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EDITORIALS

FACTORS INVOLVED IN OPENING UP THE FIELD OF UNUSED ELEMENTS[1]

In attempting to classify the accepted elements so that one group, or pseudo-group, contains those elements designated "unused," or "little used," one is confronted with many difficulties. The prime difficulties involve the purpose of the classification and the extent of the use.

Over one-third of the accepted chemical elements have no serious commercial uses at present as elements or compounds. These are given below, classified according to the periodic system for convenience:

ELEMENTS OR COMPOUNDS UNUSED OR LITTLE USED

0	1	2	3	4	5	6	7	8	Unclas.
He	Rb	Be	Sc	Ge	Cb	Se		Ru	Pr
Ne	Cs	Sr	Y		Yb	Te		Rh	Nd
A			La					Os	Sm
Kr			Ga						Eu
Xe			In						Gd
Nt			Er						Dy
			Tl						Tm
									Lu
									Tb

About one-half of these have been discovered within the last thirty years. Those so recently made known are usually classified under the two groups of "rare gases" and "rare earths."

Attention is directed to the melting points and specific gravities of four of the rare-earths.

MELTING POINTS	SPECIFIC GRAVITIES
Ce = 623° C.	La = 6.15
La = 810° C.	Pr = 6.48
Nd = 840° C.	Nd = 6.96
Pr = 940° C.	Ce = 7.04
Al = 660° C. Ag = 960° C. } Given for comparison	

Cerium has about the same density as tin (7.3), but all four readily oxidize on exposure to air. Cerium is between lead and tin in its physical appearance, but harder than tin; lanthanum acts much like metallic calcium, its oxide combining readily with water to form the hydroxide, being air slaked, as is lime.

The word "rare" so applied above—as is the case with many words of qualification—has changed its meaning in the light of very recent investigations, although the "rare gases" are found in the atmosphere in the following proportions:

NAME	ATOMIC WT.	1 VOL. IN
Helium	4.0	2,450 vols. air
Neon	20.0	808 vols. air
Argon	39.9	105 vols. air
Krypton	81.8	746,000 vols. air
Xenon	128.0	3,846,000 vols. air

Some of the elements mentioned above are by no means so uncommon now and may be had in commercial quantities. Below is a table containing these and some other elements. Many of these have been known for a long time; they are not now used extensively, but invite application.

ELEMENTS NOW AVAILABLE COMMERCIALLY BUT LITTLE USED

0	1	2	3	4	5	6	7	8	Unclas.
A	K	Ca	B	Si	As	Se	Br	Co	
		Sr	Y	Zr	Cb	Te	I	Pd	
		Ba	La	Ce	Ta				
		Cd		Th					

Now that we have seen the field, let us see what are some of the factors involved in cultivating it. In some cases we lay the lack of use of the elements at once to the scarcity of known occurrences. Haber has shown that osmium is the best catalyzer for making ammonia from its elements, but von Welsbach, who devised the osmium-filament lamp, has calculated that there are only a few hundred pounds of osmium available in the periphery of our globe. When, however, we remember that carbon is but 0.21 per cent while silicon is 25.3 per cent of the crust of our earth for a depth of ten miles, including the waters on the earth and its surrounding atmosphere, according to Clarke's calculations, we know that our present utilization of the elements commercially bears but little relation to their total quantity. With some striking exceptions, man has found more or less ample sources of the elements or their compounds when it has been shown that our civilization required them. Tungsten, thorium, vanadium, and radium only need be mentioned in illustration. It is not the small percentage in which these elements occur, for palladium exists in nickeliferous pyrrhotites in quantities too small to be detected by even refined chemical analysis, but it accumulates in the slimes of nickel refineries and is thus obtained in some quantity. The price fixed by possession is the deterrent in the development of the use of palladium, a fact of no individual immorality—quite human perhaps—but contrary to the laws of economics. Some ten years ago one large corporation possessing a store of palladium was approached by some technologists, supported by good repute, with the idea of working out uses for that by-product. The owners said they were not interested in spending a thousand dollars on the investigation—they did not mind spending the money, but they would not be a party to lowering the price of the material in their possession, the inevitable result of extending its use. This principle is well illustrated in the history of metallic aluminum and thorium oxide whose market quotations have fallen to one one-hundredth and two one-hundredths, respectively, what they were one generation ago.

On account of its great resistance to atmospheric oxidation and moisture and to the effect of sulfuretted gases, palladium has been employed for the inner mechanisn of chronometers and watches, for the construction of fine balance-beams, for the division scales of delicate apparatus, and for surgical instruments. It has been used for coating silver goods, and for electroplating searchlight mirrors, for soldering platinum, and in dental preparations. Palladinized asbestos, palladium sponge and palladium black are most efficient catalytic substances for reducing purposes.

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[1] Author's abstract of an address before the Joint Meeting of the New York Sections of the American Electrochemical Society, the American Chemical Society and the Society of Chemical Industry, at The Chemists' Club, New York, February 6, 1914.

This well known fact may be flashed from the housetops without any fear of coagulating the clouds of litigation hovering over the oil-hardening situation in this country, as the parties referred to still own the palladium.

Some of these "unused" elements will be used, if the prices are made more reasonable. A very important factor in reducing the market prices of these substances is an improvement in methods of extraction. This may be illustrated in the case of the rare-earths, not with the intention of leading the reader into that maze, but because it shows how modern tools have served the purpose and gives suggestions for needed extension with other elements in that class of "meta-elements," as Crookes termed them.

Monazite sand is essentially a phosphate of the rare earths containing variable amounts of thorium, usually 4–6 per cent. The problem of obtaining thorium compounds from that source—315,000,000 Welsbach mantles was the world's output in 1913—depends upon: (1) Solution, usually by baking, with concentrated sulfuric acid and leaching (very fine grinding of the sand was an essential preliminary); (2) The rare earths and thorium were then thrown out as oxalates to remove the last trace of phosphoric acid; (3) The mixed oxalates were brought into solution with the destruction of the oxalic acid and the thorium precipitated; or, the oxalates were treated with ammonium oxalate, whereby the nonahydrated-thorium-tetra-ammonium oxalate went into solution. This thorium salt was subsequently converted into nitrate. With all this procedure, the price of thorium salts steadily declined until it seemed to reach a limit.

Muthmann and Weiss conceived the plan of distilling off the phosphorus and converting the metallic elements present into carbides. The resultant mass is hard and is very expensive to grind in order subsequently to dissolve it. The writer later produced calcium carbide within the mixture of other carbides, using the unground monazite sand. This mass when thrown into water crumbled at once to a powder from which the suspended milk of lime is readily washed. The residual mass goes into solution in commercial hydrochloric acid from which the thorium may be precipitated at once in a form readily soluble in nitric acid. The cerium may be thrown out of the solution from the thorium precipitate and tons of oxalic acid are not destroyed or locked up in the large quantities of rare-earths accumulated awaiting the development of uses.

Muthmann and Weiss and Hirsch in this country have applied the Hall process for the isolation of metallic cerium, whose use is now practically limited to pyrophoric alloys. The price of metallic cerium in Germany has recently fallen from $60 to $5 per kilogram.

Very recently it has been proven to be distinctly profitable, according to separate patents of Soddy and Hahn, to separate meso-thorium compounds in the process of extracting and purifying the thoria. Mesothorium rivals radium in some of its applications in radio-surgery.

The three instances cited above are given for another reason. The ideas were worked out by three college professors. Laborers must be provided for clearing the field, whether the toil be that of working out new processes to so reduce the cost of a material as to admit of its application to uses already known to exist, or devise uses not now known for by-products quoted at fictitious prices, but which do not appear at such supposititious values in the annual financial statement.

Undoubtedly the best way to work out problems of the utilization of "undeveloped elements" is to attack them in such well-equipped and splendidly manned research laboratories as are maintained by the General Electric Co., the General Chemical Co., the Eastman Kodak Co., and others, but their upkeep involves large expenditures. Many college and university professors would welcome a subsidy for work of this character, which should be scientific, dignified, and help keep the wolf from the door. We commend for your perusal the amusing "Confessions of a College Professor's Wife," in a recent number of *The Saturday Evening Post*. We do not mean that the college professor is prepared to or should go into the factory, but he can work at an idea, which should later be developed, if it has merit, on a commercial scale by the technical chemist or chemical engineer of the works. Elaboration of this proposition, which is not novel with the speaker, is not necessary here. Suffice it to say that one so selected would bring to the problem a degree of ignorance that might be stimulating and a freedom from tradition which would admit of a display of imagination necessary to utilize material which is commercially abundant.

H. B. Baker has said somewhere, "Nothing can be of more value to science than the exhaustive study of one particular action."

Weiss and Neumann have found that compressed zirconium is a conductor, whereas previous statements have been that it was non-conducting. There is need for reviewing many such statements that are handed down in the literature. Aluminum is sonorous, according to so many text books. Very pure aluminum, such as that used by the late Professor Mallet in the determination of its atomic weight, is not sonorous. If aluminum is sonorous, it is not pure.

Stewart in his charming book on "Recent Advances in Physical and Inorganic Chemistry," in referring to 1887 and the following years of feverish activity in physico-chemical research, led by Arrhenius, van't Hoff and the elder Ostwald, says: "To some extent this wave appears to have spent its force. At the present day physical chemistry, except in the hands of a few exceptional researchers, has degenerated into a means of attacking the problems of pure chemistry instead of opening up new fields; and consequently there is a certain tendency to decry the subject as a mere means to an end, and not a living branch of science. This is, perhaps, an exaggerated view; but it cannot be denied that physical chemists of the present day are not animated by the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject." Bancroft acknowledges that there is some truth in this criticism, but asserts, "The difficulty is that most people are still struggling under the limitations imposed deliberately and consciously by Ostwald. Once these are broken through, nobody will have any cause to complain of the wave having spent its force." Stewart further says:

"It is an extremely fortunate coincidence that as the first movement declined, a second and perhaps more powerful one had succeeded it. This second movement rose with even greater rapidity than pure physical chemistry, and yet at the present day we appear to have touched only the fringe of the subject of radioactivity; so that we may look forward to a long career of fruitful investigation still before us in this department of chemistry."

The problems of sub-atomic or electronic universe have presented themselves and at once we begin applying these new ideas to utilitarian purposes. The cryogenic laboratories have accumulated fractions from tons of liquefied air. Collie found that the neon, obtained thus incidentally, luminesces under the influence of the Hertzian waves. A tube of neon serves as a detector of the nodes and loops, glowing brilliantly under the influence of the latter, as if it were excited by an induction coil. Claude's tubes of neon thus excited, offer a most pleasing light and perhaps later on will prove to be an economical source of artificial illumination.

Quantities of argon are now available from liquefied air. There are indications that, on account of its inertness, we may shortly see tungsten incandescent lamps, as Whitney puts it, with "the vacuum jam-full of argon" instead of nitrogen.

Troost and Onvrard have stated that they had succeeded in causing argon to combine with magnesium vapor. Neither Rayleigh, Ramsay, nor Moissan were able to secure any evidence of the formation of compounds of argon, however. Many reactions unobserved on the laboratory scale are found to occur when dealing with large quantities of substances, through long periods of time. If this were not true we should have even greater difficulty in accounting for the occurrence of such inert gases as helium in malacome, cleveite and thorianite. It is thus barely possible that in time we shall find compounds of argon produced in the large scale operations of burning the nitrogen of the air, as carried on so successfully in Norway at present. A use of compounds of argon may then be found.

The development of radioactivity has projected us into an undreamed of realm of thought and new interests. The phenomena of radiology are closely allied to those of radioactivity. The use of Röntgen rays in medicine has been attended by not a few difficulties. Among them the so-called "hardness" and "softness" of the rays. The former are penetrating and affect tissues far below the surface, sometimes favorably and sometimes unfavorably. The "soft" rays affect the epidermis. In the use of "hard" X-rays tubes for deep treatment, it is necessary to screen the skin with various thicknesses of aluminum, or lead, etc. For treatment of skin affections only, there have been no satisfactory means for screening out the penetrating rays, consequently a problem has been the production of "soft" rays with a minimum of "hard" rays. X-ray tube glass is usually a potash or soda-lime silicate. Lindemann found that by substituting lithium for potassium the rays were "softer." He then substituted beryllium for calcium, and finally boron for silicon. Lithium-beryllium-boron-glass shows over thirty per cent reduction in the empirical molecular weight. Windows of this glass let into X-ray tubes give the "soft" rays desired. It would be interesting to see the effect with a potassium-barium-zirconium-glass.

Application of the newer electronic conceptions of valence, especially when associated with residual affinity with the development of methods for changing valence according to our wishes, will unquestionably cause many of these unused elements and many of those now most used to assume new properties. Attention may be directed to one qualitative illustration. Pure lead does not plate on iron. When molten lead is caused to flow to and fro as a conductor of a low-voltage high-amperage alternating current for variable periods of time, usually several hours, it then plates iron, as may be seen from samples very recently so plated under the supervision of the writer. While the process is not perfected, it points a way which may serve as a hint in seeking uses for such elements as cadmium, selenium, and tellurium.

CHARLES BASKERVILLE

ORIGINAL PAPERS

PAINT FILMS AS PROTECTIVE COATINGS FOR CONCRETE.

By E. E. Ware and S. M. Schott[1]

Received December 9, 1913

The extensive use of concrete as a building material for all types of construction has naturally been accompanied by numerous failures of greater or less importance. These examples have been seized upon by manufacturers of competitive material and have been brought to the attention of the public through wide publicity, causing a doubt to arise in the minds of some as to the permanence of concrete construction. However, with the better understanding of the possibilities and the limitations of this material, it has been possible to very nearly eliminate the causes of failure that were mainly responsible for the difficulties experienced by the pioneers in the use of concrete construction.

But we are confronted by a cause of disintegration still little appreciated by the concrete engineer—lack of constancy of volume in concrete after setting. Although the tendency to failure from this cause is more apparent in stucco and other light construction, where mixtures rich in cement are used, monolithic work is by no means free from the effects of this lack

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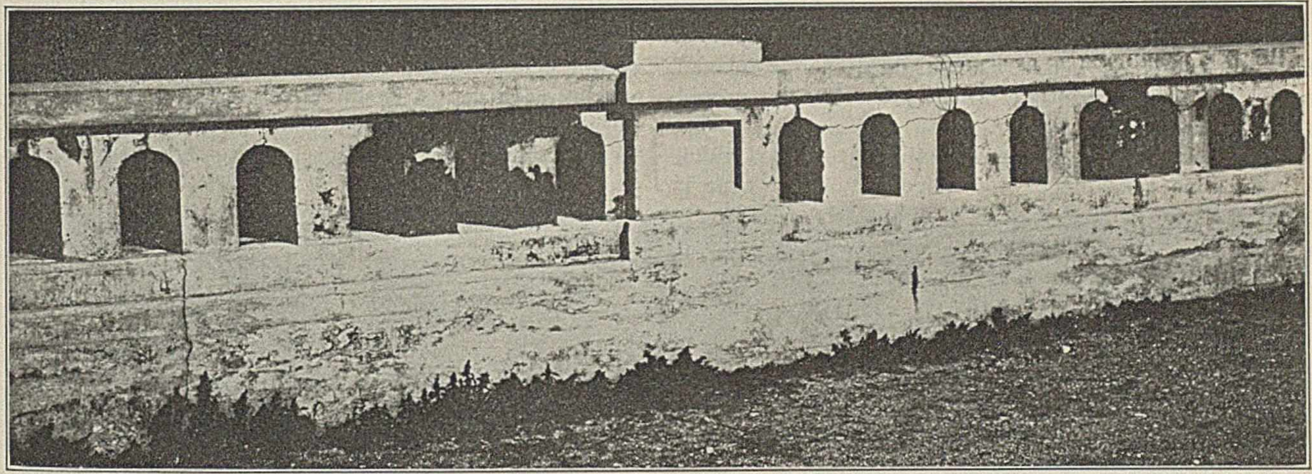
[1] Holder of Paint Fellowship, Acme White Lead and Color Works, 1911–1912.

of constancy of volume, and we find failure cracks whose presence can be accounted for only by the assumption of a differential expansion in the different members of the structure.

White[1] has shown that the changes in volume due to changes in temperature are small as compared to the changes due to the alternate wetting and drying of the concrete, and that these latter changes are sufficient to cause failure in many cases. Figs. 1 and 2 show representative failure cracks of this type.

Another source of trouble in which water plays a part, is the electrolytic effect of stray currents on the steel reinforcement in concrete. This corrosion of the reinforcement could not take place in perfectly dry concrete.[2] The elimination of these two causes of disintegration in concrete is strictly a problem in waterproofing.

Waterproofing materials for use with concrete are divided into four general classes: membrane, integral, surface washes, and oil paint films.



Courtesy of Prof. A. H. White

Fig. 1

Wig and Bates[3] have made an extensive study of waterproofing materials, and their work seems to show that none of the integral or wash waterproofings are efficient in preventing the absorption of moisture, although they may prevent the percolation of water through the concrete.

Recent work[4] seems to have demonstrated that volume changes are caused by adsorbed water, and that the presence of waterproofing within the concrete has very little effect upon the ultimate percentage change, and that its only effect is to retard the rate of absorption.

The use of an impermeable membrane on the exposed side of the concrete would very efficiently prevent the passage of water to the concrete, and would, therefore, prevent the resultant disintegration due to either moisture, volume changes or to electrolysis. However, in the majority of cases it is not feasible to use an asphalt felt membrane, so we are limited to the use of the somewhat less efficient but more suitable paint film.

Without doubt paint films can be compounded that will be practically impervious to water; but they must, in the case of concrete coaters, be also able to stand the saponification action of lime leached out from the concrete, as well as be insensitive to the attack of the weather.

Manufacturers have made attempts to solve the problem of putting out a satisfactory concrete coater; but there has been a decided tendency to lose sight of the fact that first of all the paint must be of such a nature as not to lose its elasticity or impermeability through the influence of the weather. The paint must possess all of the weather-resisting qualities of any paint designed for outside work, in addition to being able to meet the conditions peculiar to this particular service.

Concrete coaters may be classified in general: (1) coaters compounded from materials inert to the action of alkali; (2) coaters whose vehicles carry considerable amounts of free organic acids; (3) coaters compounded with the idea of getting a hard and perfectly impenetrable surface; (4) those coaters whose virtue lies mainly in the elastic and only slightly permeable film formed from the good drying oil which constitutes the major portion of the vehicle.

The first class may contain neutral gum varnishes, petroleum products, may be of a casein base, or may be made up from a cementing pigment.

Experimental data as well as practical experience with paint films for general service work have established the fact that the vehicle for any paint should be selected with a view to getting the maximum of elasticity in the dried film, recognizing that any additions that tend to harden the film will, at the same time, increase the brittleness and accelerate the disintegration.

Paints of the second class are quite common and appeal strongly to the average user, inasmuch as the free acid is supposed to serve the double purpose of neutralizing any lime that may be present and at the same time sealing the pores of the concrete with the

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[1] *Proc. Am. Soc. for Test. Mat.*, **1911**.

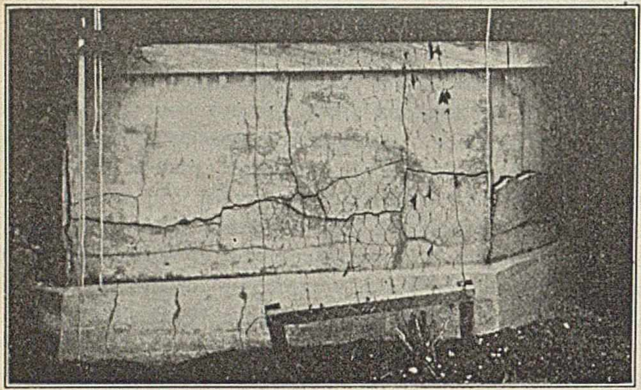
[2] Rohland, *Wasser u. Abwasser*, **5**, 504. O. Berndt, *Beton u. Eisen*, **11**, 1st Supplement. C. de Wyrall, *Proc. Int. Assn. Test. Mat.*, **2**, 20.

[3] Bur. Standards, *Technologic Paper* **3**.

[4] White, Private Communication. Jesser, *Tonind. Ztg.*, **37**, 535–8.

precipitated lime soap. The free acid of this type of paints is sometimes an added fatty acid, and sometimes the unneutralized resin acid of a varnish mixed with the oil as a constituent of the vehicle.

Cathcart[1] claims that the soaps used in waterproofing have a disintegrating influence on linoxyn. This will apply as well to the insoluble soaps formed in the neutralization of the lime by the free fatty acid of the second type of coater.



Courtesy of Prof. A. H. White

Fig. 2

In an attempt to determine the extent to which the reactions take place when a coater of this type is applied to a concrete or stucco surface, some samples of oil were subjected to parallel tests. The oils were as follows:

No. 1. Raw linseed oil.

No. 2. The same oil to which had been added a small amount of fatty acid.

No. 3. The same oil to which had been added 20 per cent of rosin varnish containing a considerable amount of unneutralized rosin acid.

Each of these samples of oil was shaken at intervals for three weeks, with three different pigments, calcium carbonate, calcium hydrate, and Portland cement. To each of these was added about 10 per cent of water, and the whole was diluted to double its volume with kerosene. A fourth set was shaken with dry Portland cement.

Table I shows that the acid constituents act as completely on Portland cement as they do on calcium hydrate, while they act very slowly on calcium carbonate and unhydrated Portland cement.

Assuming the same conditions to hold under actual conditions of service, there will be an action between the acid of the coater and the cement at the surface of the concrete, which will give a film of lime soap at the surface, to which the paint film must cling. This action is all near the surface, for there is present within one-sixty-fourth inch of the surface of an ordinary concrete sufficient lime compounds to neutralize all the acid content of the common cement coater. These coaters show themselves to be inefficient as neutralizers, and the life of the film cannot be long when they have nothing better with which to bond than a skin of insoluble soap.

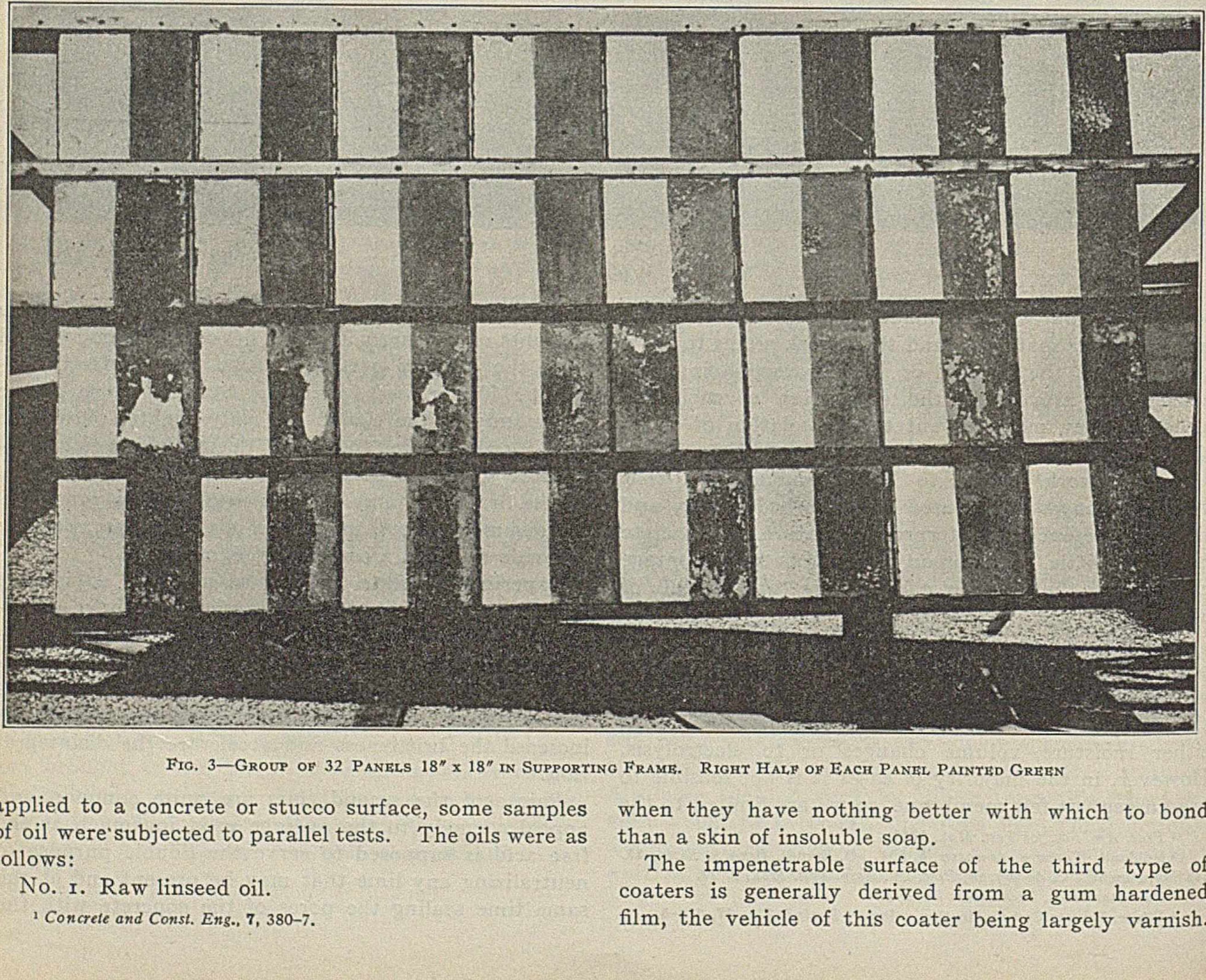


Fig. 3—Group of 32 Panels 18″ x 18″ in Supporting Frame. Right Half of Each Panel Painted Green

The impenetrable surface of the third type of coaters is generally derived from a gum hardened film, the vehicle of this coater being largely varnish.

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[1] *Concrete and Const. Eng.*, 7, 380–7.

TABLE I

	LINSEED OIL			OIL AND ACID			OIL AND VARNISH		
	Acid	Sapon.	Iodine	Acid	Sapon.	Iodine	Acid	Sapon.	Iodine
Original	1.90	113.0	122.2	9.1	105.5	111.1	6.7	105.4	118.9
Calcium carbonate	1.3	118.4	123.3	7.9	109.9	111.9	6.1	110.8	122.8
Calcium hydrate	0.1	114.1	122.6	0.2	104.7	114.5	1.2	105.5	125.8
Dry cement	1.0	115.6	122.3	4.7	105.0	111.6	2.7	109.4	125.4
Wet cement	0.2	114.2	122.6	0.3	105.0	113.2	0.4	103.1	125.6

The tests on iodine absorption were made as a more or less accurate check on the evaporation of the thinner during shaking and centrifuging.

The paints of this class really possess the faults of both the first and the second classes, for the resins of the varnishes are at least in part acid, while as a whole the hard film is subject to the same accelerated disintegrating influences as affect any nonelastic film.

With an idea of studying the efficiency of the different types of coaters, a few of the more widely advertised ones were purchased, and together with some made up in the laboratory, were applied to surfaces of concrete and stucco, and given an exposure test that has extended over about two years time.

The exposure panels were each eighteen inches square and two inches thick, reinforced by expanded metal, and held within a frame built up from 1/4 inch x 2 inch steel band, to insure them against breakage. The backs of the panels were covered with galvanized iron in order that there should be no water entering from the back of the panel, and that the conditions should be as nearly as possible the same as those existing in an ordinary structure. The paint films were subject, then, to the saponifying action of only such lime as would leach out with the water that might have passed through the film pores, or through cracks that had developed in such films as were unable to stand the weather. If a paint film be water-tight it should be free from the action of lime just so long as it remains in perfect condition; but when it begins to show cracks, then with the access of water to the underlying concrete and its subsequent evaporation from the surface, lime will be brought to the under surface of the film.

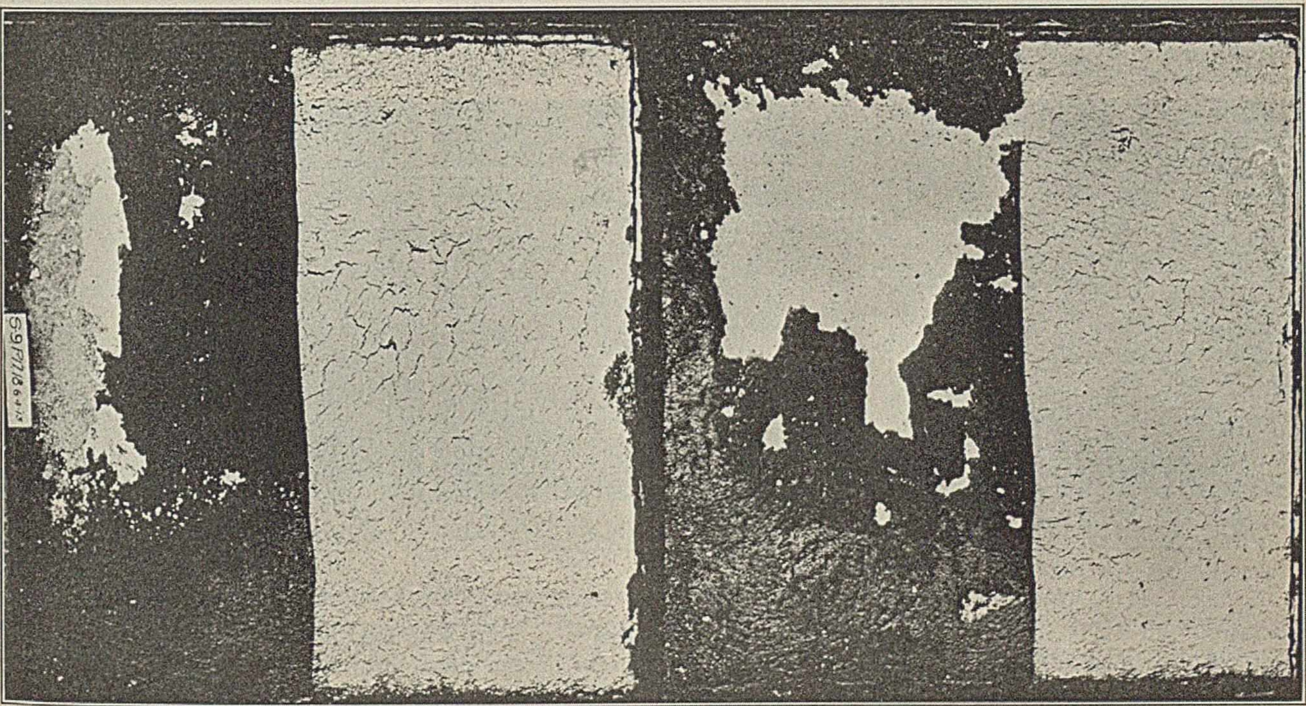

FIG. 4—PAIR OF PANELS SHOWING COMPLETELY DISINTEGRATED PAINT FILM

In these tests, each paint was assigned to two panels: one made up from a mix of one part cement to three parts river sand, and one panel of a rich stucco mix, one part lime, two parts cement and five parts river sand. The panels were made up indoors and allowed to set for three weeks before the paints were applied. During the first two weeks of this time the panels were kept damp; but they were allowed to dry a full week in order that there might not be present in the concrete, when the paint was applied, moisture that would prevent proper penetration of the paint and give an imperfect bond between the paint film and the concrete surface. The second coat was applied after the first coat had become thoroughly dry, the time intervening varying from three to seven days.

During the time of exposure, the panels were carried on a frame inclined about 20° from the vertical, with the painted surface of the panel facing south. Fig. 3 shows the complete group of panels with their supporting frame. The frame occupied such a position on the roof of the laboratory as would insure the tests being free from the influence of laboratory fumes.

After having been exposed to the weather for a period of one year, each panel was coated over one-half of its surface with a green paint whose pigment was a mixture of chrome yellow and prussian blue. This paint served as a very good indicator of the extent to which lime leached out to the surface, the presence of lime being indicated by a yellow spot. In order not to influence the porosity of the underlying film too much, only one coat of the green was applied. In cases where the paint on the panel was disintegrated badly, an attempt was made to prepare the surface for the coat of green paint by brushing off the loosely adhering scales. Even then, in some cases the condition for painting was decidedly unsatisfactory. This emphasizes the importance of using in the first place, a paint which, upon disintegration, will present a proper surface for repainting, for it is a well recognized fact that no paint coat can last indefinitely any more on concrete than on wood or metal. Ladd's[1] work has shown this to be an important consideration in the permanent protection of wooden structures, and the same conditions apply to the protection of concrete.

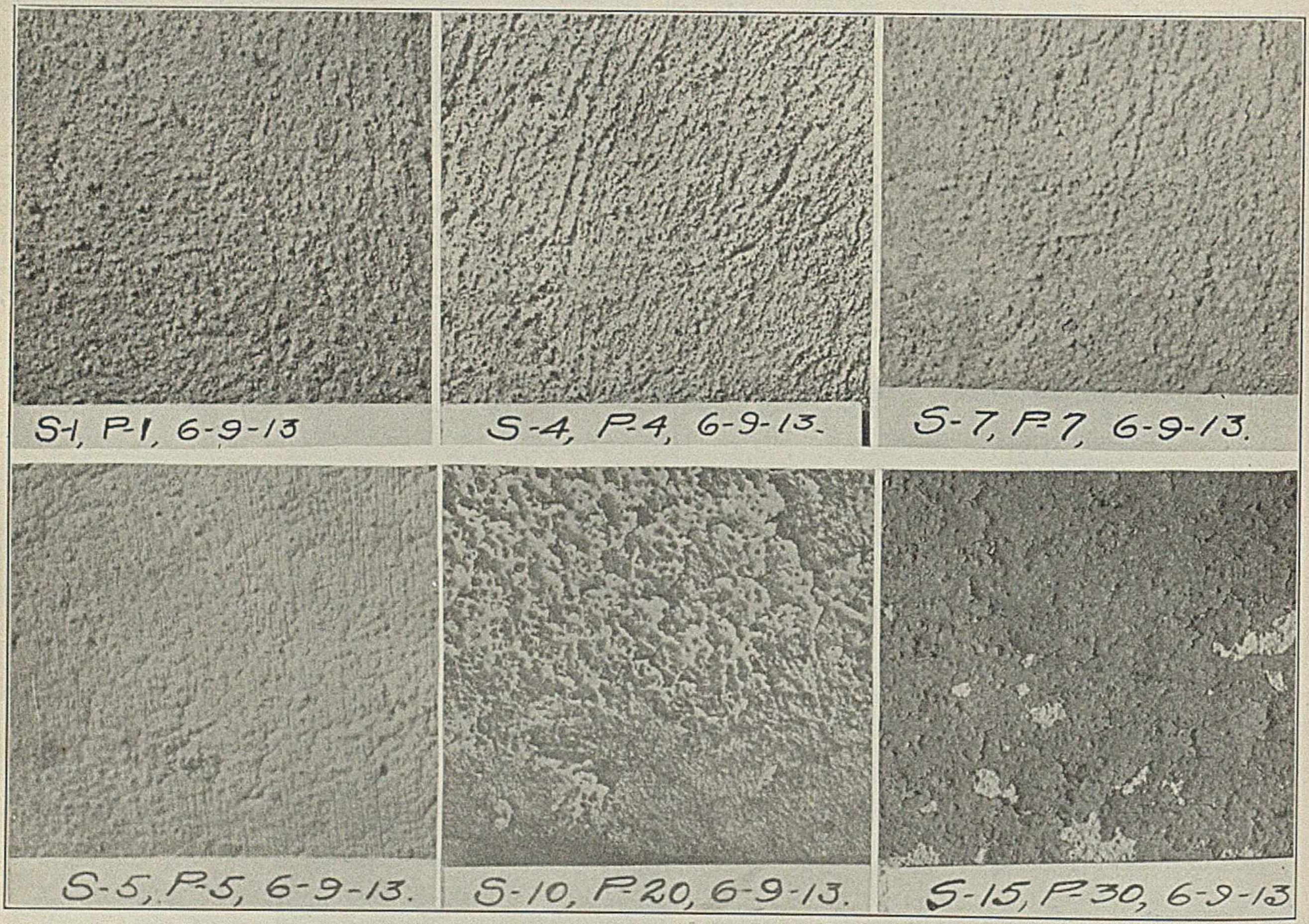

Fig. 5—Typical Illustration of Surface Condition. About 3/4 Size

Table I gives a summary of the condition of the various panels at the end of two years.

Panels Nos. 3, 11, 4, 12, 25 and 26 were painted with coaters carrying considerable amounts of fatty acid or unneutralized resin acid. The disintegration of these films was early and complete, and was not closely enough characteristic to warrant a classification according to the type of disintegration. The paints for Panels Nos. 3 and 11 carried, in addition to the fatty acid, a small amount of cement as a constituent of the pigment. While the colloidal silica formed in this way may have been efficient in sealing the pores of the concrete, the fatty acid evidently affected the film, whose early disintegration would not permit these films to be classed as efficient protection for concrete surfaces.

The paints on panels Nos. 6, 14, 17, 18, 19, 20, 21, 22, 31 and 32 depend for their efficiency on the presence of a neutral gum varnish. These panels all exhibited very early disintegration of the coater. This disintegration was, for the most part, characterized by heavy scaling and flaking, which in some cases left parts of the panel entirely free from paint within a short time.

Coater No. 5, on panels Nos. 5 and 13, was very heavy bodied and did not spread at all freely. The small amount of vehicle present was neutral in character, the material acting more like a cement than a paint, there being little tendency to form a true paint film. These panels retained their coats fairly well, although they at all times showed a high degree of porosity as indicated by the tendency to absorb any water applied to the surface. This coater might serve well as a decorative paint; but it is probably of com-

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[1] Bulletins of North Dakota Agricultural Experiment Station.

paratively little value as a protection to the concrete surface upon which it may be applied.

The coaters on panels Nos. 27 and 28 help to prove the contention that non-drying oils do not make good substitutes for linseed oil in paints, for they were among the first to show a tendency to disintegrate.

The vehicles of the paints applied to panels Nos. 1, 2, 7 and 15 were made up very largely of drying oil, the content of varnish being small, and the mineral oils being confined to the thinners. These panels were, to all appearances, the most efficiently protected of any in the test. This is true particularly of panels Nos. 1 and 2, which were prime coated with mild process white lead and oil and finished with a special outside white made up of a composite pigment, with the linseed oil vehicle carrying a small amount of varnish as a hardener.

TABLE II

Coater No.	Panel No.	Amt. applied in grams (1)	Amt. applied in grams (2)	Type of Coater	Condition. 2 yrs.	Condition. 1 yr.	Approximate Life	Condition of Green Paint
1	1	51	64	4	Good	Good	3 yrs.	General bleaching
1	9	45	45					
2	2	22	39	3	Gone	Very poor	4 mos.	Spotted
2	10	26	36					
3	3	25	43	2	Very poor	Poor	8 mos.	Spotted
3	11	25	42					
4	4	27	43	2	Very poor	Poor	8 mos.	Large spots
4	12	28	38					
5	5	79	68	1	Fair	Good	2 yrs.	Spotted
5	13	78	70					
6	6	61	..	1	Gone	Very poor	6 mos.	Not many spots
6	14	52	..					
7	7	66	57	4	Fair	Good	2 yrs.	Free from spots
7	15	43	36					
8	8	62	62	3	Gone	Very poor	4 mos.	Few spots
8	16	53	67					
9	17	51	60	1	Gone	Gone	3 mos.	Disintegrated
9	18	70	46					
10	19	55	66	1	Gone	Gone	3 mos.	Disintegrated
10	20	48	59					
11	21	63	64	1	Gone	Gone	3 mos.	Disintegrated
11	22	48	56					
12	23	58	50	3	Gone	Gone	3 mos.	No spots
12	24	49	45					
13	25	30	..	2	Gone	Very poor	6 mos.	Few spots
13	26	25	..					
14	27	27	..	1	Gone	Poor	6 mos.	No spots
14	28	..	..					
15	29	48	..	2	Gone	Fair	12 mos.	No spots
15	30	37	..					
16	31	50	..	1	Gone	Very poor	6 mos.	Few spots
16	32	50	..					

These two panels were subjected to an especially severe test, in that they were exposed at the back during the greater part of the test, the protecting galvanized iron covers having been removed from these particular panels at the end of three months exposure. This permitted water to get in from the back of the panel, which, had the pores of the concrete not been perfectly sealed, would have caused a decided saponification of the linoxyn film, for the water would naturally have evaporated from the side of the panel exposed to the sun, and in this evaporation would have deposited considerable lime within the film. Had the lime come to the surface in any quantities it must have saponified the film, as linoxyn is extremely sensitive to alkali,[1] both sodium hydroxide, and calcium hydroxide attacking it in the cold.

SUMMARY

Assuming water to be an important agent in the disintegration of concrete and stucco, there is a necessity for a system of waterproofing that will prevent absorption. The film coaters most nearly fill such a specification, where the surfaces are to be at all ornamental.

No coating compound can be successful that will disintegrate under the influence of the weather. This eliminates from consideration any material that would not be classed as a good coater when applied to other materials than concrete.

Although linoxyn is readily saponifiable in the cold, there is not, under ordinary conditions, enough lime carried out by the small amount of water that may penetrate a paint film in good condition, to cause disintegration of the film. This is emphasized by the fact that the disintegration of the paint film under observation in this work is no more pronounced on a rich lime stucco than on a cement sand concrete.

The absence of stains on the green paint tests in the cases of some of the panels whose coaters showed disintegration at the time of application of the green, would indicate that the lime at the surface of the panels had become pretty well carbonated during the first year. Any stucco exposed to the weather for a year's time can be coated satisfactorily with a good outside paint.

A successful concrete coater should be compounded on the same basis as is used for a satisfactory outside paint for wood, with only such adjustments in composition as tend to make it more nearly impervious, and these must not be made at the expense of the elasticity and general durability of the film.

The panels of these tests are to be repainted with the original materials, and a further set of experiments are in progress in which measurements of the expansion and contraction of the individual panels will be made.

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THE COMPARATIVE VALUE OF A CALCIUM LIME AND A MAGNESIUM-CALCIUM LIME FOR WATER SOFTENING

By EDWARD BARTOW AND CLARENCE SCHOLL

Received December 4, 1913

On the market there are limes made from calcium limestones and limes made from magnesium-calcium limestones. The latter is favored by masons because they think it has a smoother plasticity. The claim has been that magnesium-calcium lime is as good as calcium lime for water softening. While we believed that the claim for magnesium-calcium lime was unwarranted, we were glad to make some laboratory experiments to definitely settle the question for ourselves.

We could find but little data concerning the effect of a magnesium-calcium lime for water softening.

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[1] Andes, "Drying Oil and Boiled Oil," p. 33.

We found a record[1] of a sawdust filter impregnated with magnesia used for the removal of calcium salts.

In a paper on the efficiency of lime,[2] Mr. W. F. Monfort states that only the available lime (CaO) should be considered in lime purchasing.

Removal of magnesium from water is mentioned frequently in the literature and a better "flock" is obtained when magnesium is present in solution. This, however, has nothing to do with the effect of magnesium present in lime.

We used for our experiments the water from the University of Illinois water supply. This water is typical of deep drift well waters of central Illinois. An analysis shows that it contains 22 parts per million of carbon dioxide, CO_2; 128 parts per million of calcium carbonate, $CaCO_3$; 90 parts per million of magnesium carbonate, $MgCO_3$; and 86.8 parts per million of sodium carbonate, Na_2CO_3. Previous experiments[3] have shown that 276 parts per million (equal to 16.0 grains per gallon, 2.3 pounds per thousand gallons) are required to soften the water.

The limes used were furnished by the Ohio and Western Lime Company from their plants at Bedford and Huntington, Indiana. The Bedford lime, the Oxide, is a calcium lime containing very little magnesium. The Huntington limes, one oxide and one hydrate, are magnesium-calcium limes containing a large quantity of magnesium. The analyses of the limes are given below:

THE ANALYSES OF LIMES

		Calcium lime (Bedford)	Magnesium-Calcium Lime (Huntington)	
Substance	Formula	Per cent	Hydrated Per cent	Oxide Per cent
Calcium oxide	CaO	95.60	47.42	53.71
Magnesium oxide	MgO	0.84	33.20	37.60
Ferric oxide	Fe_2O_3	0.02	0.15	0.09
Aluminium oxide	Al_2O_3	0.85	0.55	0.86
Silica	SiO_2	0.29	0.03	0.00
Carbon dioxide	CO_2	0.18	3.44	0.65
Water	H_2O	2.24	15.20	7.08
Total		100.02	99.99	99.99

METHOD OF PROCEDURE—A number of portions of water of one liter each were treated with emulsions made from the three limes. The emulsions were of such strength that 1 cc. contained available calcium oxide, equivalent to 5 mg. $CaCO_3$. The available calcium oxide was determined by subtracting from the total calcium oxide the amount of calcium oxide necessary to combine with the carbon dioxide, CO_2, in the lime. Fifteen portions of water were softened to different degrees by adding amounts of the emulsion varying by 10 cc. each from 10 to 150 cc. Two portions were softened by adding amounts less than 10 cc. After adding the emulsion the portions were thoroughly shaken and allowed to stand over night. Each solution after filtration was analyzed. The alkalinity to phenolphthalein and methyl orange, calcium, and magnesium were determined. Results are expressed in terms of calcium carbonate ($CaCO_3$), to simplify calculation. Corrections were made for volume increase due to water added with the emulsion.

TABLE I—EXPERIMENT WITH CALCIUM LIME
Results are expressed in parts per million equivalent to $CaCO_3$

		Alkalinity			
No.	CaO added	Phenolphthalein	Methyl orange	Calcium	Magnesium
0	0	0	332.0	128.8	108.3
1	12.5	12.1	342.0	152.7	...
2	25	14.1	340.0	141.0	...
3	50	14.1	315.1	129.1	123.3
4	100	14.3	297.8	102.7	124.5
5	150	30.9	263.9	70.5	119.5
6	200	41.6	239.2	43.7	116.5
7	250	50.4	199.5	29.7	110.0
8	300	63.5	197.2	18.1	98.2
9	350	66.4	199.0	25.2	96.8
10	400	71.1	192.2	31.6	86.3
11	450	72.0	163.5	21.4	54.0
12	500	70.0	147.4	22.3	38.5
13	550	73.3	128.8	22.2	25.1
14	600	105.7	141.1	43.6	11.3
15	650	138.1	158.2	74.3	12.8
16	700	182.8	205.2	140.5	11.5
17	750	...	...	178.9	11.0

TABLE II—EXPERIMENT WITH MAGNESIUM-CALCIUM LIME
Results are expressed in parts per million equivalent to $CaCO_3$

		Alkalinity			
No.	CaO added	Phenolphthalein	Methyl orange	Calcium	Magnesium
0	0	0	332.0	128.8	108.3
1	12.5	0	335	139.6	138.0
2	25.0	0	318	113.9	144.3
3	50	8.1	301.0	65.7	160.3
4	100	49.0	289.7	34.0	186.0
5	150	72.1	292.5	...	216.0
6	200	85.3	303.7	24.4	210.3
7	250	109.2	277.2	21.1	195.8
8	300	118.7	265.0	21.3	184.3
9	350	113.4	224.7	17.5	144.8
10	400	99.4	200.9	21.3	117.8
11	450	80.7	165.7	21.4	79.0
12	500	81.4	154.0	25.1	61.0
13	550	79.9	119.9	21.1	32.3
14	600	76.2	114.2	26.8	29.0
15	650	97.2	128.8	42.5	11.5
16	700	132.2	159.6	70.9	10.3
17	750	193.2	216.2	126.8	10.3

A study of the analytical data obtained shows the action of the two limes in softening water. (Compare Tables I and II, and the figure.) All the comparisons are based on the calcium oxide content of the limes. Both limes react first with the free carbon dioxide and there is an increase in the calcium content of the water. After the carbon dioxide is used up there is a decrease in the calcium content, the decrease being much more marked in the case of the magnesium calcium lime. While the calcium is more rapidly removed by the magnesium calcium lime, an equivalent of magnesium goes into solution. There is a more rapid decrease in the methyl orange alkalinity when calcium lime is used, the interchanging of calcium for magnesium leaving the methyl orange alkalinity nearly constant. The phenolphthalein alkalinity increases more rapidly with the magnesium calcium lime due to the additional magnesium hydrate added. The magnesium reaches a maximum of 216 parts per million (as $CaCO_3$) when the calcium content approaches the minimum. The magnesium after reaching a maximum rapidly decreases

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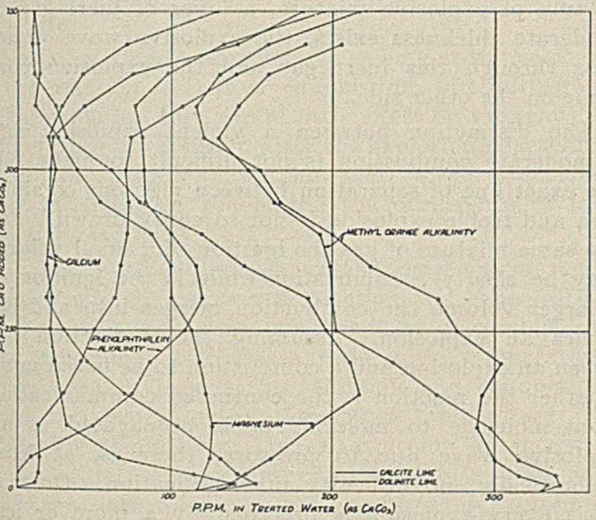
[1] *J. Soc. Chem. Ind.*, **1**, 176.

[2] *Engineering News*, **68**, 889.

[3] Univ. of Ill., *Bulletin State Water Survey*, Series 7, **98**; *Ill. Soc. Eng. & Surv.*, **24**, 213.

in amount until the minimum is reached at the point of complete softening. At the point of complete softening the methyl orange alkalinity also reaches the minimum while the phenolphthalein alkalinity is increasing. From the point of maximum softening all the constituents except the magnesium increase. The magnesium does not increase, none being added with the calcium lime and that present in the magnesium-calcium lime is not dissolved.

SUMMARY—The difference between the action of calcium and magnesium-calcium limes is that magnesium replaces the calcium until a minimum of calcium carbonate is reached. It also reacts with magnesium acid carbonate forming magnesium carbonate. With the addition of more lime all of the magnesium is precipitated as hydroxide.



Water Softening by Calcium and Magnesium—Calcium (Dolomite) Lime

The softening of water is evidently dependent on the content of available calcium oxide and therefore all lime used for water softening should be bought on the basis of the quantity of available calcium oxide. Moreover, it is not advisable to purchase lime containing magnesium because the magnesium is without value for softening and increases the amount of sludge to be handled.

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LOWER LIMITS OF COMBUSTIBLE AND EXPLOSIVE MIXTURES OF GASES AND AIR[1]

By E. E. Somermeier

Received Nov. 21, 1913

The prevention of explosions in mines and the successful operation of many industrial and metallurgical processes are to a large degree dependent upon definite information regarding the combustible and explosive properties of mixtures of gases and air. Much of the information on this subject found in the literature is indefinite, contradictory and incomplete or of limited application and the data are so scattered and in such unserviceable form that their proper correlation, interpretation and application is not at all easy.

It is the purpose of this article to discuss the conditions under which gaseous mixtures may become combustible or explosive, to analyze the various factors which constitute these conditions, to indicate a method for calculating the lower limits of combustible and explosive mixtures and to compare the results of these calculations with existing experimental data. Additional data bearing upon this question will be presented in a subsequent paper.

As a preliminary to the discussion it will be necessary to define with some care the terms which enter largely into the discussion.

IGNITION TEMPERATURE

(1) The ignition temperature may be defined as the temperature to which a mixture of gas and air or gas and oxygen must be raised in order to produce an appreciably rapid chemical reaction.

(2) The more usual definition of ignition temperature is the temperature to which a portion of a mixture of gas and air or gas and oxygen must be raised in order that chemical reaction may take place throughout the entire gas. This definition implies a self-sustaining reaction and its application is limited to combustible and explosive mixtures. It makes no distinction between the ignition temperature of combustion and the ignition temperature of explosion and on this account it is not adequate. The temperature of ignition of combustion and the temperature of ignition of explosion are two distinct temperatures corresponding to two different reaction velocities and a division into two separate definitions is desirable.

(*a*) The ignition temperature of combustion is the temperature to which a portion of a gas mixture must be raised in order that combustion may take place and the reaction be propagated throughout the entire mass of gas.

(*b*) The ignition temperature of explosion is the temperature to which a portion of a gas mixture must be raised in order that an explosion may occur and be propagated throughout the entire mass of gas.

The first definition is of importance as defining the temperature necessary to bring about a reaction. The latter definitions are, however, the ones of practical importance since they are the actual temperatures necessary to produce a combustion or an explosion for a given mixture under a given set of conditions.

THE IGNITION TEMPERATURES OF COMBUSTION

According to Dixon and Coward,[1] the temperatures to which various gases and air or gases and oxygen must be heated in order to secure ignition when mixed are as follows:

Gas	Oxygen	Air
Hydrogen	580–590°	580–590°
Carbon monoxide	637–658°	644–658°
Methane	536–700°	650–750°
Ethane	520–630°	520–630°

These values are for a pressure of one atmosphere.

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[1] Presented in outline to the Columbus Section of the American Chemical Society, January 23, 1913.

[1] *Chem. News*, **99** (1909), 139.

Diminishing the pressure of the reacting gases to one-half atmosphere raises the temperature of ignition about 5 degrees. Increasing the pressure 2 atmospheres lowers the ignition temperature by about 30 degrees.

In securing these values the two gases were heated in separate tubes and were then mixed and given an opportunity to react before any appreciable cooling had occurred. Each gas was raised to the same temperature and under these conditions an excess of either one or the other gas caused little difference in the required ignition temperature. The values given include the temperatures of ignition of both rich and poor mixtures of gas with air and with oxygen. As will be seen from the table, carbon monoxide and hydrogen have practically the same ignition temperature with air as with oxygen. These values are the temperatures at which active reaction takes place and correspond to the first definition of ignition temperature. The experiments do not, however, take into account at all whether or not the reaction is self-sustaining and on this account the results do not necessarily represent the actual ignition temperatures of combustible mixtures. They are, however, of value as a basis for the discussion of these temperatures.

IGNITION TEMPERATURE OF EXPLOSION

Probably the most reliable values are those given by Falk.[1] These values for ignition temperatures were secured under very high pressures and hence while they probably represent the required ignition temperatures of the explosive wave they do not necessarily express very closely the temperatures necessary to start explosive reactions and originate the high pressure explosive waves. Falk's values for the ignition temperatures of different explosive mixtures of hydrogen and oxygen and of carbon monoxide and oxygen are as follows:

$H_2 + O_2 = 514°$
$2H_2 + O_2 = 540°$
$H_2 + 2O_2 = 532°$
$H_2 + O_2 + 4N_2 = 637°$

$2CO + O_2 = 601°$
$4CO + O_2 = 628°$
$CO + O_2 = 631°$
$2CO + O_2 + 2N_2 = 685°$

These values are for pressures of from 30 to 40 atmospheres. The data were obtained by quick compression of the mixtures to the point where the increase in pressure raised the mixture to a temperature high enough to cause ignition and explosion.

DIFFERENCE BETWEEN COMBUSTION AND EXPLOSION

That the temperature of ignition and the temperature of explosion are two separate temperatures corresponding to two different reaction velocities is perhaps best shown by discussing in some detail the difference between combustion and explosion.

During combustion the ignition is communicated direct from molecule to molecule and the zone of combustion spreads as a continuous advancing flame, and if, during the comparatively slow reaction of combustion, the advancing zone of combustion meets an appreciable layer of inert gas the flame is extinguished and combustion ceases. In an explosion the high pressure developed by the initial explosion starts a detonating or explosive wave which, traveling with great rapidity (in the case of hydrogen 2 miles a second), produces a very high pressure in the gas. The gas being raised to the ignition temperature by this high pressure, ignites and furnishes further energy for continuing the propagation of the explosive wave. During the explosion the ignition may be considered as originating at a great number of separate points along the explosive wave, and if a column of hydrogen and air 2 miles long were to be exploded, the time of the ignition of the portion farthest from the point of origin would be only one second later than that at the origin of the explosion. While a practically continuous mass of igniting gas would exist from end to end of the column, the ignition would not be a continuous propagation from molecule to molecule; and if, in the column of explosive mixture, a layer of inert gas of moderate thickness exists, the explosive wave would pass through this inert gas and the explosion continue on the other side.

The distinction between a violent explosion and a moderate combustion is not difficult to make but the exact line of separation between vigorous combustion and feeble explosion is not so easily drawn. For the same mixture of gas the ignition of a small volume may be clearly a combustion while in the ignition of a larger volume the combustion merges into and becomes an explosion. Assuming the distinction between an explosion and a combustion to be based upon whether the reaction is the continued communication from molecule to molecule or is propagated as an explosive wave due to pressure, there is, at least theoretically, no difficulty in classification. On this basis every explosion is preceded by a more or less brief period of initial combustion.

With a large quantity of gas a combustible mixture is an explosive mixture, since when combustion is once started one of three conditions must result. The reaction decreases in rapidity, is constant, or increases in rapidity. If the rate decreases, the reaction is not self-sustaining and the mixture is not combustible. Under actual conditions a combustion at an exactly constant velocity is not likely to occur; accordingly, any combustible gas will have an accelerated velocity of reaction, and with a considerable amount of gas present an explosion will occur.

VELOCITIES OF COMBUSTIBLE AND EXPLOSIVE REACTIONS

If the temperature of ignition of combustion and the temperature of ignition of explosion are clearly recognized as corresponding more or less closely to differences in the velocities of the reactions, it follows that, for any particular mixture of gas with air or with oxygen and under any given set of conditions, there must be a minimum and a maximum rate of velocity of combustion. If the rate of reaction is less than the minimum the gas is incombustible or will not burn under the given conditions. If the rate of reaction reaches or becomes greater than a certain maximum the pressure developed produces a temperature sufficient to start ignition throughout the gas and the combustion becomes an explosion. Just what the velocity of the

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[1] *Jour. Am. Chem. Soc.*, **29** (1907), 1536.

reaction will be at any given instant for any given mixture or for any given set of conditions is dependent upon a number of factors, the effects of which will be considered in detail. Some of these factors are as follows:

(1) The thermal conductivity of the gases.

(2) The initial temperature of the reacting mixture.

(3) The initial pressure of the reacting mixture.

(4) The thermal capacity of the container.

(5) The amount of excess of either reacting gas over the ratio giving the maximum speed of reaction.

(6) The amount of inert gases or products of combustion present, such as nitrogen, carbon dioxide, and water vapor.

(7) The heat of the reaction.

(8) The volume of the reacting mixture.

(9) The length of time that the reaction has been in progress.

Nos. 1, 2, 3 and 4 are effective as long as the velocity of the reaction is that of combustion, but during an actual explosion they are of little effect on the ignition temperature of explosion after the explosion is actually under way. They have, however, a very decided effect in aiding or preventing the occurrence of the explosive reaction.

An excess of either gas or the presence of inert gases retards the velocity of reaction and hence raises the ignition temperature whether it be of combustion or of explosion. An increase in the initial temperature of the mixture lessens the radiation and conduction losses and hence lowers the actual temperature required for combustion. In an explosion an increase in the initial temperature of the mixture does not lower the actual ignition temperatures of explosion, but since it lessens the additional heat required to bring about the occurrence of the reaction, it lowers the limit of the amount of combustible gas necessary to be present and makes the gas correspondingly more explosive.

For example, a given mixture of gas of a composition such that at 0° the mixture does not undergo combustion, may, upon an increase in temperature, become not only combustible but actually explosive, because an increase in initial temperature is equivalent to so much more heat generated by the reaction, and may so accelerate the rate of reaction as to change the gas from an incombustible mixture into a combustible and explosive one. On the other hand, a diminished initial temperature increases the conduction and radiation losses and also increases the temperature required for combustion, since with a large radiation and conduction loss the rate of reaction must be accelerated, or the mixture will not support combustion. In an explosion the pressure developed is so high that small differences in the initial pressure are of little effect if an explosion is once started, but a diminished initial pressure may effectively prevent the explosion from beginning since the increased conduction and radiation losses at diminished pressure may prevent a combustion reaction from accelerating into an explosive one.

EFFECT OF RADIATION AND CONDUCTION LOSSES

During the initial stage when the speed of combustion is slow, radiation and conduction losses are correspondingly large. For the same temperature conditions the radiation and conduction losses for equal intervals of time may be represented by the spherical surface of the advancing combustion zone, which surface increases with the square of the radius; and if radiation and conduction losses be represented for the first second by c, for the second second they will be $4c$, for the third second $16c$, etc. Meanwhile the gas burned, or the total heat generated, is as the cube of the distance the combustion zone has advanced, and at the end of the first second, if it be represented by d, at the end of the second second it will be $8d$, at the end of the third second $64d$, etc. From these values, it is apparent that for equal temperature conditions, the radiation and conduction loss, if 50 per cent during the first second, will be only about 25 per cent during the second second and about $12^1/_2$ per cent during the third second, etc. This diminishing of the percentage of radiation and conduction losses leaves more heat available for further raising the temperature of the reacting gases, and hence for an acceleration of the combustion reactions above the initial rate. This raising of the temperature of the reacting gases above the initial ignition temperature, is accompanied also by increased radiation and conduction losses and the actual percentage decrease of these losses is not quite as rapid as figured above.

EFFECT OF PRESSURE ON RATE OF REACTION

A rapid increase in the rate of the combustion reaction is accompanied by an increase in pressure of the reacting gas which in turn further accelerates the rate of reaction. Dixon and Coward[1] show that an increase in pressure from one atmosphere to two atmospheres lowers the required ignition temperature for combustion about 30°, from which, if the temperature of the reacting gases remains the same, doubling the pressure is equivalent in its effect on the rate of combustion reactions to raising the temperature 30°, which as will be shown later corresponds to an eightfold increase in the rate of reaction.

EFFECT OF DUST ON REACTION VELOCITY OR ON IGNITION TEMPERATURE

All gas reactions are accelerated by contact with solids and the effect on the ignition temperature of exceedingly fine dust particles in the gas should be taken into account. It is well known that hydrogen and oxygen in contact with fine palladium will rapidly unite at temperatures below 100° and if extremely fine particles of palladium were to be in suspension throughout a mixture of oxygen and hydrogen, it might be explosive at ordinary temperatures. Very fine dust of any kind has the same effect to a greater or less degree and the effect of dust in coal mines is threefold: (1) The very fine particles may accelerate the ignition reaction and hence lower the temperatures of ignition. (2) The coal particles, being themselves combustible, increase the thermal value of the gas

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[1] *Chem. News*, **99** (1909), 139.

and correspondingly less methane or other combustible gas is required to form an explosive mixture. (3) The particles, in being raised to the ignition temperature of the gas, absorb heat and in the case of the coarser dust this absorption of heat may more than counteract any acceleration effect due to surface effect upon the gas reaction. In the case of non-combustible dust as rock dust, the retarding effect may so far exceed the accelerating influence as to render gases less combustible or explosive, while if the dust is exceedingly fine the conditions may be reversed and the mixture may become more explosive. Experimental results by Abel[1] on the effect of fine magnesium oxide upon the explosive properties of mixtures of methane and air showed an appreciable increase in the explosive quality of the gas.

The Explosions in Mines Committee[2] in their third report disagree with Abel's results and state that as the result of an extended series of experiments it found no appreciable effect produced by fine incombustible dust and that the actual effect of the presence of such incombustible dust is to render a gas and air mixture less explosive. Experiments by Dixon and Campbell[3] show errors in Abel's work and their results agree with the Explosion in Mines Committee's report, that the presence of incombustible dust does not make a gas mixture more explosive.

The findings of the Explosion in Mines Committee and the results obtained by Dixon and Campbell apparently disprove Abel's conclusions and indicate that the danger from rock dust has been greatly exaggerated. These experiments, however, do not necessarily disprove the general statement that the presence of exceedingly fine dust particles does accelerate gas reactions and it is entirely possible that their experiments if repeated on gas mixtures containing exceedingly fine dust particles of other kinds might show an increase in explosive properties due to the presence of inert dust. If the dust itself is combustible the increase in the explosive properties of the gas due to the presence of the dust is unquestioned.

EFFECT OF INCREASE IN TEMPERATURE ON RATE OF REACTION

According to Ostwald, in many chemical reactions, the rate of reaction is doubled by an increase of 10°. If this rate of increase holds true throughout a range of 100°, the reaction velocity of a gas having an initial ignition temperature of 700°, if raised to 800° would increase approximately a thousandfold. The radiation and conduction loss at 800° as compared with that at 700° is not more than in the ratio of about 5 to 3. Hence, in comparison with the increase in the speed of reaction, the increase in radiation and conduction loss is of minor importance.

The minimum velocities of reaction of combustion and of explosion and the corresponding ignition temperatures of combustion and of explosion, are different for different mixtures and different conditions. The velocity of combustion must be sufficient to keep the reaction self-sustaining and, since the requirements for being self-sustaining are dependent upon the combined influences of all the factors mentioned, it is evident that the actual velocity and hence the actual ignition temperature are different for every different set of conditions. The maximum velocity of combustion and the ignition temperature corresponding to this velocity are likewise different for each particular set of conditions. The maximum velocity of combustion and the corresponding ignition temperature may be considered as the minimum velocity and the minimum temperature required to produce an explosion. It follows, therefore, that any particular temperature of ignition of combustion and any particular temperature of ignition of explosion can be accurately stated only for some definite mixture under some definite set of conditions.

SUMMARY

In order to be adequate, statements regarding the ignition temperature of a gas mixture must be explicit as to whether the temperature of combustion or the temperature of explosion is meant. Also the particular mixture of the gas with oxygen or with air must be stated as well as data as to the presence of inert gases and the initial temperature and the initial pressure.

THERMAL REQUIREMENTS FOR COMBUSTION AND EXPLOSION AND THE CALCULATION OF THE COMPOSITIONS OF COMBUSTIBLE AND EXPLOSIVE MIXTURES

While the values for ignition temperatures vary with differences in conditions, the experimental data available are sufficient to serve as the basis for the theoretical calculations of the composition of combustible and explosive mixtures. This calculation involves the heat of combustion, the temperature of ignition and the thermal capacity of the reacting gases. A brief discussion of this last factor is advisable.

THERMAL CAPACITY OF GASES

The thermal capacity of a gas for any given temperature range is the amount of heat required to raise it through this range, and is the product of its mean specific heat, the number of degrees of temperature through which it is raised, and the number of unit quantities heated. Tables of thermal capacity afford an easy and ready means for determining the sensible heat contained in the different reacting gases or in the products of combustion for different temperature intervals. The tables may be calculated to any basis desired, as for example the thermal capacity of the gas per gram molecular volume, or the thermal capacity of the gas per gram, or per pound, or the thermal capacity per gram or per pound of one of the constituents.

The thermal capacity of some of the common gases from 0° to temperature t° is given in the following table. The values are in small calories per gram molecular volume of gas under constant pressure, and are derived from the general formulas given by Lewis

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[1] Report to the Secretary of State for the Home Department, March 23, 1881. For review of this see *Colliery Guardian*, **105** (1913), 812.

[2] *Colliery Guardian*, **105** (1913), 848.

[3] *Jour. Soc. Chem. Ind.*, **32** (1913), 684–687.

and Randall.[1] These formulas are based upon the work of Holborn and Austen, Holborn and Henning and Pier. They are the best data available on the specific heats and thermal capacities of gases.

TABLE OF THERMAL CAPACITIES

Temperature ° C.	O_2, N_2, CO	H_2	CO_2 SO_2	H_2O	CH_4	$2t$ calories
0	0000	0000	0000	0000	0000	0000
50	340	338	448	422	504	100
100	682	679	910	843	1038	200
150	1027	1022	1386	1263	1602	300
200	1375	1367	1877	1684	2196	400
250	1725	1715	2380	2104	2820	500
300	2077	2064	2897	2526	3474	600
350	2432	2416	3426	2950	4158	700
400	2789	2770	3966	3377	4872	800
450	3148	3125	4512	3804	5601	900
500	3512	3485	5081	4237	6390	1000
550	3876	3845	5650	4671	7179	1100
600	4243	4209	6239	5112	8028	1200
650	4613	4573	6828	5556	8877	1300
700	4986	4942	7436	6008	9786	1400
750	5360	5311	8043	6462	10695	1500
800	5738	5685	8667	6927	11664	1600
850	6116	6058	9290	7394	12633	1700
900	6501	6436	9929	7875	13662	1800
950	6885	6814	10567	8357	14691	1900
1000	7273	7196	11219	8857	15780	2000

Column 7 gives the value for $2t$ calories which is the amount by which the thermal value at constant pressure must be diminished to obtain the thermal value at constant volume. For example, the thermal capacity of one molecular volume of air at 600° at constant pressure is 4243. At constant volume it is $4243 - 2(600)$ or 3043.

LIMITS OF COMBUSTIBLE MIXTURES

In calculating the composition of a mixture that will support combustion, the thermal capacity of a mixture should be calculated at constant pressure, since in combustion without explosion the gases have time to expand. In calculating the lower limit of a combustible mixture the heat which must be supplied by the combustion may be considered as equal to the quantity lost by radiation and conduction plus the thermal capacity of the mixture of gas and air at constant pressure when raised from the initial temperature (t) to the ignition temperature (t'). The higher (t) the less the loss due to radiation and conduction at the temperature (t'), and hence (t') decreases as (t) increases. The difference, $(t' - t)$ being smaller, the thermal capacity of the products of combustion is smaller and less combustible gas is required to be present in the mixture. In general, an increase in the initial temperature (t) lowers the ignition temperature (t'), decreases the difference $(t' - t)$, lowers the thermal requirements for combustion conditions and as a result lowers the limit of combustible gas required in order to have a combustible mixture.

LIMITS OF EXPLOSIVE MIXTURES

In calculating the composition of an explosive mixture the thermal capacity of the mixture should be taken as at constant volume, since with an explosion traveling at a high velocity the gases have little opportunity to expand. Loss of heat by conduction is a small factor during an explosion but the quantity of heat generated must be sufficient not only to sustain but to greatly increase the ordinary rate of combustion. For example, in the combustion of a six per cent mixture of methane in air the heat generated by the combustion of the first volume of the mixture is sufficient to heat about three volumes of additional mixture to the ignition temperature of combustion and the heat generated by the combustion of these three volumes is sufficient to raise 9 volumes of mixture to this ignition temperature. The increase being a geometrical one, the rate of the reaction quickly changes the combustion into an explosion.

In an explosive reaction the heat developed by the explosion cannot be less and as a matter of fact considerably exceeds the thermal capacity of the gas or products of combustion heated from the initial temperature (t) to the ignition temperature of the explosive mixture (t'). In determining the lower limit of an explosive mixture, assuming one volume of mixture, the equation may be written as follows: Heat developed by combustion of X volume of gas equals the radiation and conduction loss plus the thermal capacity of X volumes of gas plus $(1 - X)$ volumes of air from temperature (t) to temperature (t'), X being the unknown amount of combustible gas necessary to be present, and t' the ignition temperature. With radiation and conduction losses quite small and with a known value for t', the value of X is readily calculated.

For example, assuming t equals 0° and t', the temperature of an explosive mixture of methane and air, as 850°, the value of X is determined as follows: X molecular volumes of methane on combustion gives $X(191{,}200)$ calories. This equals the thermal capacity of X molecular volumes of methane and $(1 - X)$ molecular volumes of air from 0 to 850° at constant volume, or $X(191{,}200)$ equals $X(10{,}933) + (1 - X)(4416)$. Therefore, $X = 2.4$ per cent.

Assuming 750° as the ignition temperature of combustion, a 2.4 per cent mixture of methane in air will not support combustion as shown by the following considerations:

0.024 molecular volumes of methane on combustion gives 4589 calories. The thermal capacity of 0.024 molecular volumes of methane plus 0.976 molecular volumes of air from 0 to 750° at constant pressure equals $0.024(10{,}695) + 0.976(5{,}360) = 5488$ calories, or a deficiency in heat of 900 calories. The theoretical amount of methane required for combustion at 750° is calculated as follows:

X molecular volumes of methane on combustion give $X(191{,}200)$ calories. This equals the thermal capacity of X molecular volumes of methane plus $(1 - X)$ molecular volumes of air from 0 to 750° at constant pressure; or $X(191{,}200)$ equals $X(10{,}695) + (1 - X)(5360)$, from which it follows that X equals 2.9 per cent.

With an initial temperature of 30° (86° F.) about $^1/_{25}$ less of methane will be required or about 2.3 per cent for an explosive mixture and 2.8 per cent for a combustible mixture. The experimental values for

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[1] *Jour. Am. Chem. Soc.*, **34** (1912), 1128.

the lower limits of an explosive or combustible mixture of methane and air are usually given as from 5.5 to 6 per cent of methane. Assuming the value 5.5, the excess gas over the calculated amount required for combustion is 5.5 — 2.8 = 2.7 per cent, and the excess gas over the calculated amount required for explosion is 5.5 — 2.3 = 3.2 per cent. These values indicate that during combustion and for the temperature assumed, 750°, 50 per cent of the heat liberated is available for radiation and conduction losses and for accelerating the reaction; while during an explosion for the temperature assumed, 850°, with radiation and conduction losses practically negligible, nearly 60 per cent of the entire heat liberated is expended in accelerating the reaction or in increasing the pressure of the gas.

CALCULATION OF LOWER LIMITS OF COMBUSTIBLE AND EXPLOSIVE MIXTURES OF HYDROGEN AND AIR

Assuming an ignition temperature of 600° the calculation for a combustible mixture is as follows: In one volume of mixture let X equal the volume of hydrogen and $1 - X$ the volume of air. Then $X(58,100)$, the calories of heat developed, equals the thermal capacity at constant pressure from 0° to 600° of X volumes of hydrogen plus $(1 - X)$ volumes of air, which equals $X(4209) + X(4243)$. From this it follows that X equals 7.3 per cent. With an initial temperature of air and gas at 30° (86° F.) the thermal capacity of the mixture is about $^1/_{20}$ less than this value; therefore, $^1/_{20}$ less of hydrogen or only 6.9 per cent will be required to furnish the necessary heat units.

Assuming an ignition temperature for explosion of 700° C. and neglecting radiation and conduction losses, the lower limit of an explosive mixture of hydrogen and air is obtained by taking the thermal capacity of the gas at constant volume and is found as follows: Let X equal the hydrogen present in one volume of the mixture; then the heat produced by the combustion of the hydrogen, equals the thermal capacity at constant volume of X volumes of hydrogen, plus $1 - X$ volumes of air heated from 0 to 700°. In figures this is as follows:

$X(58,100) = X(3,542) + (1 - X)(3,586)$, in which the value of $X = 6.2$ per cent.

With an initial temperature of air and gas at 30° the thermal capacity of the mixture is about $^1/_{25}$ less than this value; therefore, $^1/_{25}$ less hydrogen or only 6 per cent will be required to furnish the necessary heat units. The calculated values, 6.9 per cent and 6.0 per cent, are slightly too high, owing to the fact that the thermal capacity of the products of the reaction, $H_2 + \text{air}\ (^1/_2\ O + 1.9\ N_2) = H_2O + 1.9\ N_2$, is lower than the capacity of the unburned gas, hence after the reaction and after the products have been raised to the temperature of ignition there is a surplus of heat which is available for heating a small additional amount of unburned mixture or for heating the products to a temperature higher than the ignition temperature.

From the table of thermal capacity the capacities from 0° to 600° before and after the combustion of one molecular volume of hydrogen with oxygen to form water vapor are as follows:

Capacity of unburned gas, $H_2 + 1/2\ O_2 = 4209 + 1/2\ (4243) = 6331$
Capacity of water vapor formed = 5112
Excess = 1219

This excess (1219 calories) is a little over 2 per cent of the total heat liberated by the combustion of one molecular volume of hydrogen (58,100 calories). Therefore, the calculated values of combustible and explosive mixtures, 6.9 and 6.0 per cent, are correspondingly 2 per cent, or $^1/_{50}$ too high. Making this correction the values are about 6.8 and 5.9 per cent. The thermal calculations on methane and air are subject to a similar correction, which, however, amounts to only 470 calories per molecular volume of methane burned or 191,200 calories, which is less than $^1/_4$ per cent of the total heat produced and is more of theoretical interest than of practical importance.

TEMPERATURE REQUIRED FOR IGNITION FOR COMBUSTION COMPARED WITH TEMPERATURE REQUIRED FOR IGNITION FOR EXPLOSION

In the foregoing calculations the ignition temperature of combustion for a mixture of hydrogen in air is assumed as 600° and the ignition temperature for combustion for a mixture of methane in air is assumed as 750°. These values are approximately Dixon and Coward's highest values for ignition temperatures, which for hydrogen and air are 580° to 590° and for methane and air 650° to 750°. The ignition temperatures of explosion of hydrogen and air and methane and air are assumed as 100° higher than the ignition temperatures of combustion. These values are not to be regarded as exact but serve merely as a basis of calculation and for discussion of explosive conditions. The value 700° assumed for hydrogen is 186° higher than Falk's value for the ignition temperature of explosion for a 50 per cent mixture of hydrogen in air and 67° higher than his value for the ignition temperature of a 16 per cent mixture of hydrogen in air.

If temperature alone were the cause for the greater rapidity of an initial explosion reaction compared with a combustion reaction, the temperature required to start an explosion necessarily would be very considerably higher than that required to sustain combustion. However, as has been already shown, the high pressure during an explosion is an important factor in producing ignition of the gas at independent points throughout the mass. During combustion the large radiation and conduction losses, which losses are practically absent during an explosion, necessarily raise the actual temperature at which the combustion reaction is self-sustaining considerably above that which would be required if these losses are absent. Taking the influences of these factors into account it is conceivable that the temperature necessary to start and sustain a continuous combustion reaction actually may be as high or higher than the required ignition temperature of an explosion reaction after the explosive wave is once started.

VALUES OBTAINED BY THERMAL CALCULATIONS COMPARED WITH ACTUAL VALUES

In ordinary combustion, as has already been stated, the products of the reactions are necessarily heated considerably above the temperature actually required to produce the reaction. Otherwise the conduction and radiation of heat to adjacent molecules of unburned gas and air would not be sufficient to raise any of them to the actual combining temperature, and in thermal calculations for combustion where the heat evolved is assumed as equal to the thermal capacity of the reacting gases raised to the ignition temperature, the calculated value for the amount of combustible gas required must be lower than the amount actually required. If on the other hand, the amount of combustible gas actually required to produce an explosive mixture is made the basis of a thermal calculation, the value obtained for ignition temperature of the mixture is higher than the actual temperature required to cause chemical reaction to take place in the mixture. The effect of radiation and conduction losses is to raise the required ignition temperature and to increase the amount of combustible gas required to produce a self-sustaining combustion.

In general, any thermal equation based on the temperature at which two gases will unite if raised to that temperature will give a result for the amount of combustible gas required lower than that which will be obtained experimentally.

Likewise, any thermal equation for combustion which balances if it is based on experimental data actually obtained on gas mixtures that support combustion must give a value for the ignition temperature higher than the temperature at which combustion takes place.

POTENTIAL EXPLOSIVE PROPERTIES OF GAS MIXTURES

The results of thermal calculations based upon the temperature at which actual chemical reaction takes place fixes the lowest limits of the amount of combustible gas required for a given set of conditions. Any increase in amount of combustible gas over this lower limit or any change of conditions may make the mixture at least potentially combustible or explosive. The theoretical value of 5.9 per cent as the lower limit of an explosive mixture of hydrogen in air and the value of 2.4 per cent as the lower limit of an explosive mixture of methane in air are based on ignition temperatures of 700° for hydrogen and 850° for methane. Falk's value for the ignition temperature of explosion of a 16 per cent mixture of hydrogen in air is only 637°, from which it appears that the assumption of 700° as the ignition temperature with approximately a 6 per cent mixture is probably not too low. Natural gas and gas in coal mines frequently contain 10 to 15 per cent ethane which has an ignition temperature of combustion as low as 520° and has about twice the heating value of methane volume for volume, which makes a 2 per cent mixture of natural gas at least as explosive as a 2.4 per cent mixture of methane. From these considerations it is apparent that any mixture of over 6 per cent of hydrogen in air and of over 2 per cent of natural gas with air may be at least potentially explosive.

The results obtained in the laboratory with explosive mixtures are presumably obtained with practically dust-free gas and hence with gas having a high ignition temperature. Furthermore, in laboratory tests the results are usually obtained with mixtures rich enough to ignite and explode without any accelerating influence analogous to blow-out shots, local explosions of rich mixtures, etc.

In mines and factories the mixtures of gas and air are very liable to contain appreciable quantities of fine combustible dust and therefore may have appreciably lower ignition temperatures and be correspondingly more explosive. Any mixture of gas which is potentially explosive is to be regarded as dangerous, as in mines or in other localities there is always the possibility of conditions changing to such an extent that a potential explosion may become an actual one.

SUMMARY

The data in the literature regarding the explosive properties of gas mixtures are often incomplete and misleading. Definite knowledge is of importance in securing safety in mining and other industrial operations. This knowledge can be made more usable if the various factors bearing upon the question are collected and their effects analyzed.

In order to discuss the problems involved it is desirable to define with some exactness some of the factors and to consider in detail the difference between combustion and explosion.

The ignition temperature of a mixture is the temperature to which it must be raised to bring about an appreciably rapid chemical reaction. Ignition temperature of combustion or explosion is the temperature to which a portion of the mixture must be raised in order that a combustion or an explosion may be propagated throughout the entire mixture. Ignition temperature of combustion and ignition temperature of explosion are two distinct temperatures corresponding to two different reaction velocities. The minimum velocity of a combustion reaction is the lowest velocity at which the combustion is sustained and below which the combustion flame is extinguished. The maximum velocity is the highest velocity for combustion beyond which the reaction becomes explosive. Combustion is produced by direct transfer of energy from molecule to molecule. In an explosion the heat produced by a rapid initial reaction raises the pressure high enough to start an explosion wave, the pressure of which raises the gas to its ignition temperature and the reaction takes place throughout the entire mixture. The exact value for ignition temperature of combustion and for ignition temperature of explosion is affected by changes in initial temperature of the gas, by changes in the initial pressure, and by radiation and conduction losses, and is different for every mixture and for every set of conditions. In order that a gas mixture may support combustion or be explosive the heat produced by the reaction must be more than sufficient to raise the products of combustion and any inert gases or any excess air present to the ignition temperature of the mixture. Having given the heat of the reaction and the ignition temperature, the calculation of the lower limits of combustible and explosive mixtures of gas is comparatively easy. These theoretical calculations, if based on the temperature at which a reaction will take place, give results for the amounts of combustible gas required lower than the results found by experimental means, as the experimental results necessarily include enough additional combustible gas to overcome the effect of radiation and conduction losses. The values by theoretical calculations while lower than actual values are useful in that they show the potentially explosive properties of a mixture and any potentially explosive gas is to be regarded as dangerous.

Assuming ignition temperatures of combustion of 600 and 750° and ignition temperatures of explosion of 700 and 850° for mixtures of hydrogen in air and of methane in air and determining the amount of each required to satisfy the thermal requirements of the reaction for these temperatures, and assuming combustion as occurring at constant pressure and explosion as occurring at constant volume, the theoretical lower limit of a combustible mixture of hydrogen in air is 6.8 per cent and of methane in air is 2.8 per cent and the theoretical lower limit of an explosive mixture of hydrogen in air is 5.9 and of methane in air is 2.4 per cent.

In a succeeding paper entitled "Partial and Intermittent Combustion of Gas," the writer gives the results of some experiments undertaken in order to obtain further experimental data upon these limits and also to try to harmonize the different experimental values found in the literature, which for air and hydrogen range from 5 to 10 per cent and for air and methane range from 3.2 to 6 per cent.

The writer desires to express appreciation and indebtedness to Dr. W. E. Henderson of the Department of Physical Chemistry for advice and suggestions.

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A NEW METHOD FOR DETERMINING THE VALUE OF DISINFECTANTS

By C. A. Duyser and W. K. Lewis

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Since the chief function of a disinfectant is to kill bacteria or other micro-organic growth, its commercial value may be measured in terms of either of two quantities—*first*, the time required for a disinfectant of definite dilution to destroy a predetermined bacterial culture; *second*, that certain dilution necessary to kill the bacteria of this culture in a definite interval of time. But bacteria are living organisms having more or less an individuality. Not only are there many different strains or types of each organism, but the same culture of bacteria may differ in many of its characteristics from day to day. Hence it is impossible to employ as an analytical standard for determining the killing power of disinfectants an organism which may vary in its vitality, or a culture which may be heterogeneous as to the vitality of the individual bacteria present. The other alternative is to agree upon a certain chemical compound of known composition, and which may be obtained with ease, as the standard disinfectant, and to measure all other disinfectants in terms of the killing power of this standard. Phenol is the substance more generally employed for the purpose, and the ratio of the ability of a disinfectant to kill the bacteria of a certain culture to the ability of phenol to kill the same bacteria under absolutely the identical conditions is called the "Phenol-coefficient."

There are at present three methods for measuring the bactericidal value of disinfectants, all using the above principles, but differing in details of manipulation; these are the Rideal-Walker, the Lancet and the Hygienic Laboratory Methods. Each of these, however, gives unsatisfactory results, not only when carried on by different experimenters in different laboratories, but by the same operators when carrying on his work in duplicate. Blythe[1] has called attention to this fact most forcibly, and has made a strong appeal for a more chemical method for testing disinfecting materials. We believe that the methods now in use are not sound for the following reasons: The mechanism of the reaction by which a disinfectant kills bacteria is not definitely known, but it is generally conceded that the concentration of the disinfecting solution falls in proportion as the number of living bacteria present is decreased. It is possible that the number of molecules of disinfectant is so great in proportion to the number of bacteria present that the change in the concentration of the disinfectant as the living bacteria disappear is negligible. But it is generally true in carrying out these methods that so large a number of bacteria is used that the strength of the disinfectant is materially changed as the killing of the bacteria proceeds and before the last, or more hardy individuals are killed, the disinfectant is appreciably exhausted. Misleading results are therefore obtained.

Each of the above methods provides for removing what is supposed to be a perfectly constant volume of the culture from a tube or flask by means of the so-called standard loop. This is a circular loop made by winding a platinum wire of determined size around a rod having a definite diameter. There are so many physical conditions which apparently would influence the volume of liquid such a loop would carry that it was thought of interest to determine this volume. A strong solution of iodine of known strength served as the liquid to be transferred, and a dilute solution of thiosulfate was used to measure the amount of iodine contained in each loopful. A number of loopfuls were withdrawn with great care and placed in cold distilled water. The weight of iodine in each was then determined by titration, and from this data the volume of the loopfuls calculated. When great precautions were used, the volume of one loop varied as much as 30 per cent from the mean of 25 loopfuls, and when hurriedly done the variation rose as high as 80 per cent. The volume transferred by the standard

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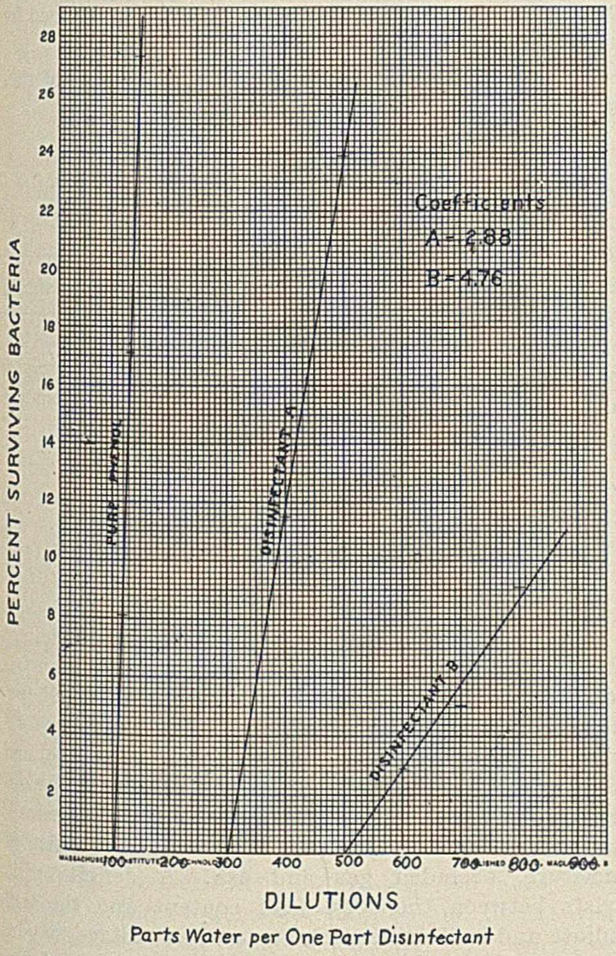
[1] Orig. Communications, Intern. Cong. Applied Chem., 1909.

loop is on the average 0.003 cc. It may be easily seen that if the number of living bacteria has been largely reduced by the action of the disinfectant it is very possible to transfer a loopful from the disinfected culture to a new culture tube which may contain no living bacteria, even though there are an appreciable number present. But even assuming, notwithstanding the law of chances, that each loopful contains a number of bacteria proportioned to the volume carried by the loop, since this volume may vary by at least 30 per cent from the mean, and may easily vary as much as 80 per cent, concordant results cannot be expected.

The use of a tube of sterile broth into which to transfer the loop of disinfected culture to determine whether or not all bacteria have been killed, is also unsatisfactory. If the tube should prove fertile there is no means of determining whether the inoculation was due to one stray survivor which happened to be in the loop and whose presence was accidental, or to a considerable number of bacteria which the disinfectant had failed to destroy.



To recapitulate, the present methods are unreliable because: (*a*) The use of an excessive number of bacteria depletes the disinfecting solution before the culture is rendered sterile. (*b*) An unknown volume is withdrawn for testing, in that the volume of the standard loop is not constant. (*c*) It is impossible to determine from the broth tube inoculated, how complete the killing was at the time the sample was withdrawn.

A method developed in this laboratory which seems to eliminate these sources of error, and which is not more laborious, is, in principle, as follows: The disinfectant to be analyzed for its relative bactericidal power is diluted with water to three or four definite concentrations, the extent of dilution depending upon its strength. Pure synthetic phenol is diluted in a like manner. Into a series of these known concentrations of both phenol and the disinfectant under consideration is placed an equal volume of a standard bacteria culture and the mixture allowed to remain an exact number of minutes. At the end of this time an aliquot part of each mixture is plated out in Petri dishes on nutrient agar and incubated until the colonies representing the surviving bacteria can be counted. At the same time plates of equal dilutions of the culture but without the disinfectant are incubated. The ratio of surviving organisms to the number present on the undisinfected plates is then plotted against the dilution, and two curves, one for the standard phenol and one for the disinfectant are obtained. From these the relative strength of the two disinfectants can be read off at any desired point on the curves, and a coefficient either for total killing or any determined percentage of killing may be calculated.

The exact manipulation recommended is as follows: One gram of the disinfectant to be analyzed is weighed accurately and diluted with sterile water to a volume of 100 cc. From this stock solution a series of dilutions is made. Since an equivalent part of each of these is later to be mixed with an equal volume of a dilute water suspension of bacteria, the strength of the series should be twice that of the final dilution desired. When nothing is known of the relative strength of the disinfectant in hand, dilutions of one part disinfectant in 200, 400, and 800 parts sterile water have been found advisable. From a 5 per cent solution of synthetic phenol a series of dilutions of one part phenol to 100, 125 and 150 parts water will give a curve covering a considerable range of killing when *B. coli communior* is used. Tubes of sterile broth and nutrient agar culture medium are prepared according to the standard methods, and a number of 10 cc. and 1 cc. pipettes and ordinary test tubes are provided.

Ten cc. of each of the dilutions of disinfectant and phenol are added to properly marked test tubes and placed in a water bath at 20° C. Ten cc. of a broth culture of *B. coli*, so diluted with sterile water that 1 cc. contains from 20,000 to 60,000 bacteria, are placed by means of a straight graduated pipette in test tubes, one more than the number of disinfectant and phenol tubes just described, and these are also placed in the water bath. This is a twenty-four hour broth culture of reaction +1, which has been transformed daily for not less than three days. When the whole has come to a temperature of 20° C. the contents of one of the tubes of disinfectant is poured into one of the tubes of bacteria and well shaken. After one-half minute this procedure is repeated with the second tube and so on through the series. At the end of five minutes, 1 cc. is withdrawn from the first tube of disinfected bacteria and added to a bottle containing 99 cc. of sterile water; one-half minute later the second tube is so treated and the others at ½ minute intervals in the same way. To the tube of bacteria in which no disinfectant was placed, 10 cc. sterile water are added and 1 cc. is transferred to a bottle containing 99 cc. sterile water. These bottles are well shaken, and duplicate Petri dishes are poured from each one, 1 cc. solution being first added to the dish followed by enough nutrient agar to make a satisfactory culture plate. When the dishes set they are inverted and allowed to incubate at 37.5° C. for 48 hours. At the end of this time the plates are counted and the ratio of the number of surviving bacteria to the number of colonies on the non-disinfected plate is determined. When plotted against the dilution two curves are obtained, types of which are shown on the accompanying plate. If a number of disinfectants are examined at the same time, it is of course not necessary to repeat the phenol series and the bacteria blank with each. The coefficient of total killing for Disinfectant A is seen to be 2.88, while for B it is 4.76.

A study of a large number of these plates shows that the curves for the so-called emulsion disinfectants are almost straight lines; at most there is but a slight curvature. Thus a small number of points will locate a line with a fair degree of accuracy and the necessity of using small increments of dilution as obtains in the older method is not here present. As is clearly shown in this plot, though desirable, it is not necessary, as in the other methods, that the most concentrated solution of the disinfectant used should produce a sterile tube or plate, that is, show total killing. If at least three points have been found to lie fairly well upon a smooth curve, the line may safely be interpolated until it cuts the axis representing complete killing and the coefficient calculated from this intersection. The results obtained may be duplicated with sufficient precision to warrant confidence in them. This is true not only of a single operation carrying on duplicate determinations, but by two analysts working separately.

	I	II
1	4.82	4.58
2	5.17	5.05
3	6.95	6.64
4	9.64	9.30
5	4.28	4.08
6	2.04	2.24

The above duplicate results obtained by the same analyst will give an idea of the degree of accuracy which may be readily attained.

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THE LEAD CONTENTS IN SUBLIMED WHITE LEAD—A CALCULATION

By John A. Schaeffer

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The composition of sublimed white lead, the basic sulfate of lead, has become a most important factor to users of this pigment. Both among rubber manufacturers and producers of paints, it is being found essential that the contents of lead oxide and lead sulfate be known, so that advantage may be fully taken of its characteristic properties. This control necessitates an analysis of the compound in the laboratory.

In analyzing sublimed white lead by the usual method, it is found that the percentage composition can be determined only by an analysis entailing lengthy manipulation, in which the content of lead oxide is directly dependent upon the accuracy of the other determinations, owing to the necessity of estimating its percentage by a calculation based upon the percentage of the other constituents present. The steps in the procedure must therefore be closely watched for slight inaccuracies at all times.

As is well known, the average composition of sublimed white lead is given as follows:

Lead sulfate	78.5
Lead oxide	16.0
Zinc oxide	5.5

That its composition varies only slightly from the above analysis during a long period of time, is shown by its comparison with an average of the entire output of the Picher Lead Company extending over five months time, an average embracing 270 total analyses.

This average shows the composition to be:

Lead sulfate	76.68
Lead oxide	17.23
Zinc oxide	5.79
	99.70

A slightly higher lead oxide and zinc oxide content and a correspondingly lower lead sulfate content is found, than in the usually stated formula. It shows, however, only slight variation. The average total percentage, consisting of lead sulfate, lead oxide, and zinc oxide, was found to be 99.70 per cent. The remaining 0.3 of a per cent is only rarely determined, and when actually sought is found to consist of moisture, occluded gas and ash. A definite ratio exists between the total lead content and the lead sulfate and lead oxide contents, and advantage may be taken of this relation for a rapid and accurate determination of the lead constituents in sublimed white lead.

In order to arrive at the short method for the analysis which is based upon a direct calculation of the lead and zinc contents, it is necessary that the usual method of analysis be considered.

USUAL METHOD ADOPTED FOR THE ANALYSIS OF SUBLIMED WHITE LEAD

DETERMINATION OF TOTAL SULFATE—Mix 0.5 gram of the sample with 3 grams of sodium carbonate in a beaker. Treat the mixture with 30 cc. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute the contents of the beaker with hot water; filter off the residue and wash until the filtrate is about 200 cc. in volume. Reject the residue. By this reaction all the lead sulfate is changed to carbonate, the sulfate being transposed into sodium sulfate, which is found in the filtrate.

Acidulate the filtrate with hydrochloric acid and add an excess of about 2 cc. of the acid. Boil, and add a slight excess of barium chloride solution (12 cc. of an 8 per cent solution). When the precipitate has well settled, filter on an ashless filter, wash, ignite and weigh as $BaSO_4$. Calculate the $BaSO_4$ to $PbSO_4$ by using the factor 2.6 when a half gram is used.

Weight of $BaSO_4 \times 1.3$ = weight $PbSO_4$.

On 0.5 gram sample the factor $BaSO_4$ to $PbSO_4$ = 2.6.

DETERMINATION OF LEAD. MOLYBDATE METHOD[1]—Dissolve 1 gram of the sample in 100 cc. of an acid ammonia acetate solution made up as follows:

Eighty per cent acetic acid	125 cc.
Concentrated ammonia hydroxide	95 cc.
Water	100 cc.

Add this solution hot and dilute with about 50 cc. of water. Boil until dissolved. Dilute to 200 cc. and titrate in the usual manner with standard ammonium molybdate solution, spotting out on a freshly prepared solution of tannic acid.

Ammonium molybdate is a slightly variable salt, but a solution containing 8.67 grams per liter usually gives a standard solution:

1 cc. = 0.01 gram Pb

Standardize against pure PbO, pure $PbSO_4$ or clean lead foil.

Deduct the lead found as lead sulfate from the total lead and calculate the residual lead to PbO.

DETERMINATION OF ZINC. FERROCYANIDE METHOD[2]—Boil 1 gram of the sample in a beaker with the following solution:

Water	30 cc.
Ammonium chloride	4 grams
Concentrated hydrochloric acid	6 cc.

If the sample is not quite dissolved the result is not affected, as the residue is lead sulfate or precipitated lead chloride.

Dilute to 200 cc. with hot water, add 2 cc. of a saturated sodium hyposulfite solution and titrate with a standard solution of potassium ferrocyanide, spotting out on a 5 per cent solution of uranium nitrate. Calculate the zinc to zinc oxide.

SULFUR DIOXIDE—Digest 2 grams of the sample with frequent stirring in 5 per cent sulfuric acid for ten minutes in the cold. Add starch indicator and titrate with *N*/100 iodine solution.

A more accurate method is to add an excess of standard iodine solution to the sample before the addition of the acid and then to titrate the excess of iodine with *N*/100 sodium thiosulfate solution.

It will be seen from the above method of analysis that the concordance of results depends upon several important factors; namely, the accurate estimation of the total lead content, the zinc content and the complete transposition of the lead sulfate present to lead carbonate with the attendant formation of sodium sulfate from which the sulfate is determined as barium sulfate. The percentage of lead oxide depends wholly upon the accuracy of these determinations, as it is never directly determined.

The following method for ascertaining the lead sulfate and lead oxide contents is based upon a calculation depending upon the percentage of total lead found. The complete analysis can be easily carried out in a half hour.

The essential requisites are the volumetric determination of the zinc present with its subsequent calculation to zinc oxide, and the volumetric determination of the total lead, regardless of the proportion of lead sulfate and lead oxide present. These volumetric determinations are carried out according to the method above outlined.

Using the percentages of zinc oxide and total lead, together with the average total, 99.70 per cent, determined from the large number of analyses, the contents of lead oxide and lead sulfate are readily estimated by the following calculation:

Total percentage of lead compounds present
= total percentage found of ZnO, PbO and $PbSO_4$ — percentage of ZnO.

Total percentage of lead compounds present
= 99.70 per cent (average total) — percentage ZnO.

Atomic weight lead	207.1
Molecular weight lead oxide	223.1
Molecular weight lead sulfate	303.1

As a hypothetical case, we can assume the presence of a 4.70 per cent ZnO and 69.00 per cent metallic lead.

Determining the percentage of lead oxide and lead sulfate present by the above formulas we find:

$$\frac{\left(\frac{303.1}{207.1} \times 69.00\right) - 95.00}{\frac{303.1 - 223.1}{223.1}} = \text{per cent PbO} = 16.68$$

$$\frac{\left(\frac{223.1}{207.1} \times 69.00\right) - 95.00}{\frac{223.1 - 303.1}{303.1}} = \text{per cent PbSO}_4 = 78.32$$

$$\frac{\left(\frac{\text{Mol. wt. PbSO}_4}{\text{At. wt. Pb}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\frac{\text{Mol. wt. PbSO}_4 - \text{mol. wt. PbO}}{\text{Mol. wt. PbO}}} = \%\ \text{PbO present}$$

$$\frac{\left(\frac{\text{Mol. wt. PbO}}{\text{At. wt. Pb}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\frac{\text{Mol. wt. PbO} - \text{Mol. wt. PbSO}_4}{\text{Mol. wt. PbSO}_4}} = \%\ \text{PbSO}_4\ \text{present}$$

A comparison of the actual results obtained by the complete analysis of sublimed white lead and its calculated composition shows that the values obtained are concordant. Indeed the only essential factors for the short method are accurate determinations of the lead and zinc contents. The removal of several steps in the analysis leads to greater accuracy coupled with a considerable curtailment of time.

A table of comparisons shows the following concordance of results:

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[1] Modification of Low's method. "Technical Methods of Ore Analysis," Low, p. 149.

[2] "Technical Methods of Ore Analysis," Low, p. 284.

No.	Analysis	Lead sulfate	Lead oxide	Zinc oxide	Total lead	Total
1	Complete	79.20	15.28	5.23	68.30	99.72
	Calculated	79.17	15.30	....	...	...
2	Complete	77.74	16.81	5.11	68.70	99.66
	Calculated	77.97	16.62	....	...	...
3	Complete	77.09	16.95	5.73	68.40	99.77
	Calculated	76.85	17.12	....	...	...
4	Complete	80.20	14.66	4.86	68.40	99.72
	Calculated	80.15	14.69	....	...	...
5	Complete	78.00	16.60	5.11	68.70	99.71
	Calculated	77.97	16.62	....	...	...
6	Complete	77.84	17.10	4.86	69.00	99.80
	Calculated	77.69	17.15	....	...	...
7	Complete	77.22	16.20	6.23	67.80	99.63
	Calculated	77.41	16.06	....	...	...
8	Complete	74.10	20.21	5.48	69.40	99.79
	Calculated	74.00	20.22	....	...	...
9	Complete	77.63	15.92	6.23	67.80	99.78
	Calculated	77.41	16.06	....	...	...
10	Complete	76.05	17.93	5.73	68.60	99.71
	Calculated	76.04	17.93	....	...	...
11	Complete	76.98	17.78	4.98	69.10	99.74
	Calculated	76.85	17.87	....	...	...

That this method will prove of value will be readily appreciated by all chemists who have to determine the percentage composition of any basic sulfate of lead, either for the purpose of meeting specifications or for accurate control of finished products.

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THE CONSTITUTION OF WHITE LEAD

By Edwin Euston

Received December 1, 1913

The usual view is that the widely used Dutch, or tan-bark stack, process of corrosion of metallic lead to form white lead results in a product containing principally a fixed and definite compound, $2PbCO_3.Pb(OH)_2$. This view is based on the physical appearance of the crust formed under the best conditions, and assumes that the higher percentage of combined carbon dioxide almost always found on analysis is due to admixed normal lead carbonate, and that the lower percentage of carbon dioxide occasionally found results from admixed lead hydroxide. It is certain that a considerable percentage of normal lead carbonate in the crystalline form ("sandy lead") is usually present in the product of the stack process, even to the extent of 5 per cent or more; and under abnormal conditions of corrosion de-hydrated lead hydroxide is found to be present in quantity sufficient even to injure the color of the white lead. The possibility, or even the probability, therefore, of either or both normal lead carbonate and some form of lead hydroxide being present in stack process white lead must be admitted. The purpose of the writer is to consider whether true white lead (the so-called basic carbonate of lead) consists substantially of a fixed and definite compound, $2PbCO_3.Pb(OH)_2$, admixed with chance amounts of normal lead carbonate and lead hydroxide, or whether some other form or forms of combination of the elements involved may not better accord with the facts.

During the long time required in the stack process to effect the commercial degree of corrosion, usually 100 to 120 days, no important control can be exercised over the process, and even in the separate tiers of the same stack, wide variations of the governing conditions of heat, ventilation, moisture and vaporization of the acetic acid occur, rendering the stack process entirely unsuitable as a means of investigating experimentally the steps in the formation of white lead and the nature of the product. Precipitation by carbon dioxide gas from basic lead acetate solution, as first suggested by Thenard as a means of forming white lead, has been found to be subject to so many difficulties of control that heretofore no results of value have been derived from this method. Yet when due care is exercised to ensure uniformity of treatment of the entire mass of solution and precipitate, when the apparatus used is of sufficient size (say, 1000 pounds product per hour), and when proper tests are known, close control of the precipitation process is attainable; and in many thousand repetitions on this manufacturing scale the writer has found that very definite results may be obtained, throwing new light on the series of changes occurring when basic lead acetate solution is subjected to the action of carbon dioxide.

For practical reasons an approximately di-basic solution of lead acetate formed from about 4 per cent acetic acid is preferable, uniformly circulated (without permitting separation of the resulting precipitate from the liquid) by spraying a number of times through an atmosphere of moderately or strongly concentrated carbon dioxide gas, at room temperature. When the precipitation is slowly performed under standard conditions, the precipitate first appearing is colloidal in character and analyses 8.6 per cent CO_2 or slightly higher, corresponding to the formula $PbCO_3.Pb(OH)_2$. When more quickly performed, the precipitate contains 9.0 to 10.0 per cent CO_2, therefore also less than the 11.3 per cent CO_2 corresponding to the formula $2PbCO_3.Pb(OH)_2$ constituting the usually accepted view of the principal compound in white lead. On continuing the treatment, the percentage of combined CO_2 increases gradually until it approximates 16.6 per cent, corresponding to the formula of the normal carbonate $PbCO_3$, after which no further precipitation and no further change in the composition of the already formed precipitate occurs. Throughout this treatment the increase in the CO_2 percentage in the precipitate is progressive and gradual, with no evidence of the formation of hypothetical intermediate compounds such as the supposed $2PbCO_3.Pb(OH)_2$, or such as $3PbCO_3.Pb(OH)_2$. The change in the solution as the available lead is precipitated is gradual, from strong alkalinity to slight acidity. Similarly, the properties of the precipitate indicate only gradual change as the process progresses, except that when the solution passes the point of exact neutrality the "apparent density" of the precipitate suddenly and sharply increases, but thereafter resumes the more gradual rate of increase which is also characteristic in the earlier stage of the precipitation. This sudden increase in "apparent density" is doubtless due to coagulation occurring when the solution becomes acid. Analyses do not indicate any fixed and definite composition of the precipitate when this sudden increase in "apparent density" occurs, as the determinations may range variously from 11.0 per cent to even 13.5

per cent CO_2. The foregoing, therefore, affords no evidence of the formation of the usually assumed compound $2PbCO_3.Pb(OH)_2$, but on the contrary shows the initial formation of a precipitate of the composition $PbCO_3.Pb(OH)_2$ and the gradual change to the normal carbonate.

Lead hydroxide is soluble in a solution of cane sugar in water. At no stage in the above described process is the separated and washed precipitate appreciably soluble in cane-sugar solution. Therefore, the precipitates described are not simple mixtures of normal carbonate and of lead hydroxide, but hold the lead hydroxide in some form of combination with all or part of the carbonate. This fact, in connection with the analyses of the first formed precipitate, shows that the first product obtained is a basic carbonate of the formula $PbCO_3.(OH)_2$. Inasmuch as the final product obtained by continuing the process to the extreme degree is $PbCO_3$, the question then becomes whether these two compounds, $PbCO_3.Pb(OH)_2$ and $PbCO_3$, when mixed in various proportions, constitute white lead, or whether other compounds must also be postulated.

As mixtures of $PbCO_3.Pb(OH)_2$ and $PbCO_3$ in proper proportions give all the intermediate percentages of combined carbon dioxide between 8.6 per cent and 16.6 per cent, no other compounds than these two need to be assumed from the point of view of composition. A mixture of one equivalent of $PbCO_3.Pb(OH)_2$ with one equivalent of $PbCO_3$ will give the average 11.3 per cent CO_2 of the heretofore assumed $2PbCO_3.Pb(OH)_2$, and the physical properties of a sample of white lead analyzing 11.3 per cent CO_2 and directly prepared are identical with the physical properties of a sample of the same average composition obtained by mechanically mixing together separately prepared equivalent quantities of $PbCO_3.Pb(OH)_2$ and of $PbCO_3$, *e. g.*, the space occupied by 20 grams of the pulverized sample settling freely under water in a 200 cc. cylinder, the amount of linseed oil necessary to form a paste, the ease of miscibility with linseed oil, also the opacity and spreading power when mixed as a paint. This same result is true for all other variations of composition between 8.6 per cent and 16.6 per cent CO_2, *i. e.*, the entire range.

The molecular volume affords further evidence that no other compounds than $PbCO_3.Pb(OH)_2$ and $PbCO_3$ are present in white lead properly prepared:

	Molecular volume	Ratio	Percentage linseed oil required to form paste	Ratio
(*a*) $PbCO_3$	57.0	1.0	7 (actual)	1.0
(*b*) $PbCO_3.Pb(OH)_2$	97.8	1.71	12 (actual)	1.7
(*c*) $2PbCO_3.Pb(OH)_2$	154.8	2.71	19 (indicated)	2.7
(*d*) $3PbCO_3.Pb(OH)_2$	211.8	3.71	26 (indicated)	3.7

The close correspondence between the ratios for calculated molecular volume and for actual oil requirement in the case of (*a*) and (*b*) is very striking. The indicated oil requirements for the hypothetical compounds (*c*) and (*d*), *viz.*, 19 per cent and 26 per cent, are entirely too high to accord with the known oil requirements of white lead of the corresponding analyses, and would imply that as the percentage of carbon dioxide in white lead increases, the oil requirement would rapidly increase until, when the normal carbonate should be reached, a sudden great drop in oil requirement would result. Certainly this is not the case, for actually the oil requirement, as the percentage of carbon dioxide increases, shows gradual reduction from 12 per cent to 7 per cent for all intermediate stages. Instead of the indicated oil requirement of 19 per cent for (*c*), therefore, this figure becomes

$$\frac{(7 \times 266.5) + (12 \times 507)}{773.5} = 10.27 \text{ per cent,}$$

which accords with the facts, provided allowance is made for gain in compactness due to the intermeshing of two sizes of particles, resulting in an actual requirement of about 9 per cent oil.

Inasmuch as the Dutch or stack process also involves the use of basic lead acetate solution and carbon dioxide gas, there is no reason to consider that the course of reactions in the stack process (in which the reactions cannot be watched) differs from the now known course of reactions in the precipitation process (in which the reactions can be watched); and, except in its comparative coarseness and granularity and its less degree of whiteness due to tan-bark and other stains, stack process lead has no characteristics different from those of a precipitated white lead known to contain the two compounds $PbCO_3.Pb(OH)_2$ and $PbCO_3$. The conclusion is clear, therefore, that white lead does not contain a compound of the heretofore assumed formula $2PbCO_3.Pb(OH)_2$, but that on the contrary white lead consists of a mixture of the two amorphous compounds $PbCO_3.Pb(OH)_2$ and $PbCO_3$, complicated in the case of stack white lead by the presence of some lead carbonate in crystalline form and occasionally some form of lead hydroxide due to abnormal conditions in the corroding stack.

EUSTON WHITE LEAD CO.
ST. LOUIS

ON THE DETERMINATION OF TITANIUM AS PHOSPHATE

By GEORGE S. JAMIESON AND RICHARD WRENSHALL

Received October 29, 1913

Several years ago Eric John Ericson[1] described a method for the determination of titanium in ferrotitanium and in ores. The method was based upon the precipitation of titanium phosphate in acid solution by the addition of ammonium phosphate and boiling, after reducing the iron to the ferrous state by means of ammonium bisulfite or sulfur dioxide. He gave the factor 0.336 for calculating the titanium from the weight of the phosphate, assuming that the latter has the formula $Ti_2P_2O_8$.

On account of the simplicity and rapidity of this method its accuracy and application have been studied in this laboratory. Some modifications of the original method have been found desirable and its application to the separation of titanic acid from alumina has been worked out. A series of eighteen experiments

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[1] *Iron Age*, Aug. 27, 1903, p. 4.

was made with standard solutions of ferric and titanic sulfates containing enough sulfuric acid to keep the salts in solution, but the quantities of free sulfuric acid present were not determined.

The standard titanium solutions employed in this research were prepared from pure potassium titanium fluoride with the exception of one solution made from a titanium oxalate of excellent quality. The titanium salts were converted into the sulfate by repeated evaporation with sulfuric acid in platinum dishes. The solutions were standardized by precipitating the titanium with ammonia from measured volumes, finally weighing the dioxide and calculating the strength of the solution in terms of titanium. The values obtained were checked by precipitating the titanium by the sodium thiosulfate method and weighing the dioxide.

In each case 15 cc. of 1 : 1 hydrochloric acid were added to measured volumes of these solutions, water was added to make the volume 100 cc., sulfur dioxide was passed through for 10 minutes, the liquid was heated to boiling and 20 cc. of a 10 per cent solution of ammonium phosphate were added. The boiling was continued for a half hour; the precipitate was allowed to settle for an hour or more; it was then filtered and washed with hot water on a Gooch crucible in which it was finally ignited for 15 minutes at the highest temperature of the Bunsen burner and weighed. The method of Ericson was closely followed here except that the Gooch crucible was used instead of paper for filtering, on account of the tendency of the precipitate to run through a paper filter. In order to make satisfactory use of the Gooch crucible, it is necessary to use moderate suction and to avoid allowing all the liquid to pass out of the crucible until thorough washing has been effected, for it is impossible to wash the precipitate after it has become compact and has cracked. Except with very small quantities of titanium, the results obtained were satisfactory. Low results were obtained when less than 0.007 gram of titanium was present, which appear to be due to the failure of the precipitate to collect in a filterable form. It probably remains in a colloidal condition. The writers have found that with such small quantities of titanium less acid must be used and after precipitation and boiling, it is advisable to let the liquid stand for at least 6 hours, then to warm on the steam bath and filter. With this treatment the loss appears to be no greater with about 0.002 gram of titanium than with larger quantities.

When an attempt was made to apply Ericson's method to some ores containing 0.5 to 8 per cent of titanium it was found that no precipitate or only a small one was obtained if the ores had been dissolved by treatment with hydrochloric and sulfuric acid and evaporation with a rather large amount of sulfuric acid instead of being dissolved by a potassium bisulfate fusion. This was evidently due to the presence of the large amount of sulfuric acid in addition to the hydrochloric acid used. Therefore, when this convenient method for dissolving titanium ores is employed, it is necessary to neutralize the sulfuric acid, best with ammonia, before proceeding with the determination. Titanium ores or minerals not decomposed by the acid treatment just described, are rendered soluble by fusion with potassium bisulfate in the usual manner.

In the analyses in the table given below, the sulfuric acid present in each solution was neutralized with ammonia before adding the hydrochloric acid; the precipitates were allowed to settle at least six hours, then the solutions were heated on the steam bath for about 20 minutes before filtering.

No.	Fe taken	Ti taken	Ti found	Error	Cc. 1 : 1 HCl used
1	0.000	0.0019	0.0018	—0.0001	1
2	0.000	0.0030	0.0027	—0.0003	3
3	0.000	0.0030	0.0034	+0.0004	3
4	0.043	0.0010	0.0010	±0.0000	2
5	0.086	0.0010	0.0009	—0.0001	3
6	0.086	0.0030	0.0029	—0.0001	3
7	0.086	0.0010	0.0009	—0.0001	3
8	0.086	0.0019	0.0011	—0.0008	6
9	0.086	0.0010	0.0002	—0.0008	6
10	0.086	0.0039	0.0032	—0.0007	10
11	0.043	0.0100	0.0101	+0.0001	5
12	0.043	0.0154	0.0152	—0.0002	5
13	0.043	0.0154	0.0151	—0.0003	5
14	0.100	0.0248	0.0245	—0.0003	15
15	0.100	0.0248	0.0244	—0.0004	15
16	0.100	0.0260	0.0256	—0.0004	15
17	0.110	0.0260	0.0258	—0.0002	15

In these experiments a volume of about 50 cc. was used instead of 100 cc., as in the case of the first series of experiments. It will be observed that in the first 10 experiments very small amounts of titanium were taken in order to determine the conditions under which they could be satisfactorily precipitated and filtered. It is evident from these experiments that when 1–3 mg. of titanium are present, it is necessary to keep the amount of free 1 : 1 hydrochloric acid down to about 3 cc. in 50 cc. solutions, otherwise low results will be obtained.

Experiments were made to find if titanium phosphate could be precipitated in the presence of tartaric acid and it was found that this could be done quantitatively although in a recent article Thornton[1] states that titanium cannot be precipitated by any reagent in the presence of tartaric acid. To the solutions containing measured quantities of titanium and ferric sulfates, about 2 grams of tartaric acid were added and enough ammonia to make them slightly alkaline. Then hydrogen sulfide was passed into the warm solutions until the iron was reduced and precipitated as sulfide. The solutions were treated with 10–15 cc. of 1 : 1 hydrochloric acid, depending upon the amount of iron present, and heated until the iron sulfide was dissolved. Then 20 cc. of the 10 per cent ammonium phosphate reagent were added and the experiments from this point were identical with those described above. In the first four experiments the ferrous sulfide was filtered off and washed with hot water containing a little ammonium sulfide, while in the last four the ferrous sulfide was not filtered, but dissolved as previously directed. No advantage was gained by removing the iron from the solution. The following results were obtained.

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[1] *Am. J. Sci.*, **34**, 214.

No.	Fe taken	Ti taken	Ti found	Error
1	0.086	0.0207	0.0206	—0.0001
2	0.043	0.0050	0.0049	—0.0001
3	0.043	0.0030	0.0024	—0.0006
4	0.043	0.0040	0.0039	—0.0001
5	0.043	0.0060	0.0059	—0.0001
6	0.200	0.0249	0.0253	+0.0004
7	0.100	0.0186	0.0186	±0.0000
8	0.100	0.0249	0.0248	—0.0001

The choice of methods for the reduction of the iron is largely a matter of personal preference, since both give equally good results as seen in the tables of test analyses given above. However it may be said that the reduction of the iron in our ammoniacal solution is somewhat quicker than that by sulfur dioxide in a hydrochloric acid solution.

In applying this method to the determination of titanium in some ores, which were previously found to be completely decomposed by acid treatment, the procedure was as follows: To 0.5 gram of very finely pulverized sample, 25 cc. of concentrated hydrochloric acid were added and the solution was heated upon the steam bath until no further action was observed. About 20 cc. of 1 : 2 sulfuric acid were added and the solution was cautiously evaporated to sulfuric acid fumes and then heated for an hour at a temperature just below the boiling point. After cooling, 30 cc. of water were added and the solution was warmed until the soluble salts had dissolved. The insoluble matter was filtered, washed three times with very dilute sulfuric acid, and finally with water at room temperature. The insoluble matter was tested and was found to be free from titanium. The filtrate was diluted to exactly 500 cc., mixed thoroughly, and aliquot parts were taken so that the ignited precipitate would not weigh over 90 mg., as it was not practical to attempt the filtration of larger amounts of this gelatinous precipitate. To each aliquot part 2 grams of tartaric acid were added and the method from this point was identical with that described above. Three titanic iron ores were analyzed with the following results.

Ore	Ti found	Ti by the volumetric method[1]
A	13.00%	13.18%
A	13.17	...
A	13.20	...
B	24.19	...
B	23.99	24.22
B	24.22	...
C	15.82	...
C	15.86	15.94
C	16.01	...

It is recommended that for the general application of this method to the determination of titanium in the presence of relatively large amounts of iron, the titanium be precipitated from a solution of about 100 cc. volume which contains 15 cc. of 1 : 1 hydrochloric acid. Furthermore, it is recommended that enough substance be taken so that at least 10 mg. of titanium shall be present in the solution.

It was found that titanium could be separated from aluminium and determined in the same manner as when iron is present, but that it was necessary to use more hydrochloric acid in order to prevent the precipitation of aluminium phosphate. The method employed was to add 1–2 grams of tartaric acid to the solution of titanium and aluminium sulfates and enough ammonia to make it slightly alkaline. (The tartaric acid was used to prevent the formation of the hydroxide.) Then a measured quantity of hydrochloric acid was added and the analysis was completed in the same way as when iron was present. A volume of about 100 cc. was used in the following experiments:

No.	AlO taken	Ti taken	Ti found	Error	Cc. conc. HCl used
1	0.063	0.0273	0.0277	+0.0004	10
2	0.060	0.0310	0.0308	—0.0002	12
3	0.070	0.0248	0.0245	—0.0003	10
4	0.063	0.0248	0.0249	+0.0001	9
5	0.110	0.0210	0.0214	+0.0004	10
6	0.100	0.0260	0.0263	+0.0003	11
7	0.120	0.0310	0.0309	—0.0001	14
8	0.060	0.0223	0.0224	+0.0001	15
9	0.060	0.0186	0.0189	+0.0003	8
10	0.050	0.0186	0.0182	—0.0004	15
11	0.070	0.0248	0.0245	—0.0003	10
12	0.060	0.0122	0.0119	—0.0003	7
13	0.050	0.0248	0.0292	+0.0044	5
14	0.100	0.0310	0.0473	+0.0163	5
15	0.150	0.0186	0.0233	+0.0047	7
16	0.100	0.0248	0.0288	+0.0040	5
17	0.070	0.0310	0.0351	+0.0041	7

These experiments indicate that with a volume of 100 cc. containing 0.05–0.15 gram alumina it is necessary to have an excess of at least 8 cc. of concentrated hydrochloric acid in order to get a satisfactory separation of the titanium.

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THE DETERMINATION OF PHENOL IN THE PRESENCE OF HEXAMETHYLENETETRAMINE AND FORMALDEHYDE

By L. V. Redman, A. J. Weith and F. P. Brock

Received December 2, 1913

During a research into the rate of condensation between phenols and active methylene groups in the production of synthetic resins it became necessary for us to find a rapid and accurate method for the determination of phenols in the presence of substances containing methylene groups, *e. g.*, formaldehyde, hexamethylenetetramine, etc.

In previous papers[1] we have described a bromination method which serves for the very accurate and rapid quantitative determination of phenol in a water solution. The method consisted in diluting the phenol to *N*/1000, in acid solution, shaking the solution for 1 minute after the bromide-bromate solution is added, then adding KI, shaking again for 1 minute and titrating the excess iodine with thiosulfate. The whole operation was carried out at 20–25° C.

The present paper deals with the determination of phenol in a water solution in the presence of hexamethylenetetramine or formaldehyde or both, using the above method with whatever modifications are mentioned later in this paper.

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[1] A modification of the method in Gooch's "Methods in Chemical Analysis," page 242.

[1] Redman and Rhodes, This Journal, **4** (1912), 655; Redman, Weith and Brock, *Ibid.*, **5** (1913), 389.

The first of these probable interfering substances to be tried was hexamethylenetetramine and the results are given in the accompanying table. Hexamethylenetetramine does not interfere in the determination of phenol by bromine when present up to 1 per cent of the total solution,[1] *i. e.*, 30 mols. of hexamethylenetetramine to 1 mol. of phenol. Much larger amounts than this have been tried. As much hexamethylenetetramine as 15 per cent of the total solution, *i. e.*, 450 mols. of hexamethylenetetramine to 1 mol. of phenol, has been added in a single determination of the phenol without changing the results. The only intermediate change noted when the hexamethylenetetramine was present in large quantities was a tendency on the part of the free iodine to form a brick-red granular precipitate, or a beautiful iridescent crystalline precipitate with the excess hexamethylenetetramine. This precipitate which is either the tetra-iodo-hexamethyltetramine or di-iodo-hexamethyltetramine dissolves up readily on the addition of the thiosulfate giving back the free iodine, and does not in any way interfere in the quantitative determination.

The presence of free formaldehyde, however, interferes very seriously with the phenol determination. Results that are 7–8 per cent too high are obtained when the total solution is one per cent formaldehyde as is shown in the table (Expts. 5 and 6). The higher the percentage of formaldehyde present the higher the results which are obtained for the phenol present in the solution until, for 40 per cent formaldehyde, bromine is absorbed in very large quantities and no precipitation of tribromphenol takes place, and the determination of phenol by this method is quite impossible.

It is evident then that if hexamethylenetetramine does not interfere with the determination, and formaldehyde does interfere, the addition of ammonia to the solution in which formaldehyde is present as an interfering substance may, by forming hexamethylenetetramine with the aldehyde obviate the trouble.

The addition of ammonia to a phenol solution containing formaldehyde was tried and the results are given in the table, Expts. 7, 8, 9, 10. If the unknown phenol solution be made 2 *N* with ammonia and the whole allowed to stand for 5 minutes, the formaldehyde is transformed over into hexamethylenetetramine or some intermediate non-interfering compound and the determination of the phenol may be made with speed and accuracy. Allowing the ammonia, formaldehyde and phenol to remain together in the water solution longer than 5 min., *e. g.*, 18 hours, before the determination is made does not affect the results as is shown in Expts. 9 and 10.

This method of determining phenol in the presence of formaldehyde would not hold if a condensing agent had been present previously or if the solution had been treated in a way which tended to form oxybenzyl-alcohol, saligeno-saligenin, etc.

In determining phenol in the presence of hexamethylenetetramine the bleaching of the starch iodide color by the thiosulfate is slightly retarded by the presence of hexamethylenetetramine and it is necessary to give a few seconds after the addition of the thiosulfate to allow the blue color time to disappear.

No.	Amount of interfering substance	Cc. of NH_3 added	Time after ammonia was added, to detn.	Cc.'s of HCl added	Cc.'s Br sol. used	Thiosulfate sol. used	Per cent of phenol determined
1	......	0	.....	6	16.92	3.42	100
2	......	0	.....	6	17.10	3.59	100
3	1 gram hexa.	0	.....	6	16.97	3.56	99.36
4	1 gram hexa.	0	.....	6	18.68	5.17	100.19
5	3 cc. 40% CH_2O	0	.....	6	17.00	2.52	106.92
6	3 cc. 40% CH_2O	0	.....	6	18.46	3.70	108.32
7	3 cc. 40% CH_2O	10	5 min.	17	16.40	2.92	99.72
8	3 cc. 40% CH_2O	10	5 min.	17	15.89	2.40	99.50
9	3 cc. 40% CH_2O	10	18 hrs.	17	16.98	3.54	99.50
10	3 cc. 40% CH_2O	10	18 hrs.	17	16.62	3.16	99.51

Water of dilution = 100 cc.
Phenol solution used = 15 cc.
Bromide-bromate sol. = 0.09970 *N*.
Hydrochloric acid = 37% solution.
N/10 ammonia = 28% solution.
Thiosulfate = 0.09825 *N*.

CONCLUSIONS

I. Phenol in the presence of hexamethylenetetramine may be determined by the method already described for the determination of phenol.

II. Formaldehyde interferes with the volumetric determination of phenol by bromine.

III. The addition of strong ammonia to the phenol-formaldehyde solution forms with the aldehyde, hexamethylenetetramine or some intermediate ammonia-aldehyde product which does not interfere with the quantitative determination of phenol.

Department of Industrial Research
University of Kansas, Lawrence

ULTIMATE ANALYSES OF COAL TAR PITCHES

By C. R. Downs

Received December 6, 1913

In connection with an investigation of coal tar pitches, the ultimate analyses of some briquet pitches were obtained.

Analyses of Three Typical Coal Tar Briquet Pitches of American Origin

	Pitch No. 1 Per cent	Pitch No. 2 Per cent	Pitch No. 3 Per cent
Carbon	92.05	92.37	93.09
Hydrogen	4.83	4.96	5.01
Nitrogen	0.95	0.61	0.89
Sulfur	0.92	1.00	0.85
Mineral ash	0.09	0.78	0.35
Oxygen (by difference)	1.16	0.28	0.00
Free carbon	33.7	31.3	26.4

Melting point 112° C., 87° C., 84° C.

The carbon and hydrogen were determined by the regular combustion method, taking proper precautions to eliminate the sulfur and nitrogen. The sulfur was determined by combustion in a bomb with oxygen under pressure (sodium peroxide being used to insure complete oxidation), and precipitated as barium sulfate. The Kjeldahl method was used for the nitrogen.

The melting points and free carbon contents of the pitches were also determined in the usual way.

Research Department Laboratory
Barrett Manufacturing Co., New York

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[1] The total solution refers to the volume after the dilution has been made with the water and acid, before adding the bromine solution.

NOTE ON THE DETECTION OF NICKEL IN FATS

By Robert H. Kerr

Received November 22, 1913

In testing samples of cottonseed oil, hydrogenated cottonseed oil, and mixtures of fats containing cottonseed oil, for nickel by the method of Boemer[1] a fugitive red color sometimes appears after the addition of the dimethylglyoxime and ammonia. This color closely resembles that obtained when a trace of nickel is present, but differs from that of nickel dimethylglyoxime, in that it is fugitive, appearing immediately after the addition of the ammonia, never before, and fading away almost entirely within a few minutes. Its appearance is apt to be very confusing, particularly to one not thoroughly familiar with it.

As there is no known inorganic body capable of giving such a reaction with dimethylglyoxime, it would appear probable that this reaction is due to some organic base contained in the oil and extracted from it by the hot hydrochloric acid. The fact that this reaction has been observed only with cottonseed oil, taken together with the well known fact that cottonseed contains numerous basic organic bodies, appears to corroborate this view. This hypothesis leads naturally to the conclusion that the trouble might best be prevented by the complete destruction of all organic matter contained in the acid extract.

Experiments have upheld this conclusion. A number of samples which had previously been found to show the fugitive red color to a marked degree have been found to show no trace of it after the destruction of all organic matter in the acid extract. As a result of this observation the following modification of the Boemer method is now proposed for the detection of nickel in fats.

Ten grams of the fat to be tested are heated on the steam bath with 10 cc. of hydrochloric acid (specific gravity 1.12), with frequent shaking for 2–3 hours. The fat is then removed by filtering through a wet filter paper, the filtrate being received in a white porcelain dish. The filtrate is evaporated to dryness on the steam bath, 2–3 cc. of concentrated nitric acid being added, after it has been partly evaporated, to insure the destruction of all organic matter. After the evaporation is complete the residue is dissolved in a few cubic centimeters of distilled water and a few drops of a one per cent solution of dimethylglyoxime in alcohol added. A few drops of dilute ammonia are then added. The presence of nickel is shown by the appearance of the red colored nickel dimethylglyoxime. The amount of nickel present may be estimated by comparing the color developed with that developed in a standard solution of a nickel salt.

A considerable number of samples, some of which had previously been found to give the fugitive color mentioned above, have been examined by this method without any instance of the appearance of color not due to nickel. The residues from the evaporation are also purer and more readily soluble than when nitric acid is not used. A larger sample of the fat may be taken if desired. If this is done the amount of hydrochloric acid used for extraction as well as the amount of nitric acid added to the filtrate should be correspondingly increased. Samples as large as 200 grams have been handled with satisfactory results.

Biochemic Division, Bureau of Animal Industry
U. S. Department of Agriculture
Washington

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[1] *Chem. Rev. Fett. u Harz. Ind.*, Jahr. **19**, Heft 9.

RECENT ANALYSES OF THE SARATOGA MINERAL WATERS. IV

By Leslie Russell Milford

Received December 6, 1913

That the restoration of the mineral waters to the Saratoga basin is being accomplished, is evident by the data which the Reservation Commission has secured since the State undertook its protective policy with regard to the springs. A great amount of information is available concerning the conditions of the springs, the influences which cause them to flow and also those which affect the flow and degree of mineralization of the water. A few years will have to elapse before the springs will have adjusted themselves to all natural conditions which were present before the gas companies began pumping the gas from the wells. Whether or not the former degree of mineralization will ever be reached cannot be stated, but a uniform head, steady flow and fair degree of mineralization has been obtained.

The amount of minerals which these waters held in solution was dependent on the quantity of carbon dioxide which impregnated the water and the pressure exerted at the mineral water vein. For over twenty years, as was stated in a previous paper, an exhaustive pumping of this gas was carried on and a great depletion of the mineral water basin took place, depriving the area of a great amount of energy which nature had furnished for the maintenance of her natural fountains. Since April, 1911, weekly chlorine and alkalinity tests have been made on these waters, by the writer, and these determinations show a fairly constant mineralization varying only with slight physical disturbances. As the main constituents of these waters are the chlorides of sodium, potassium, lithium and ammonium and the bicarbonates of calcium, magnesium, sodium, and barium, these two determinations, chlorine and alkalinity, gave a quick estimation of over 90 per cent of the total mineralization. If either of these should show a change we would have some idea from week to week concerning the condition of the springs.

DESCRIPTION OF THE SPRINGS

The Geyser Spring is situated under the old nut and bolt factory near Geyser pond. It was drilled in 1870 with the intention of securing a supply of fresh water but unexpectedly produced mineral water, the vein having been struck at about 142 feet below the surface of the ground. This spring became very famous and was frequently called the "spouting spring." Its discovery first suggested the idea of boring artesian wells for mineral water and the creation of the carbonic acid gas industry. This spring originally had a large flow and would throw a stream 25 feet above the ground. This gradually died out and the spring failed to flow for many years, so special attention was given this bore by the Reservation Commission in order to restore the flow.

Ions, Radicals and Oxides Determined. Results in Milligrams Per Liter

	Geyser spring			Washington spring		Old red spring		New red spring	Columbian spring	
	1	2	3	4	5	6	7	8	9	10
Date of analysis	——1871	Aug. 12, 1905	July 3, 1912	—— 1843	Sept. 4, 1912	——a——	Aug. 14, 1912	July 17, 1912	——a——	Apr. 9, 1913
Formula										
SiO_2	12.39	20.80	14.80	25.70	41.25	55.76	51.75	79.40	35.12	47.80
SO_4	3.00	1.40	13.08	0.69	19.96	(a)	5.35	6.39	(a)	40.13
HCO_3	5344.61	4353.20	3540.10	2192.15	1618.84	2116.55	1138.64	1463.22	1818.80	1315.08
NO_3	(a)	Trace	Trace	(a)	0.09	(a)	Trace	Trace	(a)	1.77
NO_2	(a)	None	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
PO_4	Trace	None	None	(a)	None	(a)	None	None	(a)	None
BO_2	Trace	Trace	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
AsO_4	None	None	None	(a)	None	(a)	None	None	(a)	None
Cl	6030.43	1025.10	1340.06	1909.64	468.55	923.78	226.24	541.87	2774.28	225.34
Br	29.92	11.80	13.64	5.42	2.39	(a)	2.39	8.18	Trace	8.05
I	3.59	1.00	0.76	32.54	0.19	(a)	0.46	0.30	37.12	0.07
Fe	5.26	(a)	9.46	(a)	36.60	(a)	10.72	12.56	29.96	9.18
Fe and Al	(a)	8.40	11.83	20.44	66.46	25.18	24.82	19.99	(a)	10.85
Al_2O_3	Trace	(a)	4.48	Trace	56.31	Trace	26.58	14.02	(a)	3.14
Mn	(a)	(a)	Heavy trace	(a)	None	(a)	Trace	Heavy trace	(a)	None
Ca	2913.70	116.40	426.85	357.47	231.93	428.96	190.12	281.95	288.08	217.28
Mg	424.42	60.60	116.02	190.98	100.28	120.75	53.96	73.71	132.98	74.17
Ba	18.24	2.60	4.12	(a)	1.41	(a)	2.82	2.70	(a)	1.06
Sr	3.04	Trace	0.48	(a)	None	Trace	Trace	Trace	(a)	0.10
K	222.35	29.00	136.04	2.65	78.20	61.60	32.83	38.88	Trace	47.47
Na	4123.56	2010.90	1386.65	1277.15	386.49	634.85	222.68	400.07	1878.39	234.39
Li	12.35	3.60	2.76	(a)	0.80	1.66	1.35	1.41	(a)	0.61
NH_4	(a)	11.40	14.62	(a)	2.25	(a)	2.27	3.45	(a)	1.64
Oxygen to form Al_2O_3	Trace	(a)	2.11	Trace	26.45	10.79	12.48	6.59	(a)	1.47
Oxygen to form Fe_2O_3	...	...	...	...	...	...	...	...	...	...
F	Trace	...	...	...						
Hypothetical Form of Combination										
NH_4Cl	(a)	33.80	39.40	(a)	6.68	(a)	6.74	10.23	(a)	5.15
LiCl	74.91	21.80	16.75	(a)	5.00	10.07	8.19	8.53	(a)	3.70
KCl	395.23	43.90	246.84	(a)	146.89	117.46	60.22	66.66	(a)	82.93
NaCl	9528.76	1588.80	1951.08	3148.23	643.05	1416.99	307.12	817.85	4573.71	295.59
KBr	43.88	17.50	20.00	8.07	3.50	(a)	3.50	12.00	Trace	12.00
KI	4.71	1.30	1.00	(b) 42.65	0.25	(a)	0.60	0.40	(c) 48.55	0.10
Na_2SO_4	4.44	2.10	19.36	1.02	29.52	(a)	7.91	9.46	(a)	59.34
$NaBO_2$	Trace	Trace	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
$NaNO_3$	(a)	Trace	Trace	(a)	0.12	(a)	Trace	Trace	(a)	2.43
$NaNO_2$	(a)	None	Trace	(a)	Trace	(a)	Trace	Trace	(a)	Trace
$Na(HCO_3)$	1363.26	5058.30	2238.22	139.62	452.54	282.57	362.63	275.32	288.38	358.76
$Ba(HCO_3)_2$	34.44	4.90	7.78	(a)	2.67	(a)	5.33	5.10	(a)	2.00
$Sr(HCO_3)_2$	7.27	Trace	1.14	(a)	None	Trace	Trace	Trace	(a)	0.23
$Mg(HCO_3)_2$	2553.77	364.90	704.24	1149.15	603.38	726.54	324.70	447.42	800.14	446.29
$Ca(HCO_3)_2$	2913.70	471.40	1728.78	1445.41	937.82	1734.52	768.75	1141.89	1164.84	878.58
$Fe(HCO_3)_2$	16.74	26.70	30.08	65.09	116.56	(a)	34.14	39.94	95.42	29.34
Mn_3O_4	(a)	(a)	Heavy trace	(a)	None	(a)	Trace	Heavy trace	(a)	None
Fe_2O_3	....	...	....	...	...	35.97	...	...	(a)	...
Al_2O_3	Trace	(a)	4.48	Trace	56.31	...	26.58	14.02	(a)	3.14
SiO_2	12.39	20.80	14.80	25.70	41.25	55.76	51.75	79.40	35.12	47.80
Total solids in solution (computed)	16953.50	7656.20	7023.92	6014.83	3045.54	4379.88	1968.16	2928.22	6994.73	2227.28
Residue on evaporation dried at 105° C.	(a)	(a)	5232.00	(a)	2175.00	(a)	1266.50	2138.00	(a)	1471.00
Temperature	7.8° C.	(a)	10.0° C.	7.2° C.	9.5° C.	(a)	11.1° C.	11.6° C.	10° C.	8° C.
Organic matter	Trace	...	....	...	...	...	...	...	...	...

(a), not given. (b), equivalent of NaBr reported. (c), equivalent of NaI reported.

1 = C. F. Chandler. Hydrotherapy at Saratoga by J. A. Irwin, 1892.
2 = Mineral waters of the U. S. U. S. Dept. of Agric., Aug. 12, 1905.
3,5,7,8,10 = Files N. Y. State Dept. of Health, 1912 and 1913.
4 = J. R. Chilton. Hydrotherapy at Saratoga by J. A. Irwin, 1892.
6 = Prof. Appleton Bulletin No. 32, U. S. Geological Survey.
9 = J. H. Steel. "An Analysis of the Mineral Waters of Saratoga, etc.," 1838.

Other References

Advertised analyses in various circulars.

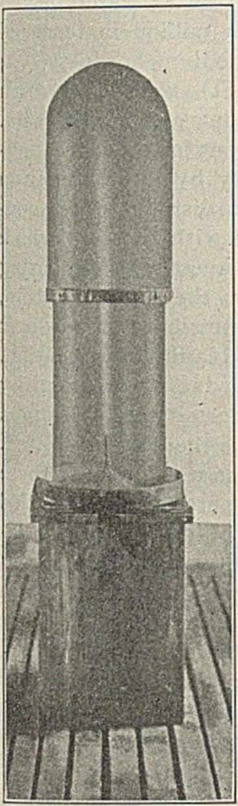
Therapeutic Saratoga—American Medical Association, June, 1902.

Mineral waters of the U. S. and their therapeutic uses by J. H. Crook, 1899.

The mineral springs of Saratoga, N. Y. State Education Dept. Museum, Bulletin No. 159 by James F. Kemp, 1912.

It was found upon careful investigation that the bore was very crooked and irregular and was filled to a considerable depth with foreign matter. It was therefore reamed to a uniform size, cleaned and explored from top to bottom in order to locate the best mineral water vein. The tubing was completed in June, 1912, and an excellent spring, spouting many feet above the level of the flow, was secured. This revival was brought about by placing water columns on the two Champion springs which were wasting about

200 gallons per minute and seemed to be the key to the control of the mineral water basin. This spring was cleaned again in April, 1913, and now has a flow of about one gallon per minute. The water is strongly mineralized, being low in chlorides but high in sodium and magnesium bicarbonates. The water is an excellent table water and is served at the spring.


Geyser Spring

Old Red Spring—This spring is situated on Spring Avenue and was discovered in 1770 or about as soon as the locality was visited by white men, being the next spring found after the discovery of the famous "High Rock." In 1784, the first bath house was erected on the property. From that time up to the acquirement of the spring by the Reservation Commission several bath houses had been built on the site of the old one and various improvements were made in the spring. The flow for many years was sufficient to maintain the baths and allow the water to be bottled. The spring had a reputation for the great curative properties of its water and was a famous resort in the days of Saratoga's popularity. When the state took over this property the bath houses, bottling house and equipment were old, crude and unsuitable for continuance under State ownership so the buildings were taken down. The spring itself was also in bad condition, the wooden tubing being neither sanitary nor permanent. In July, 1912, it was decided to retube the spring, and to avoid excavating an eight inch steel casing was inserted into the wooden tubing, and the space between the two packed with concrete. After retubing, the natural flow was slightly greater than before but was not enough to meet the demands for bathing or bottling without resorting to pumping. The spring is 22 feet deep and has a flow of about one quart per minute. The water is moderately mineralized averaging with that of the Columbian. It is one of the famous iron springs and derived its name from the red coloration due to iron which the water contained.

The New Red Spring is situated on this same property about 100 feet southeast of the Old Red Spring. It was drilled in 1885 and is 60 feet deep. The water of this spring is high in iron content and is served to the public. It has a flow of about two quarts per minute and in mineralization it approaches the Washington.

Washington Spring—This spring is situated on South Broadway just above Congress Park in the old Clarendon Hotel property. It was discovered in 1806 and is 170 feet deep. The water does not flow at the surface of the ground but is obtained by pumping. The spring had a celebrated reputation for its iron content and was used to a great extent. The property does not belong to the Commission but is owned by the St. Peters Catholic Church. Various scientific observations, which have been taken, show an improvement in this spring.

The Columbian Spring is located in the famous Congress Park, just west of the park entrance and on Broadway. It is one of the oldest mineral springs having been opened by a pioneer, Gideon Putman, in 1806. This is also a chalybeate water being closely connected with the Washington Spring as like changes in water levels are recorded simultaneously in both springs.

In April, 1913, the wooden tubing was cleaned and an iron casing inserted in it so as to insure sanitary conditions. The spring is eleven feet deep and its waters are moderately mineralized.

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THE DETERMINATION OF HARDNESS IN NATURAL WATERS

By Clarence Bahlmann

Received December 1, 1913

Lime hardness, magnesium hardness, and total hardness constitute the three primary determinations in industrial water analyses. An alkalimetrical method for total hardness by use of soda reagent is described in the American Public Health Association's Standard Methods of Water Analysis. Mention is made that errors due to solubility of the precipitated calcium and magnesium salts are not entirely obviated in this method, and that the most accurate figure for total hardness is that computed from the results for calcium and magnesium. This is true when these bases are determined gravimetrically, but when the magnesium is determined by Pfeifer and Wartha's lime water method as described in the 1905 edition of Standard Methods, the results are unsatisfactory. For this reason undoubtedly, this method has not been inserted in the 1912 edition of the above publication; in fact no volumetric method is given for either calcium or magnesium.

For many industrial purposes, rapidity in arriving at results is preferred to extreme accuracy, and simple volumetric methods are entirely satisfactory for ordinary purposes provided the deficiencies and limits of accuracy of the method are known. This paper is a summary of an investigation to ascertain the accuracy of results obtained by certain volumetric procedures for calcium, magnesium and total hardness. The tests were made upon fifteen samples of natural waters obtained from nearby rivers, springs and wells, and showing wide ranges in calcium and magnesium content as well as in organic matter.

CALCIUM HARDNESS

The ease of manipulation and accuracy of the permanganate titration of calcium oxalate suggests its applicability in water analysis. Depending upon the hardness of the water, volumes of 100 cc. to 500 cc. will give workable precipitates. Fifteen waters ranging in lime hardness from 33.8 to 360.5 parts per million $CaCO_3$ were examined. In only one instance did the volumetric result vary from the gravimetric by more than 2.5 parts per million $CaCO_3$; the average variation for the 15 samples was only 1.2 parts per million. The greatest percentage error was 3.2 per cent and, as an average, 99.6 per cent of the gravimetric results was found by the volumetric procedure. These results are in entire accord with those reported by R. B. Dole,[1] who states that it is possible to estimate calcium volumetrically to within 1 part per million (2.5 parts per million $CaCO_3$).

MAGNESIUM HARDNESS

The principle of Pfeifer and Wartha's method[2] for magnesium is that when lime water is added to a neutral solution of calcium and magnesium salts, the calcium salts remain unaltered while those of magnesium are precipitated as hydroxide, the lime water consumed being a measure of the magnesium present. The waters tested ranged in magnesium hardness from 15 to 295.6 parts per million, expressed as an equivalent amount of $CaCO_3$.

The same volume of lime water was added to all of these waters, and consequently the percentage of the added lime water consumed in the reaction increased as the magnesium hardness increased. If the accuracy of this method depends solely upon excess of precipitant, then we should expect the results to approach nearer to the true figures as the percentage of the lime water consumed in the reaction is decreased. The results, however, showed no relation whatsoever between excess of precipitant and accuracy of the volumetric results. On 4 samples (magnesium content from 15.0 to 20.9 p. p. m.) the percentage of added lime water theoretically needed to precipitate the magnesium varied only from 2.8 per cent to 3. 9 per cent, yet the volumetric results ranged from 60 per cent to 86.1 per cent of the gravimetric amounts. Of two samples of practically the same magnesium content (21.8 and 23.0 p. p. m.), the volumetric result was in one case 82.6 per cent and, in the other, 113 per cent of the true figure.

The magnesium hardness was determined twice on 6 of the samples, using 25 cc. and 50 cc. of the lime water. In this way the effect of varying excesses of precipitant upon the accuracy was studied when working with the same water. With 3 of these samples, the best results were obtained where the lesser percentage of lime water was theoretically required in the reaction, but with the other samples just the reverse was true. In the whole series, only 6 determinations gave results within 10 per cent of the correct figures, and these showed a variation in the percentage of added lime water theoretically needed of from 6.1 per cent to 57.6 per cent.

An excess of lime water is undoubtedly necessary and, while further study upon waters of the same general character might reveal certain limits of excess giving optimum results, it appears from the above work that the amount of excess varies with the nature of the water. Even under the best conditions, magnesium hydroxide is appreciably soluble, causing low results. Another factor involved is the presence and relative concentration of other dissolved salts and organic matter. It is needless to state that no reliance can be placed upon any procedure exhibiting discrepancies such as shown above by the lime water method for magnesium.

TOTAL HARDNESS

The range in total hardness of the 15 waters tested was from 48.8 to 655.5 parts per million in terms of $CaCO_3$. For waters of low or medium hardness 0.04 N soda reagent and 0.02 N H_2SO_4 were used, with harder waters, 0.1 N soda reagent and 0.1 N acid. The original titer of the soda reagent in terms of standard acid was determined not only by direct titration but by a blank determination on distilled water conducted under conditions identical with those to which the sample was subjected. As an average, when basing the value of the soda reagent upon the direct titration, only 83.7 per cent of the gravimetric total hardness was found, but on the basis of the blank determination, 95.8 per cent of the true total hardness was found by the volumetric method. The necessity of making a control determination in all cases is therefore indicated.

The same volume of soda reagent was added to these waters and it follows that the percentage of added alkali consumed increased as the total hardness increased. When only 7.2 per cent of the precipitant was used up in the reaction, the volumetric result was 100.4 per cent of the gravimetric, and the percentage of the true amounts found by the volumetric method decreased in fairly regular amounts as the percentage of soda reagent required for the reaction increased. When as much as 79.7 per cent of the added alkali was consumed, only 76.8 per cent of the gravimetric total hardness was obtained by the volumetric method.

It is evident from the above that low results are to be attributed to insufficient excess of the precipitant. Several of the samples, on which 50 cc. of 0.04 N soda reagent had been used, were examined again, using 25 cc. of 0.1 N soda reagent. This trial indicated that the best result on any one sample was always obtained where the largest excess of alkali was present. Twenty-five determinations were made upon the 15 waters and all results were within 5 per cent of the true figures when not over 35 per cent of the soda reagent was consumed in the reaction. The relationship existing between the percentage of added soda reagent theoretically required in the reaction and the accuracy of the volumetric result for total hardness is shown in the following table:

Per cent of added soda reagent theoretically required	No. of determinations	Average per cent of gravimetric total hardness found by volumetric method
0–10	2	100.4
10–20	6	99.1
20–30	4	97.5
30–40	4	96.3
40–60	4	94.1
60–80	5	89.1

It appears from this table that the best volumetric

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[1] Geological Survey, *Water Supply Paper* **236**, 28.

[2] *Z. anal. Chem.*, **1902**, 199.

results are obtained when the soda reagent is added in such quantities that not more than 20 per cent of it enters into the reaction, and that the results are within 5 per cent of the true amounts when not more than 40 per cent of the alkali is used up.

MAGNESIUM HARDNESS BY DIFFERENCE

It has been shown that the soda reagent method for total hardness is quite satisfactory for ordinary work if care be taken to have sufficient excess of the alkali present, and that the permanganate titration for calcium is very accurate. When the magnesium is computed by difference, it suffers from the errors of the 2 direct methods and low results are to be expected because the total hardness figures are themselves low, due to the appreciable solubility of normal calcium carbonate and magnesium hydroxide. With certain waters, however, very close results can be obtained by this method. Seven of the samples, showing a range in hardness encountered in the Ohio River at this locality (48 to 130 p. p. m. total hardness; 15 to 37 p. p. m. magnesium hardness), gave very satisfactory results for magnesium by difference, the average percentage of the true amount being 98.6 per cent. With waters ranging in total hardness from 136 to 655.5 p. p. m. and in magnesium hardness from 63.8 to 295.6 p. p. m., however, the average accuracy was but 90.3 per cent. In such hard waters a comparatively small percentage error in the total hardness affects the magnesium to a greater extent, especially if the sample contains a relatively small quantity of this base in comparison to the lime content.

It appears then, that with comparatively soft waters a procedure, whereby the total hardness and calcium hardness are determined volumetrically as outlined above and the magnesium by difference, is satisfactory for ordinary purposes. This method can also be applied to hard waters the general character of which is familiar to the analyst, provided he applies a correction factor determined by occasional comparisons of the volumetric with gravimetric results. Hard waters very low in magnesium as compared to calcium content will give the least satisfactory results, and the gravimetric method for magnesium must be resorted to in this case if accurate figures are desired.

SUMMARY

I. No volumetric methods for calcium or magnesium are given in the 1912 edition of Standard Methods of Water Analysis.

II. For ordinary purposes, rapidity is preferred to extreme accuracy, and volumetric methods are desired.

III. The estimation of calcium by titration with permanganate is easily and quickly performed and the results are very accurate.

IV. The estimation of magnesium with lime water is entirely unreliable.

V. The best results for total hardness are obtained when less than 20 per cent of the soda reagent is used up in the reaction, and the results will be within 5 per cent of the true amount when not more than 40 per cent of the soda reagent is consumed. The original strength of the soda reagent must be determined by a blank determination.

VI. An ordinarily satisfactory procedure for examination of waters of low or medium hardness consists in determining the total hardness with soda reagent, the lime hardness with permanganate and ascertaining the magnesium content by difference. This method can also be used for hard waters by applying a correction factor. For very hard waters containing only small amounts of magnesium, this base must be determined gravimetrically if accurate results are desired.

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THE QUANTITATIVE ESTIMATION OF THE SALT-SOLUBLE PROTEINS IN WHEAT FLOUR

By Geo. A. Olson

Received October 2, 1913

It has been repeatedly pointed out[1] that the strengths of alcohol suitable for the extraction of gliadin from flour, extracts other proteins besides gliadin. That this is unquestionably true was brought out by the writer in a previous article[2] on the estimation of gliadin in flour and gluten where it was found that the direct method for the extraction of the alcohol-soluble proteins gave considerably higher yield of nitrogen (38.3 per cent more) than could be obtained by either the indirect or coagulation methods.

Likewise it has been found[3] that 1 per cent sodium chloride extracts, besides edestin, leucosin and amino bodies, and some gliadin. Osborne[4] states that gliadin is practically insoluble in 10 per cent sodium chloride. From a quantitative point of view, it appears reasonable that a 10 per cent salt solution is the proper strength to use. But we find that a 10 per cent salt solution is impractical to work with owing to the large amount of salt present, and for this reason Teller,[5] and subsequently others, adopted strengths less objectionable. It was admitted by Teller and confirmed later by others by indirect methods that gliadin is partly soluble in 1 per cent salt solution, but just how soluble gliadin is no one has stated, nor even corrected for, when using this strength solution. A correction has been made for amide bodies by assuming that amide bodies are not precipitated by phosphotungstic acid. In the article referred to, the writer has pointed out the method for the estimation of the gliadin extracted by a 1 per cent salt solution and in connection with this the following experiments were conducted with the view of establishing a correct method for the estimation of edestin and leucosin proteins in flour.

Three different methods of procedure were adopted for the estimation of the salt-soluble proteins in flour. The first series of results was obtained by the method which is annually recommended to be followed by the

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[1] U. S. Dept. of Agr., Bur. of Chem., *Bull.* No. **81** and **90**.

[2] This Journal, **5**, 917.

[3] *Ark. Bull.* No. **53**; U. S. Dept. Agr., Bur. of Chem., No. **81** and No. **90**

[4] "The Proteins of the Wheat Kernel."

[5] *Ark. Bull.* No. **53**.

referee on vegetable proteins for the A. O. A. C.[1] with a view to its final adoption. The second series of results was obtained from a modified method of the first where the coagulable nitrogen was considered. The third series of results was obtained from a still further differentiation than that given in the second method in that the alcohol-soluble in the salt-soluble which is coagulable was considered. Besides this a series of results are given according to Method III where for comparison a 10 per cent sodium chloride solution was used instead of the 1 per cent solution.

Method I—Instead of using 5 g. of flour and 250 cc. of one per cent salt solution twice the amount was used. The mixture was shaken at intervals of 5 minutes for the first two hours and then let stand for 24 hours when filtered clear. Nitrogen determinations in the total and phosphotungstic acid precipitates were made and the difference between these two determinations was regarded as amide nitrogen. The results were as follows:

TABLE I—1 PER CENT SALT-SOLUBLE NITROGEN IN FLOUR (PERCENTAGES)

Number	Total N	Precipitated N	Amide N
O. C.	0.43	0.39	0.04
R. W. B.	0.38	0.29	0.09
B. L.	0.33	0.30	0.03
P.	0.50	0.41	0.09
L. C.	0.34	0.31	0.03
M 15.	0.40	0.36	0.04

The larger part of the nitrogen carrying bodies soluble in 1 per cent salt solution are precipitated by phosphotungstic acid. In the proposed method there is no differentiation made between the gliadin and edestin and leucosin nitrogens soluble in 1 per cent salt solution.

Method II—Instead of precipitating the salt-soluble proteins with phosphotungstic acid directly, aliquots of the salt-soluble were boiled down to within 20 cc. of liquid. The precipitate formed was filtered off and washed with water. The resulting filtrate was then treated with sufficient phosphotungstic acid, thoroughly mixed and allowed to stand one hour, when the resultant precipitate was removed and washed with water containing phosphotungstic acid. Nitrogen determinations were made in the total and the two precipitates. The difference of the sum of the nitrogens from these precipitates and the total nitrogen was reckoned as amide nitrogen. According to this method of procedure, the following results were obtained:

TABLE II—DIFFERENTIATION OF THE COAGULABLE NITROGEN IN 1 PER CENT SALT-SOLUBLE (PERCENTAGES)

Number	Total N	Coagulable N	Pptd. N	Amide N
O. C.	0.43	0.130	0.250	0.050
R. W. B.	0.38	0.045	0.230	0.105
B. L.	0.33	0.055	0.240	0.035
P.	0.50	0.125	0.275	0.100
L. C.	0.34	0.120	0.230	0.000
M. 15.	0.40	0.065	0.270	0.065

Since gliadin is appreciably soluble in 1 per cent salt solution, one would expect to find this material included with what has been generally estimated as albumin and globulin. The resulting data given in Table II do not show what portion of the nitrogenous bodies are gliadin bodies. Method II is better for the separation of the protein bodies soluble in one per cent salt solution than Method I, because the nitrogenous bodies coagulable by heat are separated from those not coagulable. The amounts of amide nitrogen obtained by difference in this method are practically identical with the amounts obtained in Method I.

The writer found in earlier investigations that it was possible to separate gliadin from the other salt-soluble proteins, and as a result of these investigations the following method for the estimation of the edestin and leucosin fractions in flour was adopted.

Method III—200 cc. aliquots of salt-soluble (10 grams of flour digested with 500 cc. of 1 per cent sodium chloride) were boiled down to within 20 cc. of liquid, then slowly evaporated to dryness on an iron hot plate. The solid was digested with 100 cc. of 55 per cent alcohol[1] by volume, filtered, then washed with same strength alcohol. The precipitate obtained was regarded as albumin. The alcohol filtrate was evaporated to within 10 cc. and 50 cc. of water added, boiled down to 35 cc., 15 cc. more water added, allowed to cool to room temperature and then filtered. The coagulum was washed with cold distilled water and reckoned as gliadin nitrogen. The coagulum filtrate was precipitated with phosphotungstic acid and reckoned as globulin nitrogen. The sum of the nitrogens obtained in the precipitates deducted from the total nitrogen leaves a small amount of unaccounted-for nitrogen which may be regarded as amide nitrogen. In Table III are given the results found according to this method.

TABLE III—INCLUDES THE ESTIMATION OF THE GLIADIN NITROGEN IN 1 PER CENT SALT-SOLUBLE (PERCENTAGES)

Number	Total N	Coag. N Insol. in alcohol	Gliadin N	Pptd. N	Amide N
O. C.	0.43	0.070	0.100	0.190	0.070
R. W. B.	0.38	0.080	0.095	0.140	0.065
B. L.	0.33	0.060	0.115	0.125	0.030
P.	0.50	0.125	0.160	0.165	0.050
L. C.	0.34	0.075	0.135	0.130	0.000
M. 15.	0.40	0.080	0.085	0.175	0.060

According to the results found and recorded in Table III it will be noted that the largest amount of nitrogen material soluble in 1 per cent salt solution was precipitated by phosphotungstic acid, which is nearly double that found in the coagulable insoluble in alcohol. The per cent of the alcohol-soluble which is coagulable is as much or more than the amount of nitrogen material insoluble in alcohol. In other words, there is very little nitrogen material extracted with 1 per cent salt solution that is not soluble in 55 per cent alcohol by volume.

In another series of experiments the same flours were digested with 10 per cent sodium chloride instead of 1 per cent solution. The method of procedure for the separation of the different nitrogen bodies was the same as that given in Method III. Owing to the large amount of salt present the alcohol separation method was tedious and slow. The various fractions for the nitrogen bodies soluble in 10 per cent salt solution are recorded in Table IV.

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[1] See proceedings of Association, issued as bulletins, Bureau of Chemistry, Department of Agriculture.

[1] Fifty per cent alcohol is just as efficient as alcohol of higher strengths.

Table IV—Includes the Estimation of the Gliadin Nitrogen in 10 Per Cent Salt-Soluble (Percentages)

No.	Total N	Coag. N insol. in alcohol	Gliadin N	Pptd. N	Amide N
O. C.	0.290	0.215	0.015	0.043	0.017
R. W. B.	0.210	0.175	0.010	0.005	0.020
B. L.	0.160	0.125	0.005	0.025	0.005
P.	0.310	0.268	0.010	0.020	0.012
L. C.	0.220	0.165	0.023	0.008	0.024
M. 15	0.260	0.203	0.007	0.040	0.010

As would naturally be expected, the per cent of nitrogen extracted with a 10 per cent salt solution is considerably less than that extracted with a 1 per cent salt solution. The reason for a much lower yield of nitrogen bodies is due to the increased concentration of the solute. It will be noted from the data given in Table IV that there is very little nitrogen material extracted which is soluble in 55 per cent alcohol by volume, and about 80 per cent of the total proteins soluble in 10 per cent salt solution are coagulated upon boiling down or increasing the salt concentration.

When the data for the total nitrogen and the various fractions obtained in the 1 per cent salt extraction are compared with those obtained in the 10 per cent salt extraction (see data in Tables III and IV), it will be noted that the amount of nitrogen material separated varies in any one group, depending upon the concentration of the solvent used for extracting these bodies. In the one case it is found that there is considerable gliadin and phosphotungstic acid precipitated nitrogen extracted, while in the other only a limited quantity is found which is not directly coagulable upon boiling the solution. The large amount of nitrogen bodies extracted by 10 per cent salt solution insoluble in 55 per cent alcohol by volume are insoluble in this strength of alcohol, owing to the concentration of the salt present. In Table V the sum of the figures given in Tables III and IV for alcohol insoluble and phosphotungstic acid precipitated nitrogen are compared with each other. In addition the total nitrogen in the 10 per cent salt solution with the gliadin correction has been included.

Table V—Results for Alcohol Insoluble and Precipitated Nitrogen in 1 and 10 Per Cent Salt-Soluble (Percentages)

No.	1 Per cent NaCl Alcohol insol. and pptd. N	10 Per cent NaCl Alcohol insol. and pptd. N.	Salt-sol. N — gliadin N
O. C.	0.260	0.258	0.275
R. W. B.	0.220	0.180	0.200
B. L.	0.185	0.150	0.155
P.	0.290	0.288	0.300
L. C.	0.205	0.173	0.197
M. 15	0.255	0.243	0.253

Having a method for estimating the gliadin nitrogen that may be extracted from wheat or its product by salt solution, it will be noted from the data presented in Table V that the amount of edestin and leucosin nitrogen is the same whether the concentration of sodium chloride be 1 or 10 per cent, providing the gliadin nitrogen is accounted for.

Referring again to the data given in Tables III and IV, it will be noted that the amount of nitrogen insoluble in 55 per cent alcohol in the 1 per cent salt extract is quite small and that of the nitrogen bodies precipitated by phosphotungstic acid is very large, while in case of the 10 per cent salt solution the per cent alcohol insoluble nitrogen is very large while only a noticeable amount of nitrogen is found in the phosphotungstic acid precipitate. These facts naturally raise the question, Are we dealing with true globulins and albumins? The quantitative data obtained and the method of procedure followed indicate that the substances spoken of as globulin and albumin are only such in 10 per cent sodium chloride solution, while in lower per cents of sodium chloride there is a smaller quantity of such material.

Again, if the substances extracted from flour with 10 per cent salt solution are globulin and albumin, then either one or both of these two materials in less concentrated salt solution, or water, are wholly soluble or partly soluble in 55 per cent alcohol or alcohol of higher strengths. This thought has weight in the preceding article on the estimation of the gliadin nitrogen in flour where it was found that approximately 68 per cent of the alcohol-soluble was coagulable by the direct method and corroborated in the indirect method of procedure and subsequent analyses. The data given for the alcohol-soluble uncoagulable nitrogen, where different strengths of alcohol were used, should also be considered in connection with this view.

There is sufficient reason to believe that the globulin and albumin of wheat are appreciably soluble in diluted alcohols even in the presence of 1 per cent sodium chloride solution. And since gliadin is appreciably soluble in 1 per cent salt solution, the methods that have been followed in the past where 1 per cent salt solution is used, includes gliadin as a part of globulin and albumin nitrogen and in the direct alcohol extraction of flour albumin and globulin are included as a part of the gliadin nitrogen. With 10 per cent salt solution only a very small part of the gliadin nitrogen is considered.

The amount of gliadin nitrogen extracted in salt solution depends upon the amount of salt used, being approximately 90 per cent more in a 1 per cent sodium chloride solution than was found to be the case in 10 per cent sodium chloride. The fact that the gliadin nitrogen can be removed from the salt solution regardless of the strength of salt used up to and including 10 per cent sodium chloride, makes the 1 per cent salt extraction method, owing to the more rapid filtering, more rapid digestion, etc., the most desirable one to follow. Omitting the determination for gliadin nitrogen and making the one for amide nitrogen in its place, renders the method of procedure for the estimation of edestin and leucosin nitrogen less difficult and is as follows:

Digest 10 grams of flour with 500 cc. of 1 per cent sodium chloride solution, shaking at intervals of 5 minutes for the first two hours, then allow to stand over night in a cool place. Filter clear and use aliquots of 200 cc. each. Boil to within 20 cc. of liquid; then slowly evaporate to dryness on iron hot plate. Digest the solid mass in each beaker with 100 cc. portions of 55 per cent alcohol by volume, filter, wash precipitate on filter paper with same strength alcohol. Determine nitrogen in this precipitate by the Kjeldahl method, and after correcting for filter paper, etc., by blank determinations, the difference found should be regarded as albumin nitrogen.[1]

Evaporate the alcohol filtrate to within 10 cc., add 50 cc. of distilled water, boil down to 35 cc., then add 15 cc. more of distilled water, allow to cool to room temperature and filter. Wash precipitate with cold distilled water. Owing to the sticky nature of this material and the difficulty in transferring the same to the filter paper, it is not advisable to make this determination.

The resulting filtrate obtained in the gliadin separation is treated with sufficient phosphotungstic acid to cause precipitation of the albumin filtered and washed with distilled water containing phosphotungstic acid. Nitrogen determinations in this precipitate should be corrected for by running blanks containing filter paper washed in phosphotungstic acid. The nitrogen obtained by difference is regarded as globulin nitrogen.

The nitrogen found in the phosphotungstic acid precipitate filtrate when properly corrected for is considered amide nitrogen. The total nitrogen found as amide, globulin and albumin when deducted from the total salt-soluble nitrogen is gliadin nitrogen extracted in the 1 per cent salt solution.

CONCLUSIONS

1. One per cent sodium chloride extracts from flour edestin, leucosin and gliadin.
2. The amount of gliadin extracted by 1 per cent sodium chloride solution approximately amounts to about 29 per cent of the total proteids.
3. The amount of gliadin extracted by 10 per cent sodium chloride solution approximately amounts to about 5 per cent of the total proteids.
4. The gliadin nitrogen extracted by solutions containing sodium chloride can be determined and corrected for in making edestin and leucosin nitrogen estimations of flour and its products.
5. The amount of nitrogen bodies extracted with salt solutions and directly coagulated by heat varies with the concentration of the solvent. The 10 per cent concentration gives higher results than was found possible with a 1 per cent salt solution.
6. The nitrogen bodies soluble in salt solution are partly or wholly soluble in diluted alcohols varying with the concentration of the sodium chloride used.

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AN INVESTIGATION OF THE PRESENCE OF FURFURAL IN CIDER VINEGAR

By Agnes A. Anderson

Received November 15, 1913

That pure cider vinegar contains volatile reducing substances has been known for some time and several methods have been given[2] for eliminating these substances in order to get the true amount of reducing sugars. The presence of furfural in these volatile reducing substances was discovered while doing routine vinegar analyses in the Kansas State Food Laboratory. Since nothing on the subject could be found in the literature an investigation was begun to determine its presence in normal cider vinegars. The results seem to warrant publication at this time.

Twenty-eight samples of cider vinegar of known purity were tested for furfural by the aniline acetate method as given by Leach.[1] Nineteen gave a positive test, nine being negative. These vinegars were made at the laboratory and their history known. In addition to these samples some farmers' vinegars were tested with similar results. From these results it is seen that furfural may be present normally in cider vinegars and its presence does not necessarily indicate added wood acetic acid.

In the *Abstract Journal* (7, 666) appeared a method by Ronnet for detecting added caramel in vinegar. This method is based upon the formation of furfural when sugar is heated in the process of making caramel, and makes use of the Fiehe resorcinol reagent.[2]

Since it appears that furfural is normally present in some cider vinegars, its presence can again be said not to indicate adulteration from caramel. This test for caramel was applied to the vinegars of known purity and in every case an affirmative result was obtained. Four of the samples tested for caramel did not give a test for furfural upon distillation, but gave a very positive caramel test. This may be due to decomposition of the sugar during the drying on the water bath. The water bath was carefully maintained at a temperature below 70° C. to avoid this possible decomposition, so this fact adds to the unreliability of the method. Caramel was added to some of the vinegars, but the resulting tests were not different from those to which none had been added.

Table I

No.	Variety	Furfural	No.	Variety	Furfural
P1	Winesap Pomace	Neg.	18	Gano	Aff.
P2	Pomace	Neg.	P18	Gano Pomace	Aff.
3	Jeneton	Neg.	19	Jeneton	Aff.
P3	Jeneton Pomace	Neg.	20	Winesap	Neg.
6	Jeneton	Aff.	21	Jeneton	Neg.
7	Clayton	Aff.	22	Roman Beauty	Neg.
8	Black Twig	Aff.	23	Winesap	Aff.
9	York Imperial	Aff.	24	Black Twig	Aff.
10	Ben Davis	Aff.	25	Missouri Pippin	Aff.
P10	Ben Davis Pomace	Aff.	A	Unknown	Aff.
12	Limbertwig	Aff.		Pomace of above	Neg.
P12	Limbertwig Pomace	Aff.	70284	Farmers' Vinegar	Aff.
14	Winter Greening	Aff.		Rotten apples	Neg.
15	York Imperial	Aff.	70284A	Farmers' Vinegar	Neg.
17	Winesap	Aff.	9373	Farmers' Vinegar	Aff.
P17	Winesap Pomace	Neg.	5159	Farmers' Vinegar	Neg.

Table II

No.	Variety	Caramel	Furfural test
A	Unknown	Good test	Aff.
9	York Imperial	Good test	Aff.
	York Imperial + Caramel	Good test	....
70284	Farmers' Vinegar	Good test	Aff.
5159	Farmers' Vinegar	Good test	Neg.
9373	Farmers' Vinegar	Good test	Aff.
	Rotten Apples	Good test	Neg.
70284A	Farmers' Vinegar	Good test	Neg.
21	Jeneton	Good test	Neg.

The above tables give the results; duplicate determinations are not included since in every case the results checked.

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[1] Globulin does not coagulate at temperatures below 100° C. (see "Proteins of Wheat Kernel," Osborne, Carnegie issue, p. 116).

[2] This Journal, **5**, 845, 928.

[1] Leach, "Food Inspection and Analysis," p. 777.

[2] Bur. of Chem., *Bull.* **154**, 15.

CONCLUSION

I. Pure cider vinegar may contain furfural as a natural constituent. Its presence, therefore, cannot be taken as indicating added wood acetic acid.

II. Since cider vinegars may contain furfural, its presence cannot be taken as indicating added caramel.

III. Cider vinegars may give a test for caramel by the Ronnet method without containing furfural or added caramel, hence the method is not reliable.

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SOME ABNORMAL FACTORS OF SO-CALLED FARMERS' CIDER VINEGARS

By John C. Diggs

Received Nov. 19, 1913

The following analyses were made of eighteen samples of vinegar which were entered in an apple product exhibit of an apple show held in Indiana. Instructions relative to the exhibit were to the effect that only legal cider vinegars should be entered.

Analyses of Vinegars

Lab. No.	Intensity of color	Pol. 200 mm. tube	Acidity	Total solids	Total sugars as invert	Non-sugar solids	Alcohol	Ash	Alk. of ash	Sol. P_2O_5	Insol. P_2O_5	Glycerine	Lead acetate ppt.	Ash / Non-sugars
7604 B	Medium	—1.8	9.56	5.09	0.63	4.46	2.91	0.757	52	16.8	36.2	0.51	Medium	1 : 5.9
7605 B	Light	—1.6	3.73	9.64	5.97	3.67	0.61	0.460	34	10.9	19.4	0.44	Medium	1 : 7.9
7606 B	Very light	0.0	1.55	2.07	0.05	2.02	2.62	0.265	18	8.5	20.1	0.39	Light	1 : 7.6
7607 B	Light	+4.0	3.66	3.22	1.54	1.68	1.96	0.304	20	13.5	28.5	0.12	Light	1 : 5.5
7608 B	Very dark	0.0	8.23	2.06	0.35	1.71	2.16	0.388	34	19.1	21.1	0.07	Light	1 : 4.4
7609 B	Very dark	+1.4	3.92	1.73	0.78	0.95	0.35	0.358	22	5.8	30.8	0.30	Light	1 : 2.6
7610 B	Medium	0.0	5.01	2.96	0.39	1.57	0.80	0.392	24	12.5	30.1	0.23	Medium	1 : 4.0
7611 B	Dark	—0.8	5.15	3.16	1.01	2.15	0.31	0.409	16	11.2	30.1	0.25	Heavy	1 : 5.2
7612 B	Medium	+0.4	2.50	2.60	0.16	2.44	0.52	0.272	20	11.7	14.5	0.22	Medium	1 : 5.5
7613 B	Medium	—0.4	3.88	4.66	1.05	3.61	0.28	0.494	30	20.4	32.3	0.39	Heavy	1 : 7.3
7614 B	Very dark	—0.6	10.25	4.47	0.75	3.72	0.28	0.552	48	24.7	32.6	0.18	Heavy	1 : 6.7
7615 B	Medium	—1.2	5.53	5.37	0.31	5.06	0.07	0.313	32	8.4	28.0	0.25	Light	1 : 16.1
7616 B	Medium	—1.4	6.99	2.00	0.28	1.72	0.55	0.478	38	6.6	19.3	0.32	Medium	1 : 3.6
7617 B	Medium	—1.4	5.83	2.97	0.59	2.38	2.19	0.434	32	11.4	26.0	0.40	Medium	1 : 5.5
7618 B	Dark	—3.8	6.32	2.57	0.69	1.88	0.35	0.293	26	10.4	25.0	0.42	Light	1 : 6.4
7619 B	Medium	0.0	1.94	2.53	0.34	2.19	3.40	0.349	26	15.3	39.5	0.33	Heavy	1 : 6.2
7620 B	Very dark	—2.8	4.38	3.04	1.15	1.89	0.14	0.506	46	26.8	34.9	0.31	Heavy	1 : 3.7
7621 B	Medium	—2.2	4.60	3.75	1.26	2.49	0.17	0.387	44	15.8	30.8	0.06	Heavy	1 : 6.4
Minimum		+4.0	1.55	1.73	0.05	0.95	0.07	0.265	16	6.6	14.5	0.06	Heavy	1 : 2.6
Maximum		—3.8	10.25	9.64	5.97	5.06	3.40	0.757	52	26.8	39.5	0.51	....	1 : 16.1
Average		—0.64	5.13	3.53	0.96	2.47	1.28	0.411	31	16.6	27.7	0.28	....	1 : 6.1

In color the vinegars ranged from a pale yellow to a reddish brown. The bouquets of a few were excellent while in some they were practically that of dilute acetic acid.

In general the methods of analysis were those given in Bulletin 137, Bureau of Chemistry, Dept. of Agriculture. The total sugars were determined by inverting the solutions and determining the reducing sugars. Alkalinity of the ash is expressed in cubic centimeters of *N*/10 acid for ash of 100 cc. sample. Phosphoric acid is expressed in milligrams of phosphoric acid in 100 cc. The other factors are in grams per 100 cc.

DISCUSSION OF ANALYSES

The variation of the factors was remarkable. Many of these can be explained only as the result of tampering—the addition of some foreign material, dilution with water, or both.

The polarization in the 200 mm. tube ranged from +4.0° V. to —3.8° V. The positive readings undoubtedly indicated the addition of sugar or glucose. The acid content varied from 1.55 to 10.25 grams per 100 cc. The higher acid samples are impossible figures and indicate the addition of acetic acid. The lower acid values indicate dilution with water or insufficient fermentation. The total solids range from 9.64 grams, a sample very high in sugar, to 1.73 grams per 100 cc. In one sample the sugars were as high as 5.97 grams and in another as low as 0.05 gram per 100 cc. The sample having 5.97 grams of course has not been properly fermented—the alcohol fermentation having been arrested by the addition of vinegar. The highest non-sugar solid content was 5.06 grams per 100 cc. Such a factor is impossible from an apple cider and has been caused by the addition of some foreign material. Just why any one should wish to make such a concoction is a puzzle. The highest alcohol value was 3.4 grams per 100 cc. Any alcohol value above 0.6 per cent indicated that the fermentation was not as complete as it should have been. The ash of all came within the limit of the law, the highest being 0.757, the lowest 0.265 gram per 100 cc. The alkalinity of the ash varied from 16 to 52 cc. of tenth normal acid per 100 cc. sample. Eight samples were below 30 the legal minimum. The soluble phosphoric acid ranged from 6.6 mgs. to 26.8 mgs. per 100 cc. Five samples were below 10 mgs. per 100 cc., the legal standard. The glycerine content varied from 0.51 gram to 0.06 gram per 100 cc. A fully fermented cider will contain not less than 0.25 gram of glycerine and a sample containing less than that amount is not a true cider vinegar. The ratio between the ash and non-sugars should be close to 1 : 5. However, we find the ratio 1 : 16.1 for the highest and 1 : 2.6 as the lowest.

From these analyses we would call Sample 7604 fraudulent. It contains 9.56 grams of acetic acid and nearly three grams of alcohol per 100 cc., an impossible condition. Sample 7605 is slightly low in acid but has nearly six grams of unfermented sugar, indicating incomplete alcoholic and acetic fermentation. The deficiencies of Samples 7606, 7607, 7611, 7613, 7619, 7620 and 7621 are probably due to a similar cause. However, the glycerine content and alkalinity of the ash of some of these samples would indicate that they have been tampered with. Samples 7610 and 7611 have probably been watered.

SUMMARY

The results of these analyses show the uncertainty of unscientific methods in the manufacture of vinegar.

Pernicious practices exist among farmers who put vinegar on the market.

Fraudulent vinegars are often sold as farmers' cider vinegars.

Laboratories of the Indiana State Board of Health
Indianapolis

THE ANALYSIS OF MAPLE PRODUCTS. III

The Range of Variation of Analytical Values in Genuine Maple Syrups

By J. F. Snell and J. M. Scott

Received January 5, 1914

In Paper II of this series[1] it was pointed out that the usefulness of a method for the detection of the adulteration of maple syrup with pure sucrose (or with granulated sugar) depends upon two factors: (1) The limits of natural variation of the analytical value in question in genuine maple syrups; (2) the rate at which the value falls off as the proportion of genuine syrup in the mixture decreases. It was shown that in respect to the latter factor, the Canadian lead method has a decided advantage over any of the other methods. While the ash values and the Winton lead number, as determined by the original Winton method or by Ross's modification thereof, fall off approximately in proportion to the amount of genuine maple syrup, the Canadian lead number falls off at a much more rapid rate, and reaches zero in mixtures containing as much as twenty per cent of genuine syrup. But it was shown that this apparent advantage of the Canadian method is, to a large extent, counteracted by the wide range of variation shown by this value in genuine syrups.

The electrical conductivity value, determined as described in the first paper of the series,[2] resembles the total ash and the Winton lead value rather than the Canadian lead value. Its rate of fall is in general a little less than proportional to that of the maple syrup content, but its range of variation expressed in percentage of the minimum is less than that of any of the other values studied in Paper II.

The objects of the present communication are three: (1) To report the results of the analysis of 126 genuine Canadian syrups of the season of 1913. (2) To study in more detail than in Paper II the ranges of variation of the analytical data in genuine syrups, with reference to the aforesaid results and to those of Bryan,[3] Jones,[4] and McGill.[5] (3) To propose a scheme for the detection of adulteration with sucrose less laborious and more effective than those commonly used.

SOURCE AND COLLECTION OF THE SAMPLES

The territory from which our syrups were collected extends from Lake Huron to the southeastern boundary of the Province of Quebec and is, we think, fairly representative of the chief maple-producing districts of the Dominion of Canada. By province and county the sources of the syrups are as follows, the total number[1] from Ontario being 57, that from Quebec 69:

Serial numbers	Province	County	Serial numbers	Province	County
1–13	Quebec	Argenteuil	71–88	Quebec	Stanstead, Compton and Sherbrooke
14–23	Ontario	Carleton	89–94	Ontario	Elgin and Middlesex
24–31	Ontario	Middlesex and Oxford	95–99	Ontario	Grey and Bruce
32–41	Ontario	Simcoe	100–117	Quebec	Huntingdon
42–61	Quebec	Shefford, Brome and Missisquoi	118–122	Ontario	Frontenac
62–70	Ontario	Grey	123–126	Ontario	Dufferin, Wellington and Peel

The syrups represent, we think, the most varied conditions of soil and elevation, and of method of manufacture to be found in the territory in question.

In the collection of the syrups we made it a point to reduce to a minimum the danger of including any adulterated samples. Samples 1–13 were collected by the senior author in person. The other samples from the Province of Quebec were collected by the Macdonald College Demonstrators resident in the respective districts, who were instructed to take the samples direct from the woods under such conditions as to preclude the possibility of adulteration. The samples from the Province of Ontario were collected by the District Representatives of the Ontario Department of Agriculture, who are graduates of the Ontario Agricultural College, acting as local agricultural demonstrators and referees. The same instructions were issued to these gentlemen as to the Macdonald College Demonstrators and we have their personal assurances that the instructions were strictly observed. Our thanks are due to them for their kind coöperation and to the Hon. James Duff, Minister of Agriculture for the Province of Ontario, for permitting us to ask this service of the Representatives of his Department.

THE RESULTS OF ANALYSIS OF THE SAMPLES

In addition to the analytical results, we have information about the method of manufacture of each syrup, including the kind of evaporator, the kind of filter, the clarifying agents used and whether the syrup had been allowed to settle or not. Table I reports 23 typical syrups.

Moisture—The per cent of moisture is derived from the refractometer reading by use of the tables of Prinsen Geerligs as given by Bryan.[2] The refractometer used was the Féry instrument made by Adam Hilger, London, England. With this instrument, using sodium light, we found it possible to make

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[1] Snell and Scott, This Journal, **5** (1913), 993.

[2] Snell, This Journal, **5** (1913), 740.

[3] Bryan, Bur. Chem., U. S. Dept. Agr., *Bull.* **134** (1910).

[4] Jones, Vermont Agr. Expt. Sta., *18th Ann. Rept.*, **1904–5**, 315.

[5] McGill, Lab. Inland Revenue Dept., Ottawa, *Bull.* **228** (1911).

[1] Quebec produces 65 per cent, Ontario 32 per cent of the maple syrup and sugar of the Dominion of Canada.

[2] Bryan, *Jour. Amer. Chem. Soc.*, **30** (1908), 1445.

TABLE I—SELECTED ANALYSES OF PURE CANADIAN MAPLE SYRUPS OF SEASON OF 1913

NO.	EVAPORATOR	FILTERING MATERIAL	CLARIFICATION		REFRACTOMETER		MOISTURE—Per cent	PERCENTAGE ASH			SOL. ASH / INSOL. ASH	ALKALINITY OF ASH		ALKAL. SOL. ASH / ALKAL. INSOL. ASH	LEAD NUMBERS		MODIFIED MALIC ACID VALUE	CONDUCTIVITY VALUE
			Clarifying agent	Settling	Reading	Temp. ° C.		Total	Sol.	Insol.		Sol.	Insol.		Canadian	Modified Winton		
3	Patent	Felt	None	Settled	1.4583	21.0	32.84	0.76	0.49	0.27	1.81	66	64	1.03	2.16	1.87	0.70	131
24	Patent	Cloth	None	Settled	1.4457	27.0	37.83	0.97	0.55	0.42	1.31	84	130	0.65	4.25	2.53	0.85	159
29	Patent	None	None	Settled	1.4543	27.6	34.03	0.64	0.35	0.29	1.21	62	77	0.81	2.19	1.67	0.65	114
31	Patent	None	None	Not settled	1.4560	26.8	33.35	0.83	0.30	0.53	0.57	51	119	0.43	3.25	2.02	0.68	134
33	Kettle	Cheesecloth	Eggs	Settled	1.4527	23.7	35.04	1.39	0.77	0.62	1.24	102	148	0.69	6.01	3.17	1.03	230
36	Kettle	Flannel	Eggs	Settled	1.4459	24.8	37.90	1.24	0.71	0.53	1.34	103	150	0.69	5.01	3.06	0.89	205
37	Kettle	Cotton	Milk	Settled	1.4329	29.5	43.23	0.99	0.58	0.41	1.41	79	113	0.70	3.69	2.48	0.85	166
39	Kettle	Cotton	Milk	Settled	1.4436	29.4	38.54	1.27	0.65	0.62	1.05	88	150	0.59	5.51	2.91	0.91	204
40	Kettle	Flannel	Eggs	Settled	1.4581	22.0	32.86	1.01	0.65	0.36	1.81	101	92	1.10	3.90	2.73	0.38	183
43	Patent	Flannel	None	Settled	1.4566	23.0	33.39	0.62	0.35	0.27	1.30	59	69	0.86	1.88	1.55	0.41	112
44	Patent	Flannel	None	Settled	1.4569	29.0	32.82	0.61	0.45	0.16	2.81	65	48	1.35	1.98	1.41	0.70	123
61	Patent	Flannel	None	Settled	1.4328	26.0	43.56	0.74	0.35	0.39	0.90	60	98	0.61	3.01	1.83	0.56	130
81	Patent	Flannel	None	Settled	1.4534	24.6	34.66	1.01	0.43	0.58	0.74	66	145	0.46	4.92	2.86	1.06	159
89	Pans	Flannel	Eggs	Settled	1.4586	24.5	32.42	0.77	0.53	0.24	2.21	76	58	1.31	1.74	1.48	0.69	156
95	Iron pans	Cotton	None	Not settled	1.4441	22.5	38.92	1.47	0.55	0.92	0.60	87	195	0.45	7.50	3.43	1.27	202
96	Kettle	Cotton	Eggs, milk	Not settled	1.4303	23.2	44.88	1.58	0.76	0.82	0.93	102	201	0.51	7.24	4.09	1.46	219
100	Patent	None	Eggs, milk	Settled	1.4593	23.1	32.28	0.71	0.33	0.38	0.87	58	90	0.64	2.43	1.76	0.74	125
103	Patent	Felt	None	Settled	1.4298	28.6	44.70	1.21	0.45	0.76	0.59	81	150	0.54	5.83	3.08	1.02	168
105	Patent	Flannel	None	Settled	1.4602	22.0	31.97	0.85	0.64	0.21	3.05	78	76	1.03	3.02	2.23	0.76	149
115	Patent	Fine cloth	None	Settled	1.4471	22.2	37.55	0.83	0.41	0.42	0.98	59	114	0.52	3.56	2.40	0.97	134
121	Pans	Cotton	Eggs, milk	Settled	1.4575	23.2	33.03	1.25	0.64	0.61	1.05	97	137	0.71	6.22	3.19	1.01	195
124	Patent	Cheesecloth	Milk	Settled	1.4593	29.0	31.82	1.29	0.59	0.70	0.84	85	144	0.59	5.08	2.91	1.05	192
125	Kettle	Cheesecloth	Milk	Settled	1.4452	26.3	38.09	0.92	0.66	0.26	2.54	82	113	0.73	3.26	2.24	0.74	174
	AVERAGE FOR 126 SYRUPS						34.24	0.88	0.48	0.40	1.20	68	116	0.59	3.48	2.30	0.75	147
	MAXIMUM FOR 126 SYRUPS						44.88	1.58	0.77	0.92	3.61	103	201	1.35	7.50	4.09	1.46	230
	MINIMUM FOR 126 SYRUPS						30.42	0.61	0.30	0.16	0.55	51	48	0.41	1.74	1.41	0.38	112

readings upon the darkest of our samples without dilution. We clarified them by filtering through cotton wool. The quantity filtered was about 25 cc. and the time required for the cold syrup to run through the filter was about 15 to 20 minutes. To satisfy ourselves that no error was introduced by evaporation during filtration we made readings upon three of the clearest syrups before, as well as after, filtering, and refiltered four other syrups, making readings before and after the second filtration. The results obtained in these experiments were as follows:

DRY MATTER CALCULATED FROM REFRACTOMETER READINGS—PERCENTAGES

No.	CLEAR SYRUPS		No.	REFILTERED SYRUPS	
	Before filtration	After filtration		After 1st filtration	After 2nd filtration
1	63.26	63.15	1	66.97	67.04
2	67.16	67.31	2	62.92	62.87
3	55.12	55.06	3	67.06	67.20
			4	65.53	65.50

The St. Lawrence Sugar Refining Company of Montreal, through its Superintendent, Dr. C. Bardorf, courteously permitted us to make readings upon ten of the syrups with their Zeiss-Abbé refractometer for comparison with the results obtained with the Féry instrument. The results were as shown in Table II.

Analytical Results—All the data of Table I except the moisture are referred to dry matter.

The determinations of total, soluble and insoluble ash, of Canadian and modified Winton lead value, and of malic acid value were made according to the methods prescribed in the Canadian pure food standards,[1] not because these methods are in our opinion superior to others but because one of the objects of our investigation was to make a critical study of the standards for maple syrup adopted by the Canadian Government. As these determinations were made before we had obtained a refractometer, the quantity of syrup used in the lead number determinations was that containing 5 or 25 grams of dry matter as estimated from the density. The results so obtained were afterwards recalculated to the basis of 5 or 25 grams dry matter, as determined by the refractometer. In the determinations of malic acid value the washing of the precipitate was continued to a filtrate volume of 100 cc., as it was found impracticable to wash "to freedom from soluble calcium salt," as indicated by testing with ammonium oxalate. The alkalinities of soluble and insoluble ash were determined in the usual manner.[2] The conductivity value determina-

TABLE II—COMPARISON OF REFRACTOMETERS

Sample	Abbé refractometer		Féry refractometer		
	Reading 20° C.	Corresponding dry matter	Reading	Temp. ° C.	Corresponding dry matter
1	1.4587	67.25	1.4570	28.7	67.16
2	1.4498	63.40	1.4483	26.2	63.26
3	1.4310	55.25	1.4298	28.6	55.30
4	1.4471	62.25	1.4459	24.8	62.10
5	1.4473	62.35	1.4457	27.0	62.17
6	1.4349	56.95	1.4329	29.5	56.77
7	1.4318	55.60	1.4303	23.2	55.09
8	1.4482	62.70	1.4470	27.8	62.83
9	1.4631	69.05	1.4609	31.0	69.03
10	1.4588	67.30	1.4574	28.5	67.34

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[1] Canadian Order in Council G. 994, Nov. 8, 1911; McGill Lab., Inland Revenue Dept., *Bull.* **228** (1911), 5.

[2] Bryan, U. S. Dept. Agr., Bureau of Chem., *Bull.* **134** (1910), 17.

tions were made as described in Paper I of this series.[1]

TABLE III—COMPARISON OF CONDUCTIVITY VALUES AT 20° AND 25° C.

	Conductivity			Conductivity	
No.	20° C.	25° C.	No.	20° C.	25° C.
1	202	230	11	113	129
2	195	219	12	112	127
3	181	205	13	107	121
4	180	204	14	107	121
5	180	202	15	108	121
6	168	197	16	105	120
7	172	195	17	98	116
8	169	192	18	94	115
9	160	183	19	103	114
10	155	177	20	99	112
Av.	176.2	200.4		104.6	119.6
Difference		24.2	Difference		15.0
Diff. in % of value at 25° C.		12.1	Diff. in % of value at 25° C.		12.5

It is difficult to draw any positive conclusions as to the relation of these analytical results to the district or to the method of manufacture of the syrup. In general, the syrups from the Lake Huron district (Simcoe, Grey and Bruce Counties) are high in total ash, conductivity, lead values and malic acid value. But the majority of the syrups from that district were made by rather primitive methods. Kettles and pans were used there to a much greater extent than patent evaporators and the practice of clarifying with eggs, milk or soda was very common. On the other hand the samples from Elgin County, although (with one exception) made in pans and treated with clarifying agents, do not show high values, and in Dufferin, Wellington and Peel Counties the single sample, No. 124, showing high values is one made with a patent evaporator, while the syrup made in a kettle, No. 125, although insufficiently evaporated shows low values throughout. Failure to evaporate to the proper density may in some instances, *e. g.*, Nos. 24, 37 and 103, account for high ash, lead values, malic acid value and alkalinity of insoluble ash, less calcium malate being forced out of solution than in the case of syrups concentrated to a sufficiently low moisture content to meet the Canadian standard (35 per cent). The same cause, together with others, may be instrumental in raising these values in 36, 39, 95, 96 and (119).[1] A number of instances appear, also, in which high moisture content is *not* accompanied by high analytical values, *e. g.*, Nos. (45, 59), 61, (102), 115 (high in malic acid) and 125. Again,

TABLE IV—RANGE OF VARIATION OF ANALYTICAL DATA OF PURE MAPLE SYRUPS

	PERCENTAGE OF ASH				ALKALINITY OF ASH			LEAD NUMBER				
	Total	Sol.	Insol.	SOL. ASH / INSOL. ASH	Sol.	Insol.	ALKAL. SOL. ASH / ALKAL. INSOL. ASH	Canadian	Winton	MODIFIED WINTON LEAD NO.	MALIC ACID VALUE	CONDUCTIVITY VALUE
MAXIMUM:												
Bryan	1.68	1.23	1.01	3.86	122	208	1.83	...	4.41	...	1.60	...
Jones	1.32	0.72	0.78	2.6	102	145	1.67	...	....	...	1.11	...
McGill	1.38	0.79	0.75	...	...	...	...	6.56	2.38	...	1.16	...
Snell and Scott	1.58	0.77	0.92	3.61	103	201	1.35	7.50	...	4.09	1.46	230
MINIMUM:												
Bryan	0.68	0.35	0.23	0.53	41	41	0.21	...	1.76	...	0.29	...
Jones	0.77	0.45	0.25	0.7	46	55	0.45	...	..	...	0.65	...
McGill	0.69	0.33	0.12	...	...	...	...	1.37	1.05	...	0.30	...
Snell and Scott	0.61	0.30	0.16	0.55	51	48	0.41	1.74	....	1.41	0.38	112
AVERAGE:												
Bryan	1.00	0.63	0.37	1.84	75	97	0.81	...	2.70	...	0.84	...
Jones	0.92	0.58	0.34	1.78	79	83	0.98	...	....	...	0.82	...
McGill	0.89	0.56	0.33	...	...	...	...	2.83	1.75	...	0.77	...
Snell and Scott	0.88	0.48	0.40	1.33	68	116	0.67	3.48	....	2.30	0.75	147
RANGE OF VARIATION—EXPRESSED IN PERCENTAGE OF AVERAGE:												
Bryan	100	140	211	181	108	172	200	...	98	...	156	...
Jones	60	47	156	106	71	108	125	...	....	...	56	...
McGill	78	82	191	...	...	...	...	183	76	...	112	...
Snell and Scott	110	98	190	230	76	132	140	166	....	117	144	80
PERCENTAGE DEVIATION OF MAXIMUM FROM MEAN:												
Bryan	68	95	173	110	63	114	126	...	63	...	90	...
Jones	43	25	129	45	29	75	71	...	....	...	35	...
McGill	55	41	127	...	...	...	...	132	36	...	51	...
Snell and Scott	80	60	130	171	51	73	101	116	....	78	95	56
PERCENTAGE DEVIATION OF MINIMUM FROM MEAN:												
Bryan	32	44	38	71	45	58	74	...	35	...	66	...
Jones	16	22	26	61	42	34	54	...	....	...	21	...
McGill	23	41	64	...	...	...	...	52	40	...	61	...
Snell and Scott	30	38	60	59	25	59	39	50	....	39	49	24
PER CENT OF SAMPLES ABOVE MEAN:												
Bryan	42.8	42.6	38.0	46.2	42.8	42.6	44.9	...	46.6	...	44.3	...
Jones	50.0	43.8	43.8	41.7	39.6	52.1	45.9	...	....	...	40.0	...
McGill	46.1	40.0	46.1	...	...	...	...	44.9	51.1	...	52.4	...
Snell and Scott	37.3	43.7	46.8	38.1	48.4	33.3	46.8	46.0	....	44.4	42.9	39.7
PER CENT OF SAMPLES AT AND BELOW MEAN:												
Bryan	57.2	57.4	62.0	53.8	57.2	57.4	55.1	...	53.4	...	55.7	...
Jones	50.0	56.2	56.2	58.3	60.4	47.9	54.1	...	....	...	60.0	...
McGill	53.9	60.0	53.9	...	...	...	...	55.1	48.9	...	47.6	...
Snell and Scott	62.7	56.3	53.2	61.9	51.6	66.7	53.2	54.0	....	55.6	57.1	60.3

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[1] THIS JOURNAL, **5**, 740.

[1] Serial numbers in parentheses refer to syrups not included in Table I.

No. 81, although made with a patent evaporator without a clarifying agent, evaporated to the correct water content (34.66 per cent), filtered through flannel and allowed to settle, is exceptionally high in total and insoluble ash, alkalinity of insoluble ash, Canadian and Winton lead values and malic acid value. This syrup came from a bush on lime soil, a fact that may have some connection with its composition. No. (104, 114) and 121, fairly high in the same values, are also from limestone soils, but we have instances, such as Nos. 3, (4), 100, (102, 108, 111 and 113), of syrups which come from limestone soils but are not high in these analytical values.

Among these syrups there are five—Nos. 33, 36, 39, 95 and 96—which show higher conductivity values than the maximum (200) reported in Paper I. The five are all from the adjacent counties of Simcoe and Grey, Ontario. Four of the five were kettle-boiled and treated with eggs or milk or both. No. 96 received 2 eggs and 4 cups of milk to 4 gallons of syrup; No. 95 was pan-boiled and not treated with eggs or milk. Four of the five contained excess of water, but No. 33, which had the highest conductivity value, was exactly right in water content. The collector of Nos. 33, 36 and 39 wrote that "these samples were all collected from the bush where the syrup was made, so that there was no possibility of it being adulterated." The collector of Nos. 95 and 96 states that these samples also were collected from the bush and that they were "made for home use." While these results indicate the possibility of a genuine maple syrup showing a conductivity value of over 200, they also show that such a high conductivity is rare, and perhaps never occurs in a marketable syrup. The highest conductivity values found in those syrups of this collection which were made in modern evaporators are 192 and 177. The syrup that gave the former value had been treated with eggs and milk.

Table V—Summary of Results of Analyses of Genuine Maple Syrups. All on Moisture-free Basis

					Alkalinity			Canadian lead No.		Winton lead No.			
	Total ash	Soluble ash	Insoluble ash	Soluble ash / Insoluble ash	Sol. ash	Insol. ash	Alk. sol. ash / Alk. insol. ash	5 g. syrup A	5 g. dry matter B	25 g. syrup A	Modified 25 g. dry matter B	Malic acid value	Conductivity value
No. of analyses	770	770	770	655	655	655	655	456	126	528	126	1094	174(*c*)
Average	0.96	0.59	0.37	1.74	0.74	1.00	0.80	2.83	3.48	2.62	2.30	0.80	148
Maximum	1.68(*b*)	1.23(*b*)	1.01(*b*)	3.86(*b*)	1.22(*b*)	2.08(*b*)	1.83(*b*)	6.56(*m*)	7.50(*a*)	4.41(*b*)	4.09(*a*)	1.60(*b*)	230(*a*)
Minimum	0.61(*a*)	0.30(*a*)	0.12(*m*)	0.53(*b*)	0.41(*b*)	0.41(*b*)	0.21(*b*)	1.37(*m*)	1.74(*a*)	1.05(*m*)	1.41(*a*)	0.29(*b*)	110(*d*)
Difference	1.07	0.93	0.89	3.33	0.81	1.67	1.62	5.19	5.76	3.36	2.68	1.31	120
Range in % of av.	111	158	241	191	109	167	203	183	166	128	117	164	81
Range in % of min.	175	310	742	628	198	407	771	379	331	320	190	452	109

(*a*) By authors. (*b*) By Bryan. (*m*) By McGill. (*d*) In a Vermont syrup. See Paper I.
(*c*) 194 actual samples, 22 of which are reckoned as 2 in averaging. See Paper I.

CONDUCTIVITY VALUES AT 20° C. AND 25° C.

We have determined the electrical conductivity at 20° C. of ten of the syrups showing high values and of ten showing low values at 25° C. The results are shown in Table III. The maximum at 20° is 202, the minimum 94. The minimum does not occur in the same syrup as at 25°. The average of the ten high values at 20° is 12.1 per cent less than at 25°, the average of the ten low values at 20° is 12.5 per cent less than at 25°. The differences in the individual syrups range from 10.7 to 18.3 per cent of the value at 25°.

RANGE OF VARIATION OF THE ANALYTICAL VALUES

In Tables IV and V we have set forth the maximum, minimum and average results obtained in the analysis of genuine maple syrups in the four most extensive investigations that have been published. In Table IV, the range of variation of each value in the work of each investigator is expressed in percentage of the mean. Table V gives the average results and the extreme variations of the four investigations taken together, the range of variation being expressed both in percentage of the mean and in percentage of the minimum.

Some explanatory statements are necessary in reference to the data of Tables IV and V. Bryan's investigation covered 481 syrups, collected from all of the important maple-producing sections of the United States and from the Province of Quebec. The collection was made by disinterested officers, whose names are published in Dr. Bryan's bulletins. They were instructed to be present at the manufacture of the syrup, whenever practicable. The measures adopted to exclude adulterated samples from the collection appear, therefore, to have been practically identical with our own. Whether they were as successfully carried out we are, of course, not in position to judge. The variations shown in the results are, in general, much wider than those in any of the other investigations. But the territory covered was much wider and the number of samples analyzed greater than in any other instance.

The investigations of Jones embraced 48 syrups, presumably all Vermont syrups.

McGill's 456 syrups were sent in by the producers with a declaration of genuineness—a method of collection which perhaps affords less security against the inclusion of adulterated samples than that adopted by Bryan and ourselves. Like our own, McGill's samples were all from the Provinces of Ontario and Quebec. His Canadian lead number determinations were made upon all the 456 samples; malic acid determinations on 452; total, soluble and insoluble ash on 115; and Winton lead number on 47.

Bryan's "basic," *i. e.*, Winton, lead number was determined upon 25 grams of syrup and calculated to the basis of 100 grams dry matter. The figures given in our table for his average ratios of soluble to insoluble ash and of alkalinity of soluble to alkalinity of insoluble ash are the true averages of the ratios of the individual syrups. The figures given for these averages in his publication are evidently derived by dividing the average soluble ash by the average insoluble ash, and the average alkalinity of soluble by the average alkalinity of insoluble ash. This involves the assumption that the ratio of the averages of two sets of numbers is equal to the average of the ratios of the individual numbers—a proposition that is not mathematically true. Thus, instead of the figure 1.70 given in his summary for the average ratio of soluble to insoluble ash the correct average is 1.84, and instead of 0.77 for the average ratio of the alkalinities the correct figure is 0.81. Of the two kinds of malic acid value determined by him that given in our tables is the one determined by the A. O. A. C. method.

Jones has made the same error as Bryan in calculating the average ratio of soluble to insoluble ash. We have used the true average, 1.78. The ratio of the alkalinities ascribed to him has been calculated from his results. His tables give the ratios of the alkalinities of one gram soluble to that of one gram insoluble ash, but not the ratios of the actual alkalinities of the two portions of the ash.

McGill's Winton lead numbers, like Bryan's, were determined with the use of 25 grams syrup and calculated over to the basis of 100 grams dry matter, notwithstanding the fact that, consequent upon his investigation, a modified method (using instead of 25 grams of syrup, the quantity of syrup containing 25 grams of *dry matter*) was adopted for the official Canadian standard of purity. The Canadian lead number also was determined on 5 grams of syrup but calculated over to the basis of 100 grams dry matter—which again is not the method adopted as the official standard.[1] It seems probable that the malic acid value was likewise determined upon 6.7 grams of syrup and calculated to the basis of 6.7 grams dry matter, although here again the use of the quantity of syrup containing 6.7 grams of dry matter is prescribed in the standards based upon the work.

As already noted, our own results upon Canadian lead value, Winton lead value and malic acid value were obtained with the use of the quantities of the syrups which contained 5, 25 and 6.7 grams of *dry matter*, respectively. Our lead values are, therefore, not strictly comparable with any of the others, and it is doubtful also whether our malic acid values are fairly comparable with the others. Since, however, our malic acid values all fall within the limits reached in the work of the other investigators, this latter point is not of consequence. We have designated our Winton numbers "modified" and placed them in a separate column to call attention to the difference of method. To be quite consistent we ought to have done the same with the Canadian lead number.

In Table V, the averages have been calculated from the averages of the four investigations included in Table IV. The minimum conductivity value given in Table IV is that found in the syrups whose analysis is here reported. That given in Table V is the minimum found in our whole experience with genuine syrups (194 samples).

COMPARISON OF THE VARIOUS ANALYTICAL DATA

Tables IV and V appear to throw much light upon the relative merits of the various analytical data as means of detecting adulteration in maple syrup. The total ash, the soluble ash, and especially the alkalinity of the soluble ash are shown to be of relatively narrow range and, therefore, much more useful than the insoluble ash or its alkalinity. In view of the not infrequent use of soda as a clarifying agent, the narrowness of range of the alkalinity of the soluble ash is a thing that would scarcely have been foreseen.

The amount of insoluble ash shows the widest variation of all the values, not only among the investigations taken as a whole but also among the results of each individual investigator. Considering the opportunities which maple syrup has to become contaminated with clay and iron rust, this is perhaps not surprising. Considered with respect to its minimum, the amount of insoluble ash has been regarded as an important datum in the detection of adulteration in maple products. Jones found no samples below 0.25, and Bryan none below 0.23 per cent in insoluble ash. McGill, however, finds 12 out of 115 samples below 0.23 and his minimum value is 0.12—just one-half the minimum found by the two investigators in the United States. It was partly this striking divergence that induced us to undertake the present investigation. The outcome has been to confirm, at any rate to a certain extent, McGill's conclusion that the insoluble ash in Canadian syrups is not infrequently below the minimum found by Bryan. Our minimum is 0.16 and 4 samples out of 126 fall below 0.23. These low results can not have been due to overheating in the ignition. Our ash determinations were made in an electric muffle at a temperature never exceeding 650° C., as indicated by a Hoskins pyrometer. The determinations on the four samples in question were made in duplicate. In our experience treating the ash with ammonium carbonate and reheating produces no increase in weight, showing that no loss of carbon dioxide occurs under the conditions of our ash determinations. Results as low, or nearly as low, as our minimum (0.16 per cent) are, however, extremely rare. McGill has only two results, and we only two, below 0.19—a total of only 4 below 0.19 in the 770 analyses of the four investigations.

The alkalinity of the insoluble ash, although less variable than the weight, is far from being of equal value with the total or with the soluble ash figures. The ratios of soluble to insoluble ash and of alkalinity of soluble to insoluble ash are so widely variable as to appear to us scarcely worth reckoning. The malic acid value is about as variable as the alkalinity of the insoluble ash. The minimum for this value is much lower than the work of Jones indicated.

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[1] In Paper II, we have shown that direct determination of these two lead numbers upon a quantity of syrup containing a definite quantity of dry matter gives results which do not coincide with those calculated to dry matter from a fixed quantity of syrup. THIS JOURNAL, 5 (1913), 997.

The Winton lead value makes a good showing on the dry basis and, as will be shown later, a much better showing on the wet basis. The Canadian lead method yields a value of comparatively wide range, but, as we have already shown, this method has a very important advantage over all the others in another respect.

In the general comparison (Table V) the conductivity value shows the narrowest range of all the values. In view of the relatively small number of samples upon which this determination has been made we hesitate to advance too positive claims on its behalf: judging from our results, this method not only excels all others in rapidity and ease of execution but is equal to any in respect to the narrowness of range of the value in genuine syrups and but little inferior to any, except the Canadian lead method, in the rate at which the value falls off with progressive adulteration of the syrup with sucrose.

TABLE VI—COMPARISON OF WINTON LEAD NUMBER ON DRY AND ON WET BASIS

BRYAN'S SAMPLES

			Winton lead value	
Sample	County and State	Moisture content	Dry basis	Wet basis
	HIGHEST VALUES			
6401	Champaign, O.	46.71	4.41	2.35
6842	Somerset, Pa.	36.96	4.28	2.70
6301	Logan, O.	38.63	4.24	2.60
6654	Upshur, W. Va.	35.81	4.20	2.70
6399	Madison, Ind.	39.04	4.05	2.47
6278	Logan, O.	38.17	4.01	2.48
6984	Mahoning, O.	30.09	3.86	2.70
	LOWEST VALUES			
6693	Oxford, Me.	33.23	1.76	1.18
6635	Rutland, Vt.	37.70	1.85	1.15
	Average 481 samples	34.22	2.70	1.78
	Maximum		4.41	2.70
	Minimum		1.76	1.15
	Difference		2.65	1.55
	Range in percentage of average		98.0	87.0
	Range in percentage of minimum		151.0	135.0

MCGILL'S SAMPLES

			Winton lead value	
Sample	Maker	Moisture content	Dry basis	Wet basis
	HIGHEST VALUES			
iii	J. Jacques, Burgessville, Ont. (a)	33.82	2.31	1.53
iv	J. C. Skinner, Burgessville, Ont.	35.68	2.36	1.52
v	H. A. Griswold, Burgessville, Ont.	35.08	2.29	1.49
xvi	J. E. Rice, New Durham, Ont.	35.22	2.30	1.49
xviii	E. T. Chambery, Oxford Centre, Ont.	28.14	2.08	1.49
xxi	M. Sager, Vandicar, Ont.	33.62	2.25	1.49
i	G. H. Losee, Burgessville, Ont.	38.32	2.38	1.47
	LOWEST VALUES			
11	W. H. McAllister, Dutton, Ont.	34.94	1.08	0.70
207	Wilfrid Larose, Angers, Que.	36.56	1.12	0.71
392	J. F. Parsons, Barnston, Que.	34.07	1.07	0.71
176	J. Y. Williams, Wisbeach, Ont.	31.12	1.05	0.72
	Average 47 samples	34.61	1.75	1.17
	Maximum		2.38	1.53
	Minimum		1.05	0.70
	Difference		1.33	0.83
	Range in percentage of average		76.0	71.0
	Range in percentage of minimum		127.0	119.0

(a) Erroneously given as Quebec in McGill's bulletin. Burgessville is in Oxford County, Ontario.

In regard to the Winton lead number a point of curious interest is that the range of variation is narrower when the figures are referred to a definite weight of syrup than when they are reduced to the dry basis. The sample in Bryan's collection which gave the maximum "basic lead number" (No. 6401, Champaign Co., Ohio) was one abnormally high in water content (46.71 per cent). The dry basis value, 4.41, for such a syrup is equivalent to 2.35 per 100 grams syrup. A number of other syrups in Bryan's collection give higher values than 2.35 on the wet basis. (See Table VI.) The highest value on the wet basis is 2.70. This is given by three samples. Similarly, the sample which gives the lowest value on the wet basis is not identical with that which gave the lowest on the dry basis. The minimum on the wet basis is 1.15. The range of variation on the wet basis amounts to only 87 per cent instead of 98 per cent, expressed in terms of the mean; or to 135 per cent, instead of 151 per cent, expressed in terms of the minimum.

Turning to McGill's samples, we find the same state of affairs (see Table VI). The range of variation on the wet basis is 71 per cent of the average as against 76 per cent of the average on the dry basis; or 119 per cent of the minimum, as against 127 per cent.

Taking Bryan's and McGill's results together (as in Table V) we find the average Winton lead value, on the wet basis (528 samples) to be 1.73. The maximum (Bryan) is 2.70, the minimum (McGill) 0.70. Difference 2.00. Range in percentage of average 116, as against 128 for the dry basis value. Range in percentage of minimum 286, as against 320 for the dry basis value. It would appear, therefore, that the reduction of Winton lead values to the dry basis is labor misspent.

For the Canadian lead value, however, the same does not hold true. Taking McGill's results, determined on the wet basis and calculated over to the dry, we find:

TABLE VII—CANADIAN LEAD VALUE

	Wet basis	Dry basis
Average	1.91	2.83(a)
Maximum	4.68	6.56
Minimum	0.89	1.37
Difference	3.79	5.19
Range per cent of average	198.0	183.0
Range per cent of minimum	426.0	379.0

(a) We find McGill's average for moisture content to be 32.58. His moisture determinations were made by drying on asbestos fiber.

Here the dry basis has decidedly the advantage. In our own work, where the method prescribed by the Canadian standards was followed, the limits are still narrower (see Table V). But as our work embraced a much smaller number of samples than McGill's, we are not in position to decide whether the method followed by McGill (determination on 5 grams syrup and calculation to 100 grams dry matter) or that adopted for the standard (determination on the quantity of syrup containing 5 grams dry matter and multiplication by 20) is preferable.

DISTRIBUTION OF RESULTS ABOUT THE MEAN

The lower half of Table IV shows that the general tendency of the analytical values is to run below, rather than above, the mean. Comparing each investigator's results on each value, we find only 5 cases out of 34 in which the deviation of the minimum from the mean is equal to, or greater than, that of the maximum. Two of these—the ratio of soluble to insoluble ash and the alkalinity of the insoluble ash—occur in Jones' work; the other three—per cent soluble, Winton lead number and malic acid value—occur in McGill's. In regard to the number of samples falling each side of the mean we find only 3 cases out of 34 in which the number above the mean is equal to, or greater than, the number below the mean. These are Jones' alkalinity of insoluble ash and McGill's Winton lead value and malic acid values. In all three of these cases very little over half the samples are above the mean.

A SCHEME OF RAPID ANALYSIS

In the light of the preceding we venture to propose the following scheme of analysis (Table VIII), not as all-sufficient for detection of adulteration of maple syrup, but as a rapid scheme that will serve to condemn many samples and thus obviate the making of other determinations, involving additional time and labor:

TABLE VIII—SCHEME FOR RAPID ANALYSIS OF MAPLE SYRUP

	TIME REQUIRED		LIMITS OF VALUE	
DETERMINATION	Actual attention	To reach result	Extreme	Ordinary
Refractometer reading....	5 min.	5 min.	.....	.....
Conductivity value 25° C.	5 min.	5 min.	110–230	113–205
Total ash, dry basis.......	7 min.	$1^{1}/_{2}$ hrs.	0.61–1.68	0.69–1.47
Alkalinity of soluble ash, dry basis..............	5 min.	$^{1}/_{2}$ hr.	41–122	48–109
Canadian lead number, 5 g. syrup, dry basis......	12 min.	5 hrs.	1.37–6.56	1.51–4.55
Winton lead number, 25 g. syrup, wet basis........	17 min.	9 hrs.	0.70–2.70	0.76–2.47
Total time required.....	51 min.	9 hrs.		

In Paper I it was shown that the conductivity test alone served to condemn 15 samples out of a collection of 34, purchased in the Canadian West, while the additional determinations made (*viz.*, total ash, insoluble ash, alkalinities of soluble and insoluble ash and modified Winton lead number) detected only two additional cases of adulteration. Of these two both would be condemned by the total ash and one by the Winton lead number. We believe the six determinations here recommended will in many instances prove equally as serviceable in the detection of adulteration as the twelve made by us on the syrups of Table I.

The extreme limits given for the values are the highest and lowest found in any of the syrups included in Table V. Under Canadian lead number, dry basis, we have included only McGill's results and the limits given are for determination upon 5 grams syrup and calculation to dry basis. Under Winton lead number, wet basis, we have included McGill's and Bryan's results. The limits for each investigator's work singly are much narrower (see Table VI). As ordinary limits of the values we have chosen the values not exceeded in either direction by more than one per cent of the samples analyzed. Thus, in the case of the total ash (770 samples) there are not more than eight samples below 0.69 and not more than eight above 1.47. Our time estimate is in each instance the minimum required for a single determination. In some cases it might be reduced by carrying on a number of determinations simultaneously. The 9 hours assigned to the Winton lead number determination provides for 4 hours settling of the lead sulfate precipitate. All six of the determinations can be made within these nine hours.

SUMMARY

I. The results of the analysis of 126 samples of genuine Canadian maple syrup are reported.

II. The range of conductivity value for 20° C. in these syrups is determined, as well as that for 25°.

III. The range of the various analytical values in genuine maple syrups is compared with reference to these results and to those of Bryan, Jones and McGill.

IV. The values of narrowest range are the conductivity value, the alkalinity of the soluble ash, the weight of the total ash and the Winton lead number.

V. A scheme of rapid analysis is proposed, embracing determinations of the aforesaid values and of the Canadian lead number.

The expenses of this investigation were defrayed out of the Dominion Grant for the encouragement of Agriculture, 1912.

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THE EFFECTS OF THE ENSILAGE PROCESS ON THE SOLUBILITY OF FLOATS

By E. B. FORBES AND CHAS. M. FRITZ

Received October 25, 1913

One of the standard methods of adding floats to the soil is through its addition to manure, and the effect of the fermentation of manure on the solubility of floats has been the subject of discussion and experiment.

It has occurred to the writers that perhaps we might profitably add a part of the floats to the plant-food two steps further from the soil by introducing it into the silo with the fodder corn, thus gaining two opportunities for increasing the solubility of the floats, first in the ensilage process, and second in the digestive tract of the animal; and further, giving to the animal such benefit as it might be able to get from the rock phosphate in its passage through the body. We do not mean to suggest, however, that all of the floats which one might desire to add to the soil could in this way be passed through the silo and the animal.

In this test four samples of corn were prepared as follows:

1. Untreated green silage corn.
2. Silage from No. 1.
3. Green silage corn plus floats (250:1).
4. Silage from No. 3.

The silage was made in glazed earthen jars. After being sealed for 6 months the jars were opened, and the silage was found to be in perfect condition.

At the time the treated corn was sealed up the floats gave it a sandy feeling between the teeth, but in the silage from this corn the "grit" had disappeared. We were able to detect no difference in the taste, odor or appearance of the two samples of silage.

The following phosphorus estimations were made on these two samples of silage and on the fresh materials from which they were prepared.

Phosphorus in Silage Corn with and without Added Floats, and in Silage Made from the Same. Per Cent, Water-Free Basis

Product	Total P	Water-sol. P	Citrate-sol. P	Inorganic P sol. in 0.2% HCl	Total water sol. + citrate-sol. P
Untreated green silage corn..	0.200	0.151	0.020	0.086	...
	0.203	0.150	0.021	0.082	...
	0.218	0.147	0.021	0.082	...
Average................	0.207	0.149	0.021	0.083	0.170
Silage from untreated corn..	0.231	0.159	0.009	0.112	...
	0.228	0.161	0.007	0.110	...
	0.214	0.161	0.009	0.112	...
Average................	0.224	0.160	0.008	0.111	0.168
Green silage corn plus floats (250 : 1)...............	0.374	0.135	0.055	0.156	...
	0.371	0.138	0.064	0.181	...
	0.367	0.135	0.065	0.178	...
Average................	0.371	0.136	0.061	0.172	0.197
Silage from treated corn.....	0.405	0.158	0.061	0.234	...
	0.387	0.157	0.061	0.243	...
	0.361	0.155	0.059	0.235	...
Average................	0.384	0.157	0.060	0.237	0.217

The increase in total phosphorus during the ensilage process shows that there was a loss of 8.2 per cent of dry substance from the untreated corn and 3.5 per cent from the phosphated corn.

The increase in water-soluble phosphorus in the untreated corn was not quite equal (7.4 per cent) to the arithmetical increase due to the loss of dry matter.

During the ensilage of this untreated corn there was a loss of citrate-soluble phosphorus, in the residue from water extraction, which signifies a process of reversion to less soluble forms.

The one significant increase during the ensilage of the untreated corn was in the inorganic phosphorus soluble in 0.2 per cent HCl. This was much more than enough to account for arithmetical increase from loss of dry substance.

In the phosphated corn there was a loss of water-soluble phosphorus simply through the addition of the floats, that is, the water-soluble phosphorus in the fresh corn was 0.149 per cent and in the phosphated corn 0.136 per cent, which probably signifies a combination of water-soluble phosphorus of the corn with bases in the floats. This probably took place during the partial drying at 50° C., though perhaps to some extent during the subsequent storage of the sample for nearly a year before the analyses were made.

The water-soluble phosphorus in the phosphated silage was not higher than in the untreated silage. The excess of water-soluble phosphorus in the phosphated silage over the amount in the unensiled, phosphated corn was more than enough to account for the loss in dry matter, but was not as great in amount as in the silage from the untreated corn, again suggesting reversion.

The citrate-soluble phosphorus in the treated fodder and in the silage from the same was naturally higher than in the untreated corn and silage, since a part of the phosphorus of the floats was citrate-soluble. There was no increase in citrate-soluble phosphorus, however, in the residue from the water extraction, during the ensilage of the phosphated corn.

The very considerable increase in inorganic phosphorus soluble in 0.2 per cent HCl during the ensilage of the phosphated corn gives us the most significant figure of the test. In the treated corn fodder the inorganic phosphorus soluble in 0.2 per cent HCl was 46.4 per cent of the total, while in the silage from the same was 61.7 per cent of the total.

It is also of interest that the phosphated silage contained more than twice as much inorganic phosphorus soluble in 0.2 per cent HCl as the treated silage.

The total phosphorus of the floats was 12.666 per cent, the water-soluble phosphorus 0.0129 per cent and the phosphorus soluble in 0.2 per cent HCl 8.721 per cent, all on a water-free basis.

CONCLUSION—The ensilage of corn will render soluble in 0.2 per cent HCl such an amount of the phosphorus of floats, added to corn, as to constitute a practical consideration in the feeding of livestock.

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THE EFFECT OF HEAT UPON THE SOLUBILITY OF THE MINERAL CONSTITUENTS OF THE SOIL[1]

By William McGeorge[2]

Received November 5, 1913

Heating soils as a means of stimulating growth of crops is a practice established centuries ago, but owing to the difficulties encountered in its application it has not been extensively used in practical agriculture, and consequently has gradually fallen out of use. Those who have investigated the cause of this stimulation have, as was to be expected from the extremely complex nature of soils, differed in their results and conclusions. It is certain, however, that the phenomenon is not explainable by any one theory, but the action is dependent upon the chemical, biological, and physical properties of the soil.

In Hawaii certain crops are greatly influenced, both in color and vigor, by the mere burning of brush and undergrowths of guava and lantana upon the surface. In tropical soils, which receive practically no "rest," it is probable that the effects of heat are similar to those derived from cultivation and aeration. With but few exceptions it is found necessary in Hawaii to plow the new land and follow with thorough tillage at frequent intervals for several months before planting. On the other hand the same results may be accomplished by means of heat.

Investigators have studied this question from various standpoints, among these being the effect of the heat upon the solubility of the mineral constituents. However, the majority have confined their studies to phosphoric acid; several have included potash and nitrogen,

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

[2] Assistant Chemist, Hawaii Agricultural Experiment Station.

while but comparatively few have gone beyond this and determined the effect upon the remaining soil constituents. The object of the work, here presented, was to add to the information regarding the effect of heat upon all the common mineral constituents of the soil. Distilled water and fifth-normal nitric acid were used as solvents.

Probably the most valuable work on the solubility of the mineral constituents of soils is to be found among the publications of the U. S. Bureau of Soils, their work being largely confined to the use of water as solvent. In a bulletin of this Bureau[1] King gives comparative results of work upon fresh and oven-dried soils which show the effect of heating to 110° C. to be quite striking. On the average, more nitrates, phosphoric acid, sulfuric acid, carbonic acid, and silica were recovered from the oven-dried than from the air-dried soil, while the average of the chlorine determinations showed a decrease. No determinations of basic constituents are given, but it is stated that upon later investigation an increase was found in the solubility of potash, lime, and magnesia in oven-dried soils.

METHOD OF PREPARING EXTRACTS—Extracts were made upon the soils in proportions of 1 part soil to 5 of water or fifth-normal nitric acid. The conditions of the samples treated were air dry, heated to 100° C. for eight hours, heated to 250° C. for the same time and over the full flame of the Bunsen burner (in porcelain dishes). The latter were heated carefully at first to prevent dusting and finally for two hours over the full flame. Water extracts were obtained by shaking for one hour and allowing to settle twenty-four hours and then filtering. Nitric acid extractions were made by shaking for 5 hours and then filtering directly.

TYPES OF SOIL—In choosing the soils to be used in this work a series of twelve soils were chosen, which included in a general way the normal and abnormal types, both physical and chemical, occurring on the islands. These include both red and yellow heavy clays, sandy and silty soils, highly manganiferous (9.74 per cent Mn_3O_4), highly titaniferous (20 per cent TiO_2) soils, a soil containing 8.7 per cent MgO, submerged soils both in the wet and subsequently air-dried states, and finally soils both high and low in organic matter.

In this paper only the results will be discussed. The complete analytical data and a more comprehensive discussion will be found in a bulletin of the Hawaii Experiment Station.[2]

The elements determined were silica, alumina, iron, manganese, lime, magnesia, potash, sulfates, phosphoric acid and bicarbonates. The results obtained upon the solubility of the first three of these substances in water are rather inconsistent. This is probably due to the slight solubility of these elements toward this solvent. On an average the solubility of alumina and silica increased with increase in temperature up to ignition. Iron was most soluble in the air-dry sample. This latter fact is in direct harmony with former experiences, namely, that under normal conditions in Hawaii, part of the iron exists in the form of ferrous compounds. Hawaiian soils, while characteristically basic, normally give an acid reaction, due indirectly to the high clay content and its accompanying poor aeration. Further confirmation of this fact is to be found in a comparison of cultivated and uncultivated soils, in which the iron content of the latter is more soluble. Also, the solubility of iron in rice and taro soils, in the submerged state, is strikingly high, and is greatly decreased as a result of heat and its accompanying oxidation. The data obtained by using $N/5$ nitric acid as solvent disclose some very interesting facts, and give almost conclusive proof of an increase in solubility of these three constituents as effected by heat. The results indicate a gradual increase with increase in temperature up to ignition.

These effects on the solubility, especially in water, are probably referable to a number of causes. It is primarily physical, being related to an alteration of the films surrounding the soil particles and to a modification of the colloidal forms which these elements probably assume under the prevailing conditions. Dehydration and certain chemical alterations at the higher temperatures would also tend towards increasing the solubility in acids through the action of heat upon the hydrated silicates. It has long been known that certain hydrated silicates of aluminum become more soluble in acids as a direct effect of heat. The ancient art of alum manufacture took advantage of this fact. The samples highest in magnesia content show the greatest solubility of silica in $N/5$ nitric acid. The alumina was found to be most soluble in the highly organic soils and in addition proved to be considerably more soluble than the iron in every sample.

MANGANESE—The solubility of manganese in water was greatest in the samples ignited, if it be permissible to draw conclusions from an average. However, the data were somewhat inconsistent and not in harmony with field conditions as induced by cultivation; that is, an analysis of the same soil cultivated and uncultivated showed a decrease in solubility as a result of aeration. Apparently the effect of heat upon the manganese is partly chemical as well as physical.

The solubility of $N/5$ nitric acid as affected by heat shows a remarkably consistent increase in solubility up to 250° C., followed by a large decrease in the ignited samples. This is true with only two exceptions in the entire series. This element occurs in some Hawaiian soils in the form of concretions and hence is present, at least partially so, as manganese dioxide. But in the normal soils these are absent and here the manganese exists in a lower state of oxidation and hence in a more soluble form. In each instance manganites or other salts may occur to a limited extent. With one exception the oxides of manganese are quite insoluble in nitric acid, this oxide being manganous oxide (MnO). Therefore the solubility of the oxides would increase with increase in temperature, owing to a decrease in state of oxidation, MnO_2 being converted into Mn_2O_3 and Mn_3O_4, each of which are partially soluble in nitric acid for the reason that they are combinations of the oxides MnO and MnO_2. Since Mn_3O_4 contains the largest amount of MnO it is

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[1] U. S. Dept. Agr., Bur. Plant Indus., *Bull.* **26**.

[2] Hawaii Agr. Expt. Sta., *Bull.* **30**.

evident that at this temperature greater solubility in $N/5$ HNO_3 would result, due to the formation of this oxide. In addition to the above facts it is known that the action of heat on organic compounds of manganese, as well as other of its salts, is to convert them into oxides.

LIME AND MAGNESIA—From a study of the data obtained from the determinations of these two elements it was found that they were both most soluble in water in the samples heated to 250° C., increasing with increase in temperature up to 250° C., and decreasing again upon ignition. In nitric acid the lime is most soluble in the samples heated to 100° C., and least soluble in the ignited samples. The general tendency is for the magnesia to be affected in a similar way. Thus we are led to conclude that the action of weak nitric acid in no way correlates with that of distilled water. The highly organic soils proved to hold the lime in the more soluble form. It is also worthy of note that the effect of cultivation was to cause an increase in the solubility of these elements. Another important fact brought out was that even though most of the soils used in this series show, from digestion with HCl (sp. gr. 1.115), a higher magnesia content than lime, one four times as much, yet the lime with few exceptions is present in higher concentration in the extract.

The effect of heat upon the solubility of these two elements is more striking than are the results obtained from the remaining elements. It is highly probable that the increased concentration of the water extract of the sample heated to 100° C over the air-dried samples is the result of physical causes, namely destruction of the soil film and dehydration accompanied by a slight decomposition of organic matter. On the other hand the samples heated to 250° C. undergo all the above transformations more completely and in addition suffer a more complete decomposition of organic matter. Since calcium and magnesium are two elements universally combined with organic matter in the soil there necessarily follows an increase in solubility as a result of the more complete decomposition. The soils containing the highest per cent of organic matter contained these two elements in the most soluble form.

The decrease in solubility of lime and magnesia in water upon the ignited samples and in nitric acid at 250° C. and ignition is hard to explain. It is undoubtedly partly due to chemical changes in the soluble forms resulting from the decomposition of the organic matter, also in the decrease in exposed surfaces as a result of the aggregation of the soil particles and other physical factors. It is suggested that one of the chemical changes taking place is that of a replacement of the potash and soda in the silicates by magnesium and calcium, as a direct result of heating. The data obtained in this work show a decided decrease in solubility of lime and an increase in that of potash upon ignition in a majority of the samples. In addition to the above-mentioned factors a decrease in solubility at ignition would be produced by the conversion of the bicarbonates into normal carbonates, the latter being less soluble. This would, of course, be more noticeable in the water extracts.

POTASH—The soils heated to 250° C. and ignition yield the more concentrated solution of potash, the average being in favor of the ignited soils. It was found that the solubility of the potash was increased by cultivation, and that in the highly organic soil to be the most soluble. The general ideas involved in the effect of heat will be dealt with more thoroughly in the discussion to follow, and for this reason the solubility of the potash requires little comment at this point. The fixing of potash is generally held to be due to hydrated silicates and organic matter. Cameron and Bell[1] on continuously extracting a soil with water until no more potash dissolved, then grinding the sample and re-extracting, found an additional amount of potash to be removed. This they attributed to a colloidal aluminum silicate upon the surface of the particles, thus protecting them from the action of the water as well as absorbing the potash. Dehydration and decomposition would therefore materially overcome the fixing power and the potash subsequently replaced by lime or magnesia would not become refixed during a short period, and heat would also liberate more potash from the insoluble form.

PHOSPHORIC ACID—The solubility of this constituent as affected by heat indicates a minimum in the air-dry soils and the maximum in those heated to 100° C. and 250° C. It is worthy of note that phosphoric acid is more soluble in the uncultivated than the cultivated soils, and that the former decreases in solubility with increase in heat. The nitric acid extracts show a gradual increase in solubility with increase in heat, being most soluble in the ignited samples.

Phosphoric acid exists in soils in the major part combined with iron, aluminum, magnesium, calcium and organic matter. It may be in the form of basic phosphates, hydrogen phosphates, or as double phosphates in combination with more than one element. It is probably combined mostly with iron, aluminum and titanium in Hawaiian soils. Considerable work has been done upon the effect of heat upon the solubility of this constituent and attempts have been made to draw conclusions from these results as to its state of combination, that is whether organically or inorganically combined. Peterson[2] using $N/5$ nitric acid found that after oxidizing the organic matter with hydrogen peroxide there was no increase in solubility when the soil was subsequently heated to 240° C. He concluded, therefore, that the solubility of the mineral phosphates in soils is not increased up to 240° C. The results obtained from the water extracts of Hawaiian soils indicate a decrease in solubility at high temperatures due either to a chemical change to a form less soluble in water or an increase in absorbing power of the soil. The increase at 100° and 250° is undoubtedly partly due to a destruction of organic matter and to a breaking up of the colloidal film. The action of dilute nitric acid is somewhat different in that an increase in solubility upon ignition results, accompanied by that of iron, aluminum, silica and titanium. Iron and alumina

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[1] U. S. Dept. Agr., Bur. Soils, *Bull.* **30**, p. 26.

[2] Wis. Exp. Sta., *Research Bull.* No. **19**.

occur, in Hawaiian soils, to a certain extent as hydrates or hydrated silicates, and, of course, would be more or less mechanically impregnated with phosphoric acid, as well as chemically combined. The effect of heat would directly increase the solubility of these constituents in nitric acid up to ignition, at which point the decomposition of the hydrates would be at a maximum while their colloidal properties would be practically nil.

SULFATES—Heat has a very striking effect upon the solubility of sulfates, most marked in the water extracts. In this series the air-dried soils were the least soluble, those heated to 100° C. next, while the maximum was reached in those samples heated to 250° C., finally decreasing upon ignition. On the other hand the ignited samples gave the most concentrated solution with nitric acid. One surprising feature of this series is that in many instances the sulfates were more soluble in water than in nitric acid, which is probably due to precipitation subsequent to extraction in the latter.

In connection with the solubility of the sulfates it should be mentioned that part of the increase in solubility of sulfates as a result of heat is probably due to absorption of the products of combustion of the gas used in heating the soils. King,[1] however, found an enormous increase in the solubility of sulfates upon heating in an oven at 110° C., using both gasoline and kerosene, thus eliminating this factor. In addition to the destruction of organic matter, soil films, etc., it is necessary to take into consideration the effect of heat upon the various inorganic sulfur compounds. Calcium sulfate is known to exist in four forms, two being anhydrous, one more soluble than the other. Sulfur also exists in soils as sulfides, generally with iron or as sulfate in combination with iron, lime or magnesia, as well as many essential forms of organic compounds. The effect of heat would be most marked upon the organic compounds in that they would be oxidized at the higher temperature, to the dioxide or trioxide which upon treatment with water as solvent would tend to form sulfuric acid or sulfates to the extent of the soluble bases present. On ignition it is evident that sulfur, especially that organically combined, would be volatilized upon ignition. An illustration of this action is well illustrated in the soil containing the highest amount of organic matter in the series. In this sample the increase of the sample heated to 100° C. over the dry-air sample was 1600 parts per million, while in passing from 250° C. to ignition the decrease amounted to 1900 parts per million.

BICARBONATES—The results of this series indicate a slight increase in solubility at 100° C. and 250° C., followed by a decrease upon ignition. Thus it appears that heat increases the amount of bicarbonates in the soil and at the same time increases the solubility of the bases. The decrease upon ignition is probably due to the transformation of the bicarbonates into normal carbonates, thus temporarily reducing their solubility in water.

DISCUSSION—The foregoing results show that an increase in solubility of the mineral constituents of Hawaiian soils is effected by heating. It was to be expected that the results would be inconsistent, to some extent, because of the varying types of soil used. The samples represent most of the normal and abnormal types of the islands. That there are both chemical and physical factors concerned in the phenomena at hand must be admitted at the outset. However, the most important set of factors affecting the solubility of inorganic soil constituents appears to be of a physical nature.

Undoubtedly the means by which the physical factors act is through the soil moisture in its relation to the physical properties of the soil. The conditions conducive to the formation of a colloidal state and the subsequent relation of heat to the destruction of colloid are two of the most important of these factors.

It is certain that soil moisture distributes itself around the soil particles and in some instances as an impregnation within the particles. The moisture, therefore, occurs as thin films which, according to certain physical conceptions, must be held around the particle by an enormous pressure. From purely physical considerations this pressure has been estimated at several thousand atmospheres. Under such pressure the concentration of film water with reference to the mineral matter should be much greater than that of the free or capillary water in the soil.

Then the air-dried soil, the particles of which are still surrounded by a film of moisture, when shaken with water, should theoretically show the least solubility. Our results in most instances are in harmony with this assumption. But if the soil be allowed to remain in the condition and environment prevailing in submerged cultures, that is, in the presence of a large excess of water, then in time diffusion would bring about a more or less equal distribution of dissolved materials throughout the entire water present, and, therefore, the pressure of soil films would be decreased to a minimum or entirely eliminated. Hence the amount of materials going into solution in the free water present from such soils would be expected to be abnormally high. Upon air drying such soils the normal films would again appear with a resulting decrease in solubility. Subsequent heating ought then to affect these soils in a way very similar to that produced on dry land soils. The data obtained in the examination of rice soils is in harmony with this view.

Water, however, not only exercises a solvent action on minerals, but forms various hydrates, the solubility and physical character of which in some instances are greatly altered; organic as well as inorganic matter goes into solution with the result that the moisture films around the particles become solution films, holding in suspension and more or less intermingled with colloids, both organic and inorganic. The films then may be looked upon as being of a colloidal nature.[1]

Upon heating the soil to 100° C. alterations in the films would take place through evaporation and by partial dehydration of colloids thus destroying the pressure by which the film was previously held around the particles. At the temperature of 100° C. the con-

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[1] U. S. Dept. Agr., Bur. Soils, *Bull.* **26**, p. 56.

[1] No claim is made for originality in this view. The idea of soil films, colloidal films, jels, etc., has been made use of by various writers on soils.

centration of the soil moisture would also be temporarily increased, due to increase in solubility with heat. During the course of the evaporation the concentration of the soil moisture would increase to the saturation point, after which the mineral matter would be deposited on the surface of the film as evaporation went on.[1]

Also the materials held in solution in the interior of the permeable particles would be partially deposited on the surface as the water evaporated. Upon adding water to the soil after having been dried, it is probable the materials deposited from previous evaporation would be more soluble than the other mineral constituents. In addition a certain amount of oxidation and other chemical changes in the organic matter might reasonably be expected to take place, which would have some effect on the solubility of the mineral bases that tend to combine with the organic matter.

Upon shaking with water a soil previously dried, the solution then obtained should be of a greater concentration than that prepared from the air-dried soil. With the absence of soil films and a more or less altered condition of the colloids present the solvent would have more ready access to the soil particles during a short period in addition to coming into immediate contact with salts deposited on the surface of the particles. In the light of these views then the solubility of soils before and after drying becomes more intelligible.

Why several of the mineral constituents of the soil should be so markedly more soluble when heated to 250° C. than at the other temperatures is a question not easily answered. The difference in physical effects were quite noticeable in that there was a greater aggregation of particles. Again there was a more complete destruction of organic matter effected at this temperature and also it is not entirely impossible that drying at 100° C. for eight hours does not effect a complete elimination of the soil moisture and especially the water of chemical combination. It seems reasonable then that the effects of heating to 100° C. are simply magnified when heated to 250° C. added to this being a more complete destruction of organic matter, the results both physical and chemical being of the same general nature but more complete at the higher temperature. The destruction of organic constituents being more complete would necessarily increase the solubility of the mineral matter held in combination, as it is generally conceded that the organic constituents of the soil in its natural state are quite insoluble in water and acids, more especially the former. There is also evidence of the existence of fatty or resinous organic matter which would materially affect the properties of the soil film. For the decomposition of such bodies it would be necessary to heat the soils considerably above 100° C.

In addition to the above-mentioned effects of heat the relation between solid and solvent would naturally be affected by other factors. Among these, would be absorption or "fixing power" of the soil.[2] It is reasonable to expect soils with widely varying physical and chemical properties, such as the samples used in this series, to vary widely in their absorptive power. Hence it is not at all unlikely that the lack of consistency in some of the results obtained is due primarily to this factor. Not only is there lack of uniformity in the absorptive power of soils but they also show considerable selective power in the absorption of mineral constituents. Soils high in humus should tend to have a high fixing power, due to the properties of this constituent of chemically combining with minerals as well as its power of absorption, and, therefore, the effect of heat upon highly organic soils should tend to increase the solubility of the minerals. This was found to be true in the highly organic soils of the series. Another factor is that of precipitation following extraction, being the more marked in the acid extract due to a more complete extraction.

In passing from 250° C. to ignition the effects are apparently of a specific rather than general nature, which have been previously discussed. Among these are the volatilization of certain sulfur compounds, conversion of bicarbonates into normal carbonates, dehydration of silicates, etc., replacing of potash by lime and other chemical transformations. In addition there is produced a greater aggregation of the soil particles, resulting in a decrease in surface area exposed to the solvent and an accompanying change in the fixing and absorbing powers of the soil. It is possible, by application of these conceptions, to explain the majority of changes, both increases and decreases in solubility resulting from ignition.

Acknowledgments are hereby extended to Dr. W. P. Kelly, chemist at this Station, for valuable suggestions and assistance otherwise rendered.

HAWAII EXPERIMENT STATION
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[1] King (*loc. cit.*) in discussing the relative solubilities of fresh and dried soils advanced this idea.

[2] Richter (*Landw. Vers. Stat.*, **47** (1896), p. 269) found that heating the soil increased the absorptive power of the soil for water.

THE USE OF SODIUM CITRATE FOR THE DETERMINATION OF REVERTED PHOSPHORIC ACID[1]

By ALFRED W. BOSWORTH

In 1871, Fresenius, Neubauer and Luck[2] published a method for the determination of reverted phosphoric acid in phosphates which involves the use of a solution of neutral ammonium citrate, specific gravity 1.09. This method, with a change in the temperature of the solvent, has been in constant use since that time[3] with no attempt by any one to give an explanation of the chemical reaction involved. It has been quite generally believed that the neutral ammonium citrate solution possesses a selective power which enables it to separate dicalcic-phosphate from tricalcic-phosphate. This is not true, for it has been found in this laboratory that 100 cc. of the Official ammonium citrate solution[2] is capable of dissolving 1.3 grams of precipitated tricalcic-phosphate in one-half hour at a temperature of 65° C. This dissolving of the tricalcic-phosphate is accompanied by a precipitation of calcium citrate.

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[1] Read before the Association of Official Agricultural Chemists, Washington, D. C., Nov. 17, 1913.

[2] *Z. anal. Chem.*, **10**, 133.

[3] U. S. Dept. Agr., Bur. of Chem., *Bull.* **107** (revised).

This separation of calcium citrate led to the belief that the solvent action of the citrate solution was the result of a double decomposition started by the free phosphoric acid always present in an aqueous solution which is in contact with a solid phase composed of a phosphate.[1] This double decomposition might be indicated by the following:

$$CaHPO_4 + 2C_6H_5O_6(NH_4)_3 \longrightarrow (NH_4)_2HPO_4 + [C_6H_5O_6(NH_4)_2]_2Ca$$

$$Ca_3P_2O_8 + 6C_6H_5O_6(NH_4)_3 \longrightarrow 2(NH_4)_3PO_4 + 3[C_6H_5O_6(NH_4)_2]_2Ca$$

If appreciable amounts of calcium are taken into solution, calcium citrate will separate out.

$$3[C_6H_5O_6(NH_4)_2]_2Ca \longrightarrow 4C_6H_5O_6(NH_4)_3 + (C_6H_5O_6)_2Ca_3$$

A great deal of work has been done upon methods of making neutral ammonium citrate solutions and several such methods have been published. The fact that neutral ammonium citrate is very unstable and easily loses ammonia has not been sufficiently considered in this connection, however. Why should extreme care be taken to secure an absolutely neutral solution, if this solution is to lose ammonia when heated a few degrees above the room temperature? Most chemists who have used the neutral ammonium citrate solution know that ammonia is constantly given off during the half hour allowed for the solvent action to take place. The final result then, is not the action of neutral citrate but rather the action of an acid citrate. There seemed to be no theoretical reason why a solution of sodium citrate should not be just as effective a solvent and it possesses two distinct advantages. It is a more stable salt and as the base in it is not volatile the solution would remain neutral throughout the whole operation. All trouble in securing a neutral solution would be eliminated, for a solution of citric acid could be neutralized with sodium hydroxide, using phenolphthalein as an indicator, or the neutral crystals of sodium citrate could be dissolved in water, and the solution made up to the required volume.

In order to learn what the action of a solution of sodium citrate might be, one was made which was of the same molecular concentration as the Official[2] ammonium citrate solution, *i. e.*, 314 grams crystallized sodium citrate, $(C_6H_5O_6Na_3)_2.11H_2O$, per liter. This solution was used to determine the amounts of insoluble and reverted phosphoric acid in several fertilizers, Thomas slag, ground bone, ground rock phosphate, dicalcic-phosphate, $CaHPO_4$, and tricalcic-phosphate, $Ca_3P_2O_8$. The results, together with those obtained by the use of the Official citrate solution, are given in the table.

In connection with these figures, it is noticeable that the differences between the figures obtained with the two solutions are, in most cases, of the same magnitude as the variations in the figures obtained by different chemists working upon the same sample.[3] It is also interesting to know that Samples 5, 10 and 11, which show the largest differences, all contain bone. The duplicate determinations, in all cases, showed closer agreement with sodium citrate solution than with the Official citrate solution.

The Official method directs that the flask in which the reaction takes place should be loosely stoppered, during the time it is being maintained at 65° C., in order to prevent evaporation. The use of stoppers often results in the loss of a determination through the breaking of a flask. It is suggested that the flask be closed with a one-hole rubber stopper carrying an empty calcium chloride tube, 300 mm. in length, which will serve as a condenser. The use of such a condenser will not interfere with the shaking and it furnishes a vent which prevents the breaking of the flask.

The last column of the table shows the amounts of ammonia given off during the half hour of treatment with ammonium citrate solution prescribed by the Official method. This ammonia was caught in standard acid by means of an air current which was passed through the Erlenmeyer flask in which the solvent action was taking place. These figures seem to bear some relation to the difference given in the preceding column. By noticing the large amounts of ammonia given off by the Thomas slag, rock phosphate and ground bone when treated with ammonium citrate at 65° C. for one-half hour an indication as to the reason for the liberation of the ammonia may be found. The fertilizing materials, after being extracted with water, leave a residue which, in most cases, contains alkaline material, alkaline phosphates, carbonates of calcium and magnesium and oxides of other elements. These all tend to drive off ammonia from the citrate solution.

COMPARISON OF THE USE OF AMMONIUM CITRATE AND SODIUM CITRATE FOR THE DETERMINATION OF REVERTED PHOSPHORIC ACID

			By ammonium citrate		By sodium citrate			
	Total P_2O_5	Water-soluble P_2O_5	Insol. P_2O_5.	Reverted P_2O_5	Insol. P_2O_5	Reverted P_2O_5	Difference	Cc. of N/10 NH_3 liberated in 1/2 hour at 65° C.
1	10.63	6.18	1.75	2.76	2.61	1.84	0.91	14.9
2	8.73	3.76	1.42	3.55	1.89	3.08	0.47	12.7
3	9.58	6.50	0.76	2.32	1.11	1.97	0.35	10.9
4	12.33	11.90	0.02	0.41	0.00	0.43	0.02	6.5
5	14.59	1.21	4.01	9.37	9.07	4.31	5.06	12.5
6	10.92	3.76	0.58	6.58	1.11	6.05	0.53	13.5
7	11.18	8.73	0.34	2.11	0.66	1.79	0.32	16.0
8	9.61	4.24	1.62	3.75	2.80	2.57	1.18	14.2
9	7.31	0.95	2.59	3.77	4.58	1.78	1.99	10.5
10	8.79	0.00	5.22	3.57	7.78	1.01	2.56	29.0
11	19.91	1.84	6.34	11.73	14.89	3.18	8.55	23.0
12	13.07	8.42	0.22	4.43	0.77	3.88	0.55	13.5
13	11.69	4.33	3.68	3.68	4.15	3.21	0.47	16.9
Bone	20.95	0.00	13.36	7.59	15.82	5.13	2.46	14.0
Slag	17.57	0.00	9.40	8.17	15.69	1.88	6.29	65.0
Rock phosphate	29.72	0.19	27.57	1.96	28.20	1.33	0.63	20.5
$CaHPO_4$	1 gram	...	0.00	...	0.00	..	0.00	3.5
$Ca_3P_2O_8$	taken	...	0.00	...	0.00	..	0.00	14.0
Ammonium citrate heated to 65° C.								2.6
Ammonium citrate heated to 75° C.								36.0

It is realized that the small amount of evidence presented in this paper does not settle the question as to the desirability of substituting sodium citrate for ammonium citrate in the determination of reverted phosphoric acid. The subject is simply brought forward at this time in order that those chemists who are interested may give it some thought.

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[1] Cameron and Hurst, *Jour. Amer. Chem. Soc.*, **26**, 905.

[2] U. S. Dept. Agr., Bur. Chem., *Bull.* **107** (revised).

[3] THIS JOURNAL, **3**, 118 and **5**, 957. The differences between the extremes in these two cases are 1.23 per cent and 0.90 per cent, respectively.

LABORATORY AND PLANT

APPLICATIONS OF OZONE[1]

By A. Vosmaer

Ozone is generated by the action of the so-called brush discharge[2] on oxygen, the product being ozone more or less diluted with either non-converted oxygen or air, the latter being the rule in actual practice. Though the use of pure oxygen gives a higher concentration of ozone, this increase is not sufficiently high to justify the high cost of the gas. In laboratory apparatus the concentration of ozone can be run up as high as 160 grams per cubic meter, but in regular work on a larger scale it is hardly possible to get more than something like 30 and even that is rather high.

Since the cost per gram of ozone is not a linear function of the concentration, but increases rapidly with concentration, it is fortunate that ozone possesses such wonderful oxidizing powers that concentrations very much lower than those cited are quite sufficient for most purposes. For the manufacture of ozone there are now several ozonators of varying values on the market[3] and it is necessary to obtain the right kind for the purpose in mind, as it would be wasteful to generate a high concentration ozone and afterwards dilute it with air. Nearly all ordinary work can be done with a concentration of between 3 and 5 grams per cubic meter; a very large amount of work can be satisfactorily carried out with ozone of no more than about one gram, and some special applications require far less yet, down to two-tenths of a milligram, so that there is ample variety.

The only property of ozone that is of commercial importance is its remarkably strong oxidizing power, unless we consider its wonderful power as a germicide to be due to a specific property. I am inclined to do so, but there is evidence also that its germicidal value can be traced to its oxidizing power.

Before discussing the applications of ozone in detail, I wish to draw attention to some important points which govern the ozone industry: (1) Ozone is scarcely soluble in water—some say it is absolutely insoluble, which would be very improbable; others claim its solubility to be about ten times that of oxygen which latter statement seems as improbable as the former. (2) Ozone is difficult to make and when made, is difficult to keep; in fact, there is no storage question, the ozone being used when made. (3) As the gas may be considered hardly soluble at all in the ordinary sense of the word, molecular contact between ozone and the substance to be treated fails and one has to make up for it by long and very intimate mechanical contact which in practice means a special apparatus and constitutes the engineering part of the business.

A great advantage when using ozone is that its product of decomposition is a gas which is easily separated from the material that has undergone the treatment, and with which we are all familiar. It is a matter of diversity of opinion, and open to discussion, whether or not ozone when acting splits off one active atom or utilizes all three. In my opinion it is probable that it is all three.

PURIFICATION OF WATER

Years ago this most important of the possible applications of ozone originated in Holland where non-success in the sterilization of milk lead to successful sterilization of water. The interest of German scientists was soon aroused, and Frohlich of the firm of Siemens and Halske took up the work. Unfortunately, the Hollanders (Tindal and Schneller) ultimately, through lack of pecuniary funds, got on the wrong track and the business failed, not because ozone did not do the work but because Schneller did not know how to handle it. To Tindal anyhow belongs the honor of having done pioneer work in this line and later success surely owes much to his attempts.

It takes very little ozone to purify water of ordinary quality, but success depends to a large extent on the apparatus used for the purpose, not only as regards efficiency, but also with reference to purification. It is here that the time factor comes in. To accomplish purification and eventually the complete sterilization of water, it is necessary to have the water in close contact with the ozone, and to keep it so for several minutes. This is the whole secret of the work but the time factor was generally overlooked in the early attempts.

The ideal apparatus for the treatment of liquors with gases is not at all the well known scrubber, though this is used to a large extent for that purpose. In the ordinary scrubber, whether made of baffle plates or filled with coke or pebbles, the only method of obtaining a sufficient time of contact between liquid and gas is to make the apparatus so high as to increase the time required by the liquid to reach the bottom when let in at the top, but the upward stream of gas has a speed of its own which cannot be altered; this kind of apparatus does well enough for processes in which absorption is the object, but it has been introduced also in ozone applications and that was a mistake resulting in inefficiency.

The principle of the apparatus I have worked out is shown in Fig. I. Here the water inlet is at the top and the outlet at the bottom, the reverse being the case for the ozone. By checking the outlet by means of an ordinary valve, the amount of water passing through in a given time can be regulated perfectly up to the maximum; the ozone entering through 3, passes a screen or perforated plate, 5, and then goes upward until it reaches the free outlet at 4. Another perforated screen at 6 serves the purpose of absolutely preventing even the smallest particle of ozone from escaping at the bottom before it has done its work. The height of the standpipe depends upon the quality of the water to be ozonized; if it be a bad water the time of contact has to be longer than with a water of good quality, quality in this particular case referring only to the content of organic matter in solution. Of course, one would expect the height to be greatest in the case of bad water, but that is not the case; on the contrary, there is another way of prolonging the time of contact,

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[1] Abstracted by the author from a paper presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1913.

[2] *Met. Chem. Eng.*, **11** (1913), 623 and 705.

[3] *Ibid.*, **12** (1914), 36.

viz., by means of increase in diameter. For bad water, evidently, far more ozone is needed than for a good water; this fixes the diameter of the standpipe, because in order to have it work perfectly, it is absolutely necessary that the whole cross area shall be completely filled by a homogeneous mass of gas and water with practically none but surface films of water surrounding the gas bubbles. The downward motion of the water checks the upward motion of the ozone to any desired extent, the natural buoyancy of a bubble being one factor in its movement and the downward force of the water the other. In actual practice this standpipe has to have a height of some 20 or 30 feet and may be made of any suitable material, even iron when properly coated.

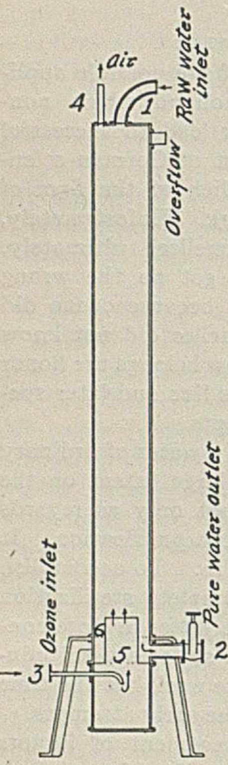

Fig. I

There are some interesting details concerning this apparatus: (1) The curious fact that its utter simplicity appeals to nobody unless it is seen in operation. I therefore used to build one of glass so as to show the whole affair outside and inside. Then the fact is evident that as long as there is sufficient pressure in the compartment under the screen 5, there is no chance for any drop of water entering; and the reverse happens at the screen 6 where the water alone passes through. This is easily explained by the assumption that a liquid and a gas cannot simultaneously pass through small openings; at 5 there is excess of gas pressure that causes the gas to take the lead; at 6 there is excess of water pressure which takes advantage of its position, the gas bubbles having no speed at all there. (2) Another thing that used to cause great surprise is that when started for the first time there is one big bubble, say one cubic foot in size, that enters into the water column but after having traveled for about 3 or 4 feet, it is entirely split up into small bubbles, the ordinary size being about one-quarter of an inch in diameter. This phenomenon, strange as it looks at first sight, is not at all extraordinary. It is entirely analogous to the fact that a vertical stream of water will invariably split up into drops; no matter what the initial size of the stream—the result is individual drops due to the surface tension of the water; in the case of the ozone the same surface tension of the water causes the enclosed gas bubbles to be of a definite size.

The apparatus described is what I would like to call perfection itself. In actual use on a larger scale it can be very conveniently altered so as to be even simpler. Instead of the inlet at the bottom through a perforated screen one can as well have a pipe come down from the top until it reaches the bottom, the whole being then more like the old-fashioned wash bottle of the chemical laboratory. I may add that I have built these sterilizing towers of different sizes, from 6 inches in diameter to 6 feet, and from 10 feet in height up to 45 feet. In all cases the economical results have been entirely satisfactory. I claim an efficiency of 99 per cent for this apparatus, the average time of contact being four minutes.

As in commercial treatments on a large scale there is necessarily an excess of the reagent, so here it is preferable to have a slight excess of ozone for certainty of results. The excess escapes at the top freely and is too slight to pay for the trouble of recovery. This detail at once proves the advantage of this style of apparatus over the scrubber. I use no more than 1 gram per cubic meter; others use 2.5 grams and as the extra concentration of ozone is not used up in the short time of contact, there is a severe loss if the excess is not recovered. The germicidal power of ozone on water is of such strength that it does not require more than one gram of ozone to treat one million grams (1 cu. m.) of water of medium quality. In a water carrying less than the equivalent of 10 milligrams of permanganate of potash, only about one-tenth this amount of ozone is needed to do the work.

Fig. II shows the bottom of a small sterilizer made of glass for demonstrational purposes, and Fig. III the whole standpipe 30 feet high and a larger size, encased to prevent freezing. I may add that I have never found the slightest difference in the amount of ozone required for purification of water in winter and that needed in summer. A one foot diameter standpipe, the size of the glass one, takes care of up to 30 cubic meters of water per hour, *i. e.*, about 8,000 gallons. I have dealt with this apparatus at length because it has given absolute satisfaction in all cases and because it is well adapted for various applications.

The problem of taking iron in solution out of water is one that often presents itself on the other side of the ocean; it can be carried out successfully by the use of air in an apparatus similar to the one just described; as shown by actual practice, the height need not be over 10 or 12 feet. A more difficult problem is to get rid of organic ferric compounds. This can be done in the same apparatus by use of ozone, the precipitated hydroxide of iron being removed by any of the well known methods.

It is quite remarkable that ozone, as a gas, actually burns up most of the organic matter in solution in water and also converts the ferric compounds to ferric hydroxide. As an additional advantage of the use of ozone for the purification of water may be mentioned the fact that any discoloration, odor or abnormal taste is removed so that the result of efficient ozone treatment is a water perfectly clear, pure, colorless and perfect from a bacteriological standpoint. Modern science does not require a water to be perfectly sterile when it has to be used for drinking. It is important to note that the dangerous pathogenic bacteria, more especially the typhoid bacillus and the cholera vibrio, have very little resistance and yield first of all to the action of ozone. What may be left after treatment are such absolutely harmless species as the *b. subtilis* or the *b. mesentericus* and in some cases spores. Fortunately water does not carry any pathogenic spore-forming bacteria.

USE OF OZONE IN THE INDUSTRIAL ARTS

This subject is not so simple or so well investigated as the former. There have been various trials of ozone in different branches of chemistry, but a good many failed, probably because the experiments were not interpreted in the right way, probably through ignorance of how to apply the new agent, perhaps also in some cases because there was no real opportunity for ozone to supplant the old agent. Certainly the fact that ozone is too expensive has been a reason for non-trial or non-success, but practically the whole field lies open. Aside from some few isolated or unknown instances, ozone has not yet entered the field of chemical industry, but it may do so at any moment.

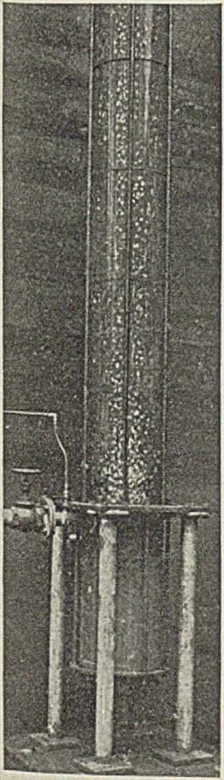

Fig. II

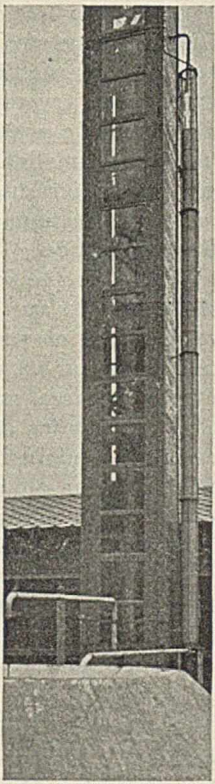

Fig. III

Its use for bleaching purposes suggests itself first. It has to compete now with that very cheap and efficient agent, chlorine, either as a gas or in the form of hypochlorites of calcium, sodium or magnesium. This competition, solely a question of price per pound, is at present decidedly in favor of chlorine. Whether or not we shall be able to improve our present method of making ozone so as to increase the yield per kilowatt hour is now an open question. The theoretical yield is over a thousand grams and we are getting no more than 10 grams under the most favorable circumstances; hence, there must be a vast improvement before ozone can exceed any other bleaching agent in value. For the present we must accept the cost of ozone as it is—about 20 cents a pound. However, one must bear in mind that it takes two atoms of chlorine to give one atom of oxygen. If my opinion is correct, and the ozone furnishes three active atoms, then 48 grams of ozone give us 48 grams of O atoms, whereas it takes 70 of chlorine to yield 16 grams of O atoms; this would be an advantage of nearly 5 to 1 for ozone, which would have to be divided by three if we must use 48 grams of ozone to yield only 16 grams of O atoms.

The advantage of chlorine over ozone however is evidently not its direct price, but the fact that for the making of ozone much electrical apparatus is required, whereas chlorine as hypochlorites can be bought in bottles or in barrels. Ozone, however, wins if we do not look solely at direct cost price, but also at quality of product. I have been treating paper pulp with ozone. The result was excellent in so far as concerns the maintenance of fiber, the ozone bleached showing a length of fiber of several times that of the chlorine bleached, but one should be very careful not to use a high ozone concentration, because strong ozone will destroy fiber just as does chlorine; the secret here lies in the proper application of a weak ozone. The bleaching of cotton fabric is even more delicate and the rule must be "Do not hurry." Beeswax is an article that is fairly high priced, and its price is considerably higher when white. The bleaching has been carried out with success but a high concentration of ozone is necessary and a long treatment must be used because there is much organic matter to be removed. The bleaching of sugar molasses solution on the other hand is very easy, but the sugar is inverted which bars this use of ozone. Its use for bleaching glue is also easy, but it deprives the glue of its sticking properties.

More success is to be expected from the use of ozone in the oil industries. Cottonseed oil when ozonized has lost its peculiar taste and smell, but a large amount of ozone must be used to get this result. Sandal wood oil responds more readily to treatment and can be deprived of its taste and bleached also.

The manufacture of white or rather colorless egg-white from blood is not so easy but I have been successful to a certain extent in this line. The bleaching of flour is not at all successful, probably because it has to be done in a dry state. The flour retains a peculiar and disagreeable taste after treatment. The manufacture of varnish from linseed oil is a promising proposition, since the resulting varnish is of remarkable transparency because the oil has not been subjected to any high temperature. It may be that under favorable circumstances the drying of the oil, say for the manufacture of linoleums, may be advantageously done by means of ozone—the advantage in this case being a considerable shortening of time of the process.

The future of ozone is brighter than ever, but we must not exaggerate its importance. If we claimed to be able to sterilize milk or butter by it we would be making false statements. Neither do I believe in its value for aging wines. The flavor of wine is of such a delicate nature and the liability of its alcohol to acidify is so great that one cannot expect any beneficial effect in this line; we all know that even ordinary oxygen will spoil good wine in a couple of hours. What then can be expected of ozone? There are perhaps hundreds of possibilities for ozone, but I do not wish to speak of any with which I have had no personal experience. All my statements come from my own experience and are thus perhaps a bit one-sided, perhaps too enthusiastic, but that is the inevitable result of 15 years' work.

PURIFICATION OF AIR FOR VENTILATING PURPOSES

I wish particularly to call attention to the fact that I do not speak here of sterilization of air, but of purification. Dry ozone has no action whatever on dry air with its millions and millions of particles of dry dust. As a means of disinfecting a sickroom, ozone, even in strong concentration and moist, is not sensible. Besides bacteria clinging to the particles of dust, there are other sources of contamination. We must consider also volatile products of respiration, perspiration and other gaseous products.

What renders a crowded room disagreeable is not the carbon dioxide of the air nor lack of sufficient oxygen, but the odor due to the above named pollutions.

Even in a non-ventilated room there is plenty of oxygen for a long time for many people. Each breath takes but a trifling part out of the available total and what makes us feel uncomfortable is not the lack of anything but the excess of bad odors of organic origin. Now ozone is an extraordinarily powerful oxidizing agent and it will take care of these disagreeable odors, harmful not in the direct sense of the word but indirectly because one is liable not to breathe freely and deeply in an atmosphere that has a nasty odor.

Some people think that ozone only masks odors, but it is not very probable that a strong oxidizing agent like ozone would suddenly lose its power, and even if it should, the mere masking would be an advantage.

Dr. Franklin, in order to settle the question of masking *vs.* oxidation, has been carrying out some very interesting and conclusive experiments to which we can only refer.[1] His conclusions are absolute and convincing in favor of oxidation.

Of course, remembering the extremely powerful action of ozone and thinking also of the delicate character of our mucous membranes, it is an absolute necessity that the concentration of the ozone shall be an exceedingly low one—certainly not over one in a million parts of air and preferably something like one in ten million parts of air when intended for continuous breathing.

The question of purification of air with ozone is two-sided anyhow: (1) There is the purification of foul air and revivifying it by ozone; (2) there is the question of ozone as a therapeutic agent, *e. g.*, in cases of phthisis in its first stages, anemia, or obesity. I am not competent to give any statements regarding these diseases, but knowing that the inhalation of ozone in a very weak concentration actually does increase the percentage of oxyhaemoglobin in the blood, I believe that this fact, easy to control, should be sufficient to point to the possibility of a beneficial effect. Even the chance of a possibility of doing something against tuberculosis should be an inducement for medical men to try so simple a treatment as ozone inhalation. As to the other side of the question, one should not lose sight of the influence of psychological conditions on physiological functions. We feel better in a room when there is no smell and to obtain that result we must ventilate to an extent far beyond the necessary replenishment of used up oxygen. What we really use ventilation for is to sweep out odors by large volumes of fresh air and if we can use ozone for that purpose we shall need far less fresh air for replenishment; this in winter means less expensive heating.

The problem of ventilation, however, is not such a simple one, as everybody who has to provide for doing it efficiently knows by experience. Sweeping out the used air has to be done by a large volume of new air which generally means a draft and usually the result is less efficient ventilation in order to avoid excessive drafts. If we try to express in grams the quantity of organic volatile matter present in a crowded space, we realize its smallness. In fact it sometimes does not amount to milligrams which explains the fact that ozone, one part in a million, is quite strong enough to take care of the destruction. We need no more than milligrams of ozone to do the work and it is a pity that unloyal objections to its use have been made, for in ozone we have a means of very cheap and efficient ventilation, since a hundred-watt apparatus will take care of the health of a large number of people. We may well remind the reader of the familiar example generally cited in text books on physics to illustrate the sensitiveness of our olfactory nerves. Asafoetida can be detected by its odor when present to the extent of one part in a thousand million million; this is an extreme case, but it is well known that it takes but very little of an odorous gaseous substance to be perceptible. In fact ozone itself is a good example since one part in ten million of air can be very easily noticed.

As to the amount of ozone required to purify the air in a room, it is safe to say that you should hardly perceive it. If there is a marked odor of ozone it proves that there is too much of it. It would do no harm, but some do not like it and from the business man's point of view, it is a wiser policy not to overdose the quantity, and thereby avoid complaints. Some people think ozone will never be used as a therapeutic because all of it is destroyed long before it has reached our lungs. I do not share that opinion for my personal experience goes to show that there actually is an increase in the oxyhaemoglobin percentage and that can be the case only when the ozone is not entirely absorbed by the mucous membranes that it passes on its way to the lungs.

In conclusion I wish to state that the actual applications of ozone are few, but the possible applications are numerous. Ozone can be had now in any quantity and quality and for a price that in many cases is less than that of other oxidizing agents.

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[1] "Ozone in Ventilation," *Heating and Ventilation*, **10**, Pt. 1, 30–35 and Pt. 2, 13–18.

A NEW VISCOMETER FOR GENERAL SCIENTIFIC AND TECHNICAL PURPOSES[1]

By Eugene C. Bingham

Received November 25, 1913

Bingham and White[2] have already published a description of a viscometer with which absolute viscosities can be measured with very great certainty. This form of apparatus is easily made, but since the dimensions of the apparatus must be accurately known for absolute measurements, the time consumed in the calibration is considerable. So for general purposes it is preferable to calculate the *absolute viscosities* from *measurements* which are only *relative*. By this procedure not only is the calibration simplified but the apparatus itself may be made simpler and less delicate to handle.

It will be urged that viscometers in great number have already been devised for relative measurements. Why another one? The answer is that relative measurements are comparatively valueless unless the results can be calculated to absolute units. It has been supposed that the relative measurements obtained by the use of instruments of the Ostwald type might be calculated to absolute units without difficulty. This is not generally true and the reason is not far to seek. In the viscosity formula for calculating absolute viscosities[3]

$$\frac{\eta}{\eta_0} = \frac{st}{s_0t_0}$$

which seems to be almost universally used, no account is made of the loss of the kinetic energy of the liquid within the capillary, this energy disappearing outside of the capillary without helping to overcome viscous resistance within the capillary. Furthermore, it can be shown[4] that this correction does not come into the calculation in such a way that it may be made to disappear. Viscometers of the ordinary type are deficient because the pressure producing the flow through the capillary is not variable at will. The result is that with very fluid substances the kinetic energy correction becomes large unavoidably, and with rather viscous substances the time of flow becomes intolerably long, necessitating the use of several instruments. With a very long period of flow the difficulties due to clogging with dust particles become very great. Applebey[5] had shown that with varying pressures, the values of st in the above formula, for a particular liquid, are only constant when the time of flow is rather great—for his particular instrument of the Ostwald type, at least six minutes. But with such sluggish flow he found that "in spite of all precautions, the tubes frequently became contaminated with dust." The necessity of the knowledge of the exact specific gravity of the liquid at each temperature where a viscosity measurement is desired lessens the convenience of this type of instrument. Both the unreliability and the inconvenience of these instruments may be avoided by using variable pressure.

THE PROPER DIMENSIONS OF AN APPARATUS FOR MEASURING VISCOSITY

The question of the proper dimensions of the apparatus should merit more attention than is usually given to this subject. A study of the best viscosity data leads one to believe that an accuracy of one-tenth of one per cent can readily be attained. If one desires values with a smaller limit of error than one-tenth of one per cent he should undoubtedly make absolute and not relative measurements. There does not exist the necessary experimental data for standardizing and testing a relative instrument for such a high degree of precision. We, therefore, assume that a relative instrument may be depended upon only to one-tenth of one per cent and that until our data are amplified, the absolute method must be used for measurements of higher precision.

With a stop-watch reading to 0.2 sec. the time of flow may be made as small as 200 sec. The volume of flow should be small for the following reasons: (1) The velocity of the liquid within the capillary should be low in order that the kinetic energy correction may be kept from becoming inconveniently large. (2) The time of flow should be small in order to economize time, and in order that the temperature may be the more easily kept constant during the time of flow. (3) Small masses of liquid come to the temperature of the bath more quickly. (4) There is also an economy of material. The minimum volume of flow is determined by our ability to read the volume with the desired accuracy. This in turn is determined by the diameter of the constricted portions of the apparatus above and below the measured volume. If, however, the constricted parts have very small bore, the effect of capillary action becomes disturbing. In particular, very viscous liquids do not drain out of the capillary, a meniscus is formed bridging across the capillary and a pressure is set up opposed to that causing the flow and the results of the measurement are then quite valueless. The troubles due to bad drainage may be minimized by having the drainage surfaces everywhere as nearly vertical as possible. In other words the change from the constricted tube to the tube of larger diameter should be made gradually. A constricted part with a bore of 0.25 cm. would have a volume of nearly 0.05 cc. per centimeter of length. Assuming that as the meniscus passes the marks, it can be read to 0.01 cm. it is only necessary to have a volume of 0.5 cc. but in order to provide a margin of safety in the construction and use of the apparatus, we have chosen 3 cc. as the volume of flow.

Testing for any error due to faulty drainage is easily accomplished. It is only necessary to test the flow of the most viscous liquid to be measured, using very different rates of transpiration. Lack of perfect drainage will show itself by the substance appearing to be more viscous at the lower rate of flow. Generally the more viscous liquids must be allowed to flow

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[1] Twentieth communication bearing on this subject. Cf. *Physical Review*, **35** (1912), 407. *Ibid.*, N. S. **36** (1913), 96; *Z. physik. Chem.*, **83** (1913), 641; *J. Chem. Soc.*, **103** (1913), 959; *J. Physical Chem.*, Feb. (1914).

[2] *Z. physik. Chem.*, **80** (1912), 670.

[3] η_0, s_0, and t_0 represent the viscosity, density and time of efflux of the liquid which is taken as standard: η, s, and t are the corresponding quantities for the liquid to be measured.

[4] *J. Chem. Soc.*, **103** (1913), 959.

[5] *Ibid.*, **97** (1910), 2000.

slowly enough so that the drainage will be complete. In the test here given, the drainage may conceivably appear to be perfect or even ultra-perfect. But this can be the case only when the flow begins with the meniscus of the liquid considerably above the upper mark, in which case the transpiration volume will be increased by a certain amount caused by drainage from the surfaces above the mark. This gain in volume will tend to offset the loss of a part of the transpiration volume which fails to pass through the capillary during the determination. Hence, it is highly advantageous to have the shape of the apparatus above the upper mark similar to that above the lower mark so that these effects may as nearly neutralize each other as possible.

The ends of the capillary are made trumpet-shaped in order to aid the drainage by avoiding horizontal surfaces and also in order to avoid the sharp corners on which filter shreds might get hung, causing clogging.

In making absolute measurements, it is customary to use a horizontal capillary. The theory for an inclined capillary is somewhat more complicated, but for relative measurements there appears to the author no reason against its use. There are some important advantages to be gained by the use of a vertical capillary. In the first place it is desirable to use a long capillary in order that the radius of the capillary may be relatively large and the kinetic energy correction relatively small and that any possible effects of the ends of the capillary may be negligible. Thus only with a vertical capillary may the limbs be kept close together, so that any small error in keeping the limbs exactly vertical will not so seriously affect the hydrostatic level in the instrument. Furthermore, the apparatus may be made stronger and more convenient to handle, and a smaller bath is required to hold it. It is not desirable to use a bent capillary, not only because of the unknown effect of the centrifugal forces but because of the danger of constrictions in the capillary at the bend. Since the velocity of flow varies as the fourth power of the radius, it will be greatly increased by a small constriction, and eddy currents will be formed at a relatively low rate of transpiration. The kinetic energy correction will also be correspondingly increased. Eddy currents cannot be tolerated even in a relative instrument and the kinetic energy correction should be kept low.

The pressure should be variable at will so that the time of flow may be kept reasonably constant. There need be no upper limit to the pressure, since liquids are practically incompressible. A pressure of 50 grams per sq. cm. can easily be read to 0.1 per cent on a water manometer, hence this may be taken as the lower limit.

As already pointed out, a long capillary is desirable, but since it is difficult to get a capillary of an exactly specified bore, it is best to pick a capillary of approximately the desired radius and then to cut the length to fit the other dimensions. Assuming that 20 cm. is a convenient length, Fig. 1 is given to show just what lengths should be taken from capillaries of different radius, the values being calculated by means of equation (1), using the above dimensions t = 200 sec., p = 50 grams per sq. cm., and V = 3.0 cc. on the assumption that the highest fluidity to be measured is 500. There is no object in following the current custom of using a variety of viscometers in measuring liquids of considerably different fluidity. All that is necessary is to have a sufficient range of pressures at one's disposal. Of course, if one is not going to measure the viscosity of very fluid substances like ether and hexane it may be best to construct an instrument which will require lower pressures, near the minimum of 50 grams given above, but this is purely a matter of convenience. In curve B of Fig. 1 we give the lengths required with capillaries of different radii on the assumption that the highest fluidity to be measured will be only 125 absolute units.

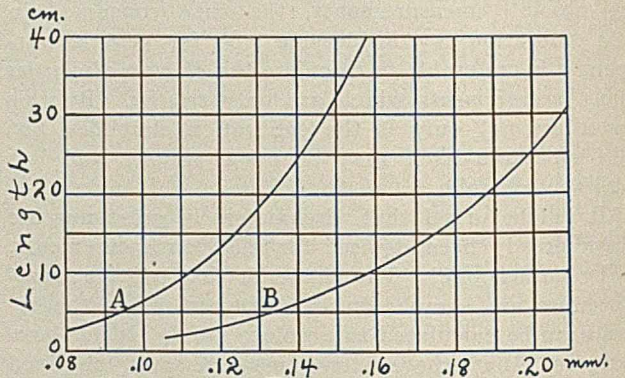

FIG. 1

Lengths required from a capillary of given radius, assuming the minimum values o t=200, p=50, and V=3, (A), when the maximum fluidity to be measured is 500, and (B), when the maximum fluidity to be measured is only 125.

THE CONSTRUCTION OF THE APPARATUS

The appearance of the viscometer is shown in Fig. 2 as drawn to scale. The capillary is made in two parts EF and GH, from non-soluble glass. The transpiration volume is contained between the two marks B and D. In constructing the apparatus it is very important that the volume of C should be similar in shape, equal in volume to the volume K, and moreover, it is important that their centers of mass be as nearly as possible at the same elevation. This is done in order that the average resultant hydrostatic head of liquid within the instrument during the time of flow may be as nearly negligible as possible. It is also important that the volume AB should be equal to the volume HJ. As the viscometer is made of thin glass in order to facilitate the passage of heat a brace is put in between the right and left limbs of the instrument in order to strengthen it. This viscometer may be obtained from Eimer and Amend of New York.

A diagrammatic arrangement of the apparatus is shown in Fig. 3. The viscometer V is shown in a bath which also contains a thermometer, stirrer, etc. At M and N are two three-way cocks for connecting one limb of the viscometer to the pressure while the other is turned to air. After a measurement, the position of the cocks is reversed and a duplicate observation is made or both cocks may be turned to air. A drying device is shown at D, and a reservoir for keeping the pressure constant is indicated at *A*. For this purpose a large glass bottle will serve, but particularly for the higher pressures an ordinary gas tank, wrapped in felt to keep the temperature steady, is convenient. The manometer *E* is conveniently filled with water but at the higher pressures mercury is required. It is best, therefore, to have two manometers, either of which may be connected to the pressure at will, but only one is shown in the figure. It has been found most convenient to read the manometer on a steel tape supported vertically against a strip of plate glass mirror. By bending both limbs of the manometer in such a way that the upper half of the right limb is directly above the lower half of the left and closed limb only one tape is required and the measurement is thus simplified. The upper part of the closed limb is prolonged upward so that all danger is obviated of the liquid in the manometer being drawn back into *A* or *D* when the pressure is removed. As shown in the figure, the pressure is obtained from a tank of compressed gas, *B*, but it may be obtained by means of an aspirator, a hand pump, or by means of a head of water. Generally it is necessary to have a check-valve, *F*, to hold the pressure once obtained. The right limb consists of tubing of very small diameter while the left limb is of large diameter. A little mercury at the bottom allows the easy passage of air to the left but not toward the right.

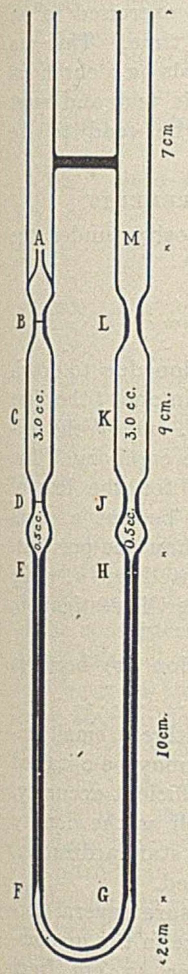

FIG. 2

In making viscosity measurements by the variable pressure method, it is neither necessary nor desirable to have every possible pressure at one's disposal. It is better to have only a few considerably differing pressures. It is desirable, therefore to have a device for giving constant pressures at the desired intervals. Such an arrangement is shown at *G*. The right limb is of large bore and contains a liquid through which the excess of gas rises in a fine stream. Other smaller pressures are obtained by allowing the gas to pass through the cocks *1*, *2*, or *3*.

It is often desired to measure the viscosity of a liquid above its ordinary boiling point in which case the cocks *M* and *N* must not open to air at *P* but, together with the open end of the manometer, they must lead to a low pressure reservoir, *C*. The air in this reservoir is maintained at a constant pressure by means of the second pressure regulator *H* like that at *G*.

The dotted part of the apparatus is not essential to the manipulation under ordinary conditions. All of the parts except the viscometer and the manometer may be made of metal so as to withstand high pressures, but glass tubing with rubber connections will serve for ordinary conditions.

If one is working at other than atmospheric pressure, it is unnecessary to add that another manometer is essential if the pressure within the reservoir *C* must be exactly known.

THE MAKING OF A VISCOSITY MEASUREMENT

After thorough cleaning, the apparatus is rinsed out with pure, dust-free water. If other liquids than water are to be introduced, dust- and grease-free alcohol and ether, and dry air which has been passed through cotton may be used for drying. The liquids may be regarded as satisfactory when dust particles cannot be seen when carefully examined in the direct rays of the sun.

The apparatus is then partially filled with the pure liquid to be measured, the liquid being introduced into the right limb. Pressure is now applied to the right limb and as the liquid passes into the left limb care is taken that no bubbles remain in the apparatus. Finally the liquid runs over into the trap at *A*. Making sure that the temperature is adjusted properly, the liquid is allowed to run into the trap until the lower meniscus reaches exactly to the point *H*, when the pressure is removed, the cock *N* being turned to air. If much liquid is in the trap it may be removed. The remaining liquid in the apparatus is the "working volume," so-called by Thorpe and Rodger.[1] Keeping the temperature constant, the left limb is now turned to pressure and while the meniscus falls from *A* to

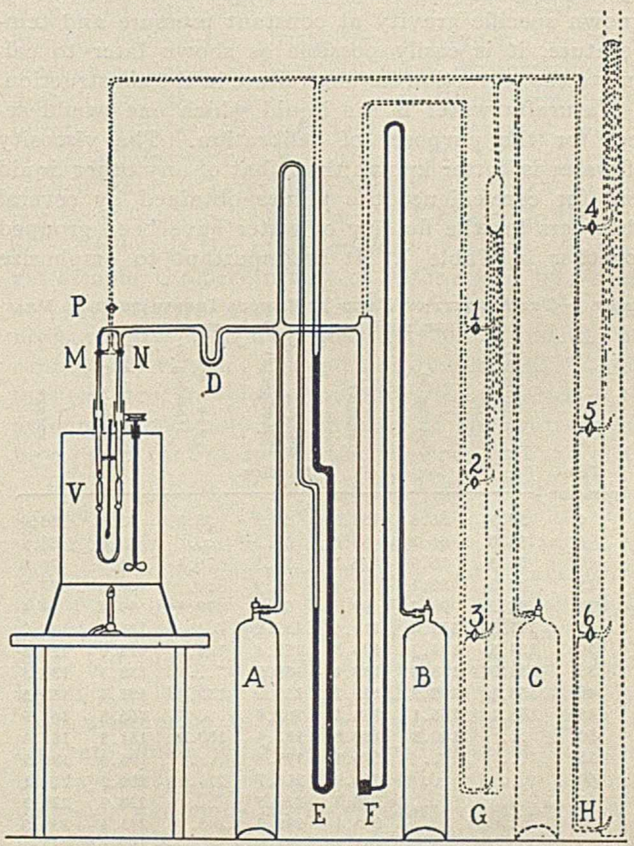

FIG. 3

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[1] *Phil. Trans.*, **185A** (1894), 397.

B the pressure and temperature of the manometer are read. As the meniscus reaches the point *B* the time record is begun and closed when the meniscus reaches the point *D*. The pressure and temperature are again read after which the left limb is immediately turned to air, before the point *E* is reached. The liquid is now in exactly the position for a duplicate reading in the reverse direction. On account of the change in volume on heating, it is necessary to adjust the working volume after each elevation of temperature.

It is evident that the duplicating observations in reverse directions will not be identical even if the pressure as read on the manometer is the same, unless the effective hydrostatic head within the instrument is equal to zero. In constructing the instrument it was intended to make this as small as possible, and by making a series of observations with a liquid of known specific gravity at constant pressure and temperature, it is easily possible as shown later to calculate the correction for any failure in the construction.

Naturally water is the liquid which one would select for the purposes of calibration. The viscosity of water is better known than that of any other liquid and for convenience the values obtained by several observers for the fluidity of water have been grouped together in Table I. It is important to emphasize here that the testing of a relative instrument with only one liquid at a single temperature is entirely unsatisfactory. Such a procedure allows all sorts of errors to creep in without any means of detection. It is best to use several liquids and a variety of temperatures in the calibration and testing. The fluidity of water increases over 500 per cent from 0° to 100°. For very fluid liquids, ether and hexane are suggested, and for very viscous liquids cane sugar solutions.[1]

Table I—The Fluidity of Water at Various Temperatures as Measured by Different Observers

Temperature	Poiseuille(*a*)	Sprung(*b*)	Slotte(*c*)	Thorpe and Rodger(*d*)	Lyle and Hosking(*e*)	Bingham and White(*f*)	Average
	Fluidity						
0	56.3	56.3	55.3	56.2	55.8	55.9	55.9
5	66.0	66.2	65.6	66.2	...	65.6	65.9
10	76.3	76.9	76.1	76.5	76.4	76.9	76.6
15	87.3	88.1	87.4	87.9	...	87.6	87.7
20	99.2	99.7	99.2	99.8	99.1	99.4	99.4
25	111.5	111.6	111.6	112.0	...	111.8	111.7
30	124.5	124.7	124.5	125.4	124.7	125.0	124.8
35	138.7	138.3	138.1	138.9	...	138.3	138.5
40	153.1	152.2	152.2	153.2	152.2	152.4	152.5
45	168.1	166.1	166.1	167.4	...	166.8	166.9
50	...	180.8	180.8	182.4	180.8	181.8	181.4
55	...	...	196.1	197.8	...	196.9	196.9
60	...	...	211.9	213.7	211.9	211.2	212.1
65	...	...	228.3	229.5	...	228.9	228.9
70	...	...	245.1	246.3	245.7	245.4	235.6
75	...	...	261.8	263.5	...	262.8	262.7
80	...	...	279.3	280.5	279.4	280.1	279.8
85	...	...	296.7	298.3	...	298.7	297.9
90	...	...	314.5	316.8	316.5	318.2	316.5
95	...	...	332.2	335.0	...	334.0	333.7
100	...	...	350.9	353.4	350.9	...	351.7

a. *Mem. présent. pars divers Savants à l'academie Roy. des Sciences de l'Inst. de France*, **9** (1846), 433. Calculation by Thorpe and Rodger.

b. *Pogg. Ann.*, **159** (1876), 1.

c. *Wied. Ann.*, **20** (1883), 257.

d. *Loc. cit.*

e. *Phil. Mag.*, [6] **3** (1902), 487.

f. *Loc. cit.*

Finally, it needs to be remarked that a correction may be required for errors of thermometer and stopwatch. Particular care needs to be exercised to see that the stop-watch keeps *uniform* time. This can be tested by timing ten-minute intervals on a chronometer. Many stop-watches fail in this test and must be discarded. Temperatures must be read to the hundredth part of a degree.

THE CALCULATION OF MEASUREMENTS

The formula for calculating viscosity under the above conditions of measurement is

$$\eta = \frac{\pi g r^4 t p}{8Vl} - \frac{mn\rho V}{8\pi t l} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where $\pi = 3.1416$, g is the acceleration due to gravitation, r is the radius of the capillary in cm., t the time in sec., p the pressure in grams per sq. cm., V the volume of flow in cc., l the length of the capillary. The second term contains the correction for the loss of kinetic energy and it should always be but a small fraction of the whole, preferably less than one per cent. The number of capillaries is represented by n, while ρ is the density of the liquid under investigation, and m is a constant equal to 1.12.

For a given instrument the equation (1) becomes

$$\eta = Ctp - C'\rho/t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Since the second term is of comparatively small importance, the value of $C' = mnV/8\pi l$ may be obtained by approximate measurement with sufficient accuracy. Knowing the values of p and t as well as the density and viscosity of the liquid used in standardization, the value of C may be readily calculated.

In obtaining the value of the pressure several corrections must be made: (1) The pressure in the manometer must be calculated in grams per sq. cm. from the known height of the liquid and the specific gravity of the liquid at the temperature observed; (2) This pressure must be corrected for the weight of the air displaced by the head of liquid in the manometer, and if the limbs of the manometer are very unequal in bore a capillary correction may be required; (3) Unless the surface of the liquid in the lower limb of the manometer is at the same height as the average level of the liquid in the viscometer, a correction must be made for the greater density of this enclosed air, which is, under pressure, than of the outside air; (4) Finally a correction must be made for the average resultant hydrostatic head of liquid within the viscometer. If the two volumes *C* and *K* in Fig. 2 are exactly similar in shape, equal in volume and at the same elevation when the viscometer is supported in its vertical position, it is evident that the gain in head during the first half of the flow will be exactly neutralized by the loss in head during the last half of the flow. Since this is never exactly the case, a correction is made as follows: Duplicate observations in reverse directions are made upon a liquid of known density and viscosity at a constant pressure and tempera-

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[1] Cf. Hosking, *Phil. Mag.*, [5] **49** (1900), 274.

ture. Let t_1 be the time of transpiration from left to right and t_2 the corresponding time from right to left. Let p_0 be the pressure, corrected except for the average resultant head of liquid in the viscometer. Let this head be equal to x centimeters of liquid as the liquid flows from left to right, so that in this case the total pressure becomes equal to $p_0 + \rho x$ but when the liquid flows from right to left the pressure must be $p_0 - \rho x$. From equation (2) we obtain the following equations.

$$p_0 + \rho x = \frac{\eta + C'\rho/t_1}{Ct_1} = \frac{\eta}{Ct_1} + \frac{C'\rho}{Ct_1^2}$$

$$p_0 - \rho x = \frac{\eta + C'\rho/t_2}{Ct_2} = \frac{\eta}{Ct_2} + \frac{C'\rho}{Ct_2^2}$$

whence

$$x = \frac{\eta}{2C\rho}\left[\frac{1}{t_1} - \frac{1}{t_2}\right] + \frac{C'}{2C}\left[\frac{1}{t_1^2} - \frac{1}{t_2^2}\right]$$

In obtaining this correction term it is sufficient to use the approximate value of C obtained by using equation (2) with p_0 in place of p. In subsequent calculations it is necessary to know the specific gravity of the liquid to be measured in order to make the necessary pressure correction and also in order to make the kinetic energy correction, but it is to be noted that if the construction of the viscometer and the measurement has been properly done these correction terms will both be small; hence, the specific gravity need be only approximately known, which constitutes a great advantage of this method.

If the viscometer is constructed of the same material throughout, the coefficient of expansion of the material need not be taken into account, as may be easily verified by introducing the coefficient of expansion into the dimensions in equation (1). But we cannot legitimately assume that the same is true of any changes in the dimensions of the apparatus due to the solubility of the glass. For this reason the time of flow of the liquids used in calibration should be redetermined occasionally. However, so far as is known to the author, the most prolonged use of a given instrument has never yet shown a change in the time of flow which could be attributed to this cause.

In conclusion, we believe that this viscometer is capable of a higher degree of precision than the forms usually employed and that at the same time it is easily made, convenient to use, and economical of time. The corrections which have been discussed are small in this type of apparatus, so that the calculation of the viscosity by means of equation (2) is simple.

Richmond College, Richmond, Va.

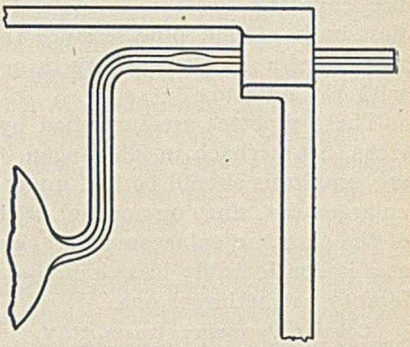
MODIFIED HEMPEL PIPETTES

By R. P. Anderson

Received November 7, 1913

The chief objection to the present form of the Hempel pipettes lies in the fact that small drops of the reagent collect in the capillary while the gas is in the pipette and are carried over into the burette on the return of the gas. This causes no appreciable error when water is used as the confining liquid, but is objectionable on account of the unsightly appearance that it gives to the burette and on account of the frequency with which the water must be changed. However, when mercury is used as the confining liquid and, as is usually the case, a small amount of water is placed on its surface, contamination of this water by the reagent will result in a change of the tension of aqueous vapor, and may influence to a measurable extent the volume of the gas.

For example, let it be assumed that there is 0.1 cc. of water on the mercury in the burette and that about 0.013 cc. of alkaline pyrogallol is carried into the burette during the absorption of oxygen. Since this reagent contains at least 0.8 gram of potassium hydroxide per cc. of solution, the resulting liquid in the burette will be approximately a 10 per cent solution of potassium hydroxide. At 20° C., the vapor pressure of water is 17.53 mm., and of a 10 per cent solution of potassium hydroxide, 16.38 mm. On the basis of 760 mm. as the total pressure of water vapor and gas sample, the percentages of water vapor by volume are, respectively, 2.31 and 2.16. At 25° C., the vapor pressures are 23.76 mm. and 22.19 mm., and the percentages by volume, 3.13 and 2.92, respectively. Therefore the error in volume caused by the presence of this amount of potassium hydroxide in the water would be 0.15 per cent at 20° C., and 0.21 per cent at 25° C.



The change in the volume of a gas sample that is caused by this contamination with reagent of the water in the burette depends, of course, upon the reagent in question and upon the care that is taken in the manipulation. In the hands of an experienced gas analyst, the error need never be as large as 0.1 per cent, but oftentimes, especially in student's work, it becomes as large as that of the preceding example.

In attempting to modify the pipettes so that the reagents would be largely retained in them during the return passage of the gas, an enlargement 3 mm. in diameter was made in the capillary tube of each pipette just below the upper horizontal portion of the frame. This enlargement serves as a trap for the small drops of reagent that are carried up to it and since the amount of reagent that collects in the capillary tube between the enlargement and the tip of the burette is small, very little, if any, reagent is carried over into the burette. However, since there is no advantage in the U-shaped capillary tube of the usual form of the Hempel pipette in the present method of manipulation[1] and since its presence increases the amount of reagent that must be retained in the trap, the pipettes were finally constructed as shown in the accompanying figure. This modification is the one that is being used in the Cornell laboratory at the present time on the absorption pipettes. The combustion pipettes are similarly constructed with the exception of the

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[1] Dennis' *Gas Analysis*, pp. 59–64.

enlargements. The length of the horizontal portion of the capillary tube is such that the pipette fits in the frame designed for the original form. This horizontal portion can be shortened somewhat by bringing the first bulb of the pipette over to the left edge of the pipette frame and changing the form of the frame accordingly. It was not thought desirable to extend the capillary tube in a vertical direction[1] from the first bulb of the pipette since that would necessitate the use of a longer capillary in making the connection with the burette.

These pipettes are furnished by Greiner and Friedrichs, Stützerbach in Thüringen, Germany. In ordering, emphasis should be laid upon the *actual* size of the enlargement, since on account of the magnifying action of the glass, an enlargement *apparently* 3 mm. in diameter is considerably less than that, and is not as satisfactory as the larger one.

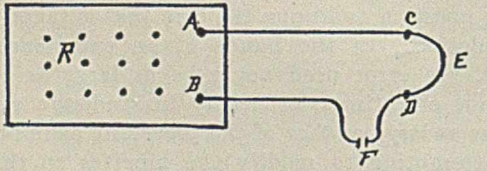
Cornell University, Ithaca, N. Y.

AN EFFICIENT METHOD FOR CUTTING GLASS

By J. I. Hardy

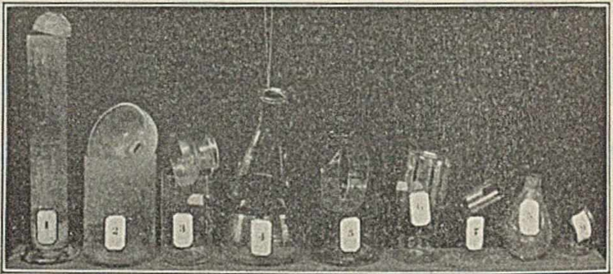
Received December 8, 1913

There is often great difficulty in satisfactorily cutting glass in the scientific laboratory, and this is especially true in the case of glassware of large diameter. There are several methods in common use. Probably the fine flame of the blowpipe applied upon a file scratch is one of the best known methods. The diamond point is often used with satisfaction. A metal rod may be bent to the shape of the object to be cut, heated red hot, and passed over the surface on the line where the glass is to be cut, then if the glass is plunged into water it will separate on this line of contact. There is a method by Kunz,[2] using an electrically heated nickel wire on a rather complicated apparatus which requires an electric current of about eleven amperes. In this method a few drops of water are applied to the heated glass, causing it to crack.



The writer believes the following method to be capable of wide application, and that the desired results can be rapidly and efficiently obtained in the average laboratory. The equipment consists of an electric system giving at least six amperes electric current, a resistance apparatus consisting of a rheostat or a bank of twelve lamps (16 c. p.) arranged in parallel, and a piece of No. 24 nickel-chromium wire. When long tubing is to be cut, a steady rest will prove helpful and can be arranged to suit the convenience of the operator. The method of procedure is as follows: Bind a piece of wire around the glassware, twisting the ends together and making sure that the wire follows the line where the glass is to be cut. This wire serves only as a guide, and may be of any inexpensive material. In the diagram, *R* indicates the bank of lamps, which is used on account of being both inexpensive and easily adjusted to definite resistance. At binding posts *A* and *B* connection is made with the electric light system of the building. Between *C* and *D* is inserted the No. 24 nickel-chromium resistance wire *E*, and *F* is the switch.

After the lamps *R* are loosened sufficiently to break their connection, the switch at *F* is turned on, and the lamps are screwed in one at a time until the wire *E* is a dull red. The glassware which has been prepared with guide wire is given a slight file scratch of about one-quarter inch length on the line to be followed in cutting, and is brought into the loop *E* and revolved two or three times, holding the nickel-chromium wire close to the metal guide. After the glassware has been revolved two or three times in the loop *E* more lamps are connected in the bank *R* until the wire *E* is a bright red. Now the wire loop *E* is held in contact with the file scratch for a few seconds until a crack is started. The glassware is now revolved, keeping the heated wire slightly ahead of the crack until the glass is cut off. If the wire cools it may be released slightly from the glass until it regains its heat.



1—Graduated Cylinder, cut above 1 L. mark.
2—2.5 L. bottle. 3—Similar to 2.
4—2 L. Erlenmeyer Flask.
5—Battery Jar, cut $^1/_4$ in. below break.
6 and 9—Jena beakers, 1 L. and 150 cc.
7—Brittle Thin-walled Tubing, poor grade of glass.

This method is very effective and can be used to cut any kind of glass from cheap bottle glass to the best Jena. It will work successfully on glassware with cylindrical, spherical or conical walls, and will cut the glass in any direction in which the guide is placed. A $2^1/_2$ liter bottle was split (after having its neck cut off) horizontally, although it required more time than any of the ordinary glass-cutting problems because of the thickness of the bottom of the bottle.

The accompanying photograph shows nine samples which were cut by this method in about one-half hour.

Agricultural Experiment Station
University of Tennessee, Knoxville

APPARATUS FOR TAKING DUST AND BACTERIA SAMPLES OF AIR

By Charles Baskerville

Received February 12, 1914

In the investigation[1] of the air of the schoolrooms of New York City, carried on with Professor C.-E. A. Winslow at the request of the School Inquiry Committee of the Board of Estimate and Apportionment, it early became apparent on account of the large num-

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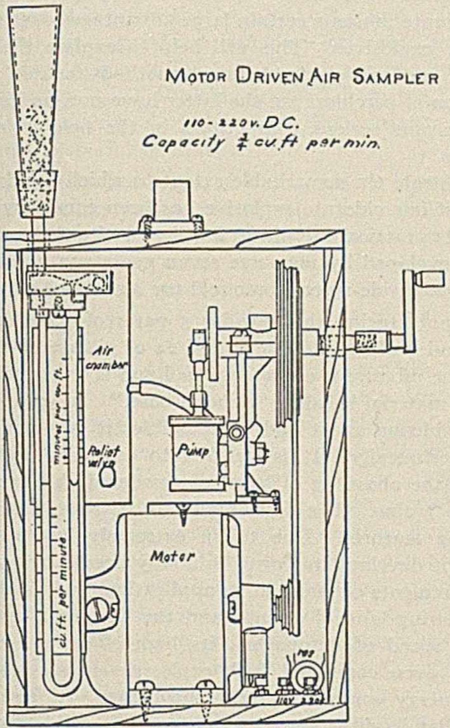
[1] See White and Campbell, *J. A. C. S.*, **27** (1905), 734.

[2] *Chem. Ztg.*, **37**, 406–407.

[1] See This Journal, this issue, p. 251.

ber of samples to be collected, in widely separated schools perhaps on the same day, that it would be necessary to depend upon some other method than one relying upon the use of a hand pump in conjunction with a gas meter. The limited time per day (school hours) available for collecting samples and the transportation of apparatus were factors of supreme importance.



After many conferences, in which the entire staff took part, Messrs. Wallace and Tiernan, Engineers, New York City, who also had a representative present, supplied us with an apparatus, which we think should be described for the benefit of those members of the Society interested in atmospheric hygiene.

The principle of the apparatus depends upon measuring volume by time. The apparatus includes an exhaust pump of the friction type run by a $^1/_{32}$ horse power motor and a measuring apparatus of compact and ingenious design. This apparatus, placed between the pump and the sampling filter, consists of an air chamber, the inlet of which is connected with the two ends of a U-tube, graduated on its distal arm. The opening of this distal arm is so reduced that the pressure at the mouth of the proximal arm is registered by a rise of the liquid in the distal arm. The whole apparatus is enclosed in an oak box fourteen inches by twelve inches, air being drawn in through an opening at the top and forced out through an opening in the side. The upper opening is fitted with a small steel cup with a rubber stopper inside, having a hole large enough to fit the constricted end of the sugar or sand filter. At the base of the cup, an extension passes through the wooden cover and screws on to the suction chamber of the machine.

The apparatus as first made was designed to draw through about three-quarters of a cubic foot of air per minute. With the resistance due to the sand or sugar, however, the time required was about three minutes per one cubic foot. The pump when first tested proved to be too noisy, so the apparatus was placed within a second box lined with felt and a muffler attached to the exhaust. This reduced the noise to a minimum. Teachers in whose classrooms we operated, were consulted, and no objections were offered to the noise made by the apparatus during class hours.

The accuracy of obtaining dust and bacteria samples by means of this form of apparatus was compared with the hand pump and meter method and approximately similar results were obtained. A further check was made by running the electrically driven pump and measuring the flow by means of standard gas meters. Both the electrical pump and the gas meters were tested and standardized by the manufacturers.

The amounts of air taken for samples for bacteria and dust with this machine were usually three feet and two feet, duplicate determinations always being made. The official methods of the Public Health Association were used in making counts of bacteria and studying the character of the dust collected.

The apparatus might be used extensively in studying the air of factories and other places where occupational diseases are to be investigated.

College of the City of New York

ADDRESSES

RECENT DEVELOPMENTS IN COMMERCIAL EXPLOSIVES[1]

E. A. LeSueur

The last few years have seen a great development in the use of safer explosives than were previously commercially available or even believed to be possible. It is my purpose to take a brief general view of the trend of development, to deal with some particularity with an explosive of rather unique character with which I have had much experience, and incidentally to outline certain advantages and disadvantages of the new types.

The most striking feature among the changes occurring in the field is the almost omnipresence of nitrate of ammonia. Although a salt of a hypothetical metal it breaks down into a gaseous mixture containing a surplus of free oxygen and no solid residue whatever and, insofar, is therefore peculiarly suited to employment in explosives. Unfortunately it is very hygroscopic and of deplorably low specific gravity so that but a comparatively small weight can be packed into a given cavity. On the other hand, its adaptability, within the above limitations, is remarkably wide and we find it associated with almost every ingredient known to explosives manufacture, and especially with nitroglycerin. So wide is the present market for this material for use in explosives that practically the entire output of the gigantic Norwegian Atmospheric Nitrate works is now delivered in the form of nitrate of ammonia, and further important developments in the cheap manufacture of this important compound are to be looked for in the very near future.

Perchlorates, and especially perchlorate of ammonia, have

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[1] Presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10–13, 1913.

numerous advocates among the inventors, but so far do not appear to have entered the market to any very great extent. Perchlorate of ammonia is obviously, from its chemical formula (NH_4ClO_4), well adapted to act as an explosive itself and at the same time provide three atoms of excess oxygen to combine with additional material. Aside from any other considerations, it possesses the serious defect of liberating considerable hydrochloric acid or a mixture of the same with chlorine. The use of certain powdered metals in the mixture serves very largely to eliminate both of the above gases.

A most profound impression has been made in the explosives trade of late years by the nitro derivatives of toluol. and especially by the various commercial mixtures of di- and trinitrotoluol now on the market. The cheddites (practically mixtures of the nitrotoluols with chlorate of soda and a vegetable oil, preferably castor oil) have achieved considerable well earned popularity, and the flood of current patent applications for explosives containing trinitrotoluol reminds one of nothing so much as of that which occurred some ten years ago for acetylene generators. Bearing in mind that trinitrotoluol possesses certain of the properties, so far as explosive effects go, of nitroglycerine itself; that it withstands water and is not affected by cold, and that it can be handled with absolute safety until blended with other materials that may increase its sensitiveness, it is not difficult to understand the enthusiasm with which it has been received by amateurs as well as by others in the explosives field. Aside from any admixture with other materials it forms, in the refined condition, an explosive of quite ideal properties for use in shells, torpedoes, mines and the like. In spite of its fierce and terrific disruptive energy, and of an enormous speed of detonation, it is a safer material to handle, transport and store than, for instance, ordinary calcium carbide. And, notwithstanding its inert behavior, it can be depended on absolutely to explode completely when exposed, in a suitable physical condition, to detonation from an adequate primer. Several European governments are now making extensive use of this intensely interesting compound. Owing to the fact that its constitution ($C_7H_5N_3O_6$) presents too little oxygen completely to combine with the carbon contents even to the monoxide form, the result of explosion is the formation of a cloud of carbon particles which will presumably have advantages in warfare both through marking the position of a shell at the instant of explosion and in obscuring the enemy's vision.

The liquid nitrotoluols are also finding an important use in connection with nitroglycerine. They greatly lower the freezing point of the latter, contribute their quota to the explosive effect, and render the resulting explosive much safer than before.

In addition to the above compounds and many others (including the nitronaphthalenes, benzenes and xylols) the old stand-by, chlorate of potash, holds its own as a prime constituent of modern disruptive powders. It may be worth while to glance for a moment at the extraordinary thermo-chemistry of the chlorates and perchlorates, the same having a vital bearing on the matters of energy developed, sensitiveness and stability of certain explosive mixtures containing them.

Chlorate of potash disengages heat energy to the extent of 93,800 calories per kilogram molecule on formation from its elements, but potassium chloride disengages 105,700 calories, or 11,900 *more* than the chlorate. The addition of three atoms of oxygen to the chloride is accompanied by the absorption of energy to this latter extent, the formation reaction being endothermic. Perchlorate contains one-third as much oxygen again as chlorate, but, instead of the addition being accompanied by a further absorption of heat, there is actually a disengagement of energy, accompanying the entry of this lone atom, of far more (19,900 calories altogether) than the entire amount absorbed when the first three atoms were added. Chlorate stands ready to fall to pieces on scant provocation and, in doing so, gives up not only three atoms of active oxygen to any combustible in the neighborhood, but 11,900 calories per kilo molecule as well. Perchlorate, on the other hand, in spite of its higher degree of oxygenation, requires more energy to drag it to pieces than does the chloride itself, and, in consequence, forms a less sensitive and less energetic constituent for an explosive than the less oxygenated chlorate.

In the light of the above, and especially in view of the fact that the besetting trouble with most modern chlorate explosives is lack rather than excess of sensitiveness, it will be seen that plain chlorate presents certain large advantages over perchlorate for many explosives. This will help to explain the fact that, although modern electrochemical methods enable the ready production of perchlorates, the latter have not, as stated above, so far become serious competitors in the field of commercial explosives.

To illustrate the remarkable extent to which the desensitizing of at least one chlorate explosive has been carried without destroying its practical usefulness I will now cite the case of an explosive developed by me some seven years ago which has been in somewhat wide-spread practical use since that time.

In manufacturing this powder 5 parts of paraffine wax are melted and 4 of ground sulfur and 22 of nitrate of soda stirred into it; the mixture is allowed to cool and is then grained. The resulting material is called "mineral base." In spite of containing an oxidizing agent and combustibles it is completely inexplosive technically. It is finished to explosive by dusting 8 parts (to the above 31 of base) of powdered chlorate of potash over the grains. The final material possesses a number of interesting features. Due to an extremely low speed of detonation it develops its power in a way peculiarly available for the requirements of many large applications such as heavy rock work, clearing land of stumps and the like; and, owing to the said low speed of detonation, its high effectiveness for these purposes, even compared with explosives possessing decidedly greater energy content, is quite surprising. Its insensitiveness is such that it withstands the impact of a steel tipped service rifle bullet fired from the regular service rifle with a standard charge behind it without response of any kind; although, due to its property of going out after being set fire to when the flame causing ignition is removed, it is possible that incipient ignition occurs during the passage of the bullet. If packed hard it is impossible to explode it by any means whatever. On the other hand, loaded loose, it is an absolutely sure fire with a No. 6 detonator even when unconfined, and, for work in earth, as in removing stumps, it is necessary to bear in mind that confinement may be negligible. When well confined in large shots in solid rock, and especially if detonated with a stick of dynamite, it will withstand any reasonable amount of packing and still give a sure fire. From its composition it will be obvious that it is non-freezing, and, indeed, owing to the paraffine wax incorporated in it becoming harder with increasing cold, it loses its porosity through being pressed into holes less readily cold than otherwise. With regard to stability, it withstands the International Stability Test (75° C. for 48 hours) with indifference, whether with moisture added or not, and some millions of pounds have been used during the past seven years, and in some cases excesses over requirements have been stored by contractors in badly constructed magazines, occasionally for years, and there has never been any sign of heating or decomposition, incipient or otherwise.

The very low chlorate content and the fact that all the other materials are used in their crude commercial condition, together with the extremely simple process of manufacture, render the cost of this powder exceptionally low. It is known under the name of R. R. Virite. A blast containing 600 fifty pound cases was fired on the Canadian National Transcontinental Railway work on the Quebec-New Brunswick border, near Notre Dame du Lac, some years ago, and the two largest blasts at Prince Rupert, the Pacific Coast terminal of the Grand Trunk Pacific, 3500 miles from Notre Dame du Lac, were also shot with it, the charges containing respectively, 1010 and 1000 fifty pound cases of the explosive. Aside from the technical importance of these blasts the spectacular effect is quite indescribable. To give an idea I may say that in the one of these shots that I witnessed the mass of broken rock that had mounted in the air about three seconds after explosion occurred, and which looked like nothing so much as a vast and spreading black tree, contained, to state it in units that will make it sound as impressive as possible, about 175,000,000 pounds. Reference to the efficiency of virite in agricultural work is contained in *Bulletin* No. 134, entitled "Land Clearing," issued from the University of Minnesota by Prof. A. J. McGuire, Superintendent of the North Central Experiment Station.

With reference to the property which this explosive, in common with very many others, has of being more difficult to explode as its porosity diminishes, I wish to point out a certain important corollary which exists in a case where the insensitiveness when closely packed reaches the point it does in a case such as the one under discussion. If compressed forcibly to a specific gravity of about 1.45 it has been found impossible to explode by any amount of detonation, no matter what the degree of confinement. This in spite of the fact that a certain small amount of local combustion occurs where the material is in direct contact with the detonator. The superficially paradoxical situation confronts us that the only condition in which the material can be exploded by hammering between hard surfaces is one in which it becomes insensitive to detonation from another explosive. By this is meant that, in order to cause explosion of the powder by hammering, it has to be packed to a maximum density before the pinching between hard surfaces necessary to cause explosion occurs. Of course what happens when the material is hammered on an anvil is that any excess over what can be pinched down to the thickness of thin paper between hammer and anvil is forced aside and only the trifling amount of powder actually so pinched goes off, and it has hitherto been found impossible by any degree of practicable impact to communicate explosion from the quantity so pinched to the rest of the mass of powder. The importance of this peculiarity in securing freedom from accidents in any case other than where the powder is exposed to detonation from another explosive will be obvious.

If we consider what is the fundamental difference between the blow of a hammer and that of a detonator we see at once why a mass of the explosive which refuses to transmit detonation, however powerful (within the enormous upper limit experimented with) when in a dense (non-porous) condition—why such material may be readily exploded when in a porous condition by a detonator although a blow from a hammer can have only a local effect. The point is that, in the former case, the blow is struck so quickly that the explosive is hammered between the products of explosion of the detonator and, if I may so express it, its own inertia, without having time for its porosity to be interfered with. The passage of a bullet exposes it to the same kind of a blow against its own inertia, but the swiftest bullet is so far inferior in speed to the velocity of the products of explosion of a detonator that it falls short, in the case of a powder of the class under discussion, of producing an explosion. There is also, of course, the essentially important feature, in the case of explosion by a detonator, of exposure to vastly greater heat than from the friction of a bullet or impact of a hammer.

The well compressed material behaves, as previously stated, in a completely inert fashion to attempts to detonate it, but mere crumbling restores it to the explosive condition. It would seem as though a technical division on the lines of classification according to safety might well be adopted to embrace explosives that require outside detonation from another explosive in order to set them off.

I must not close without making reference to liquid oxygen as a constituent of explosives. Modern methods exist for producing this element in a state of high technical purity in the liquid form at a cost extremely low compared with its cost in the combined form in any of the chemicals employed in the explosives trade, so that completely smokeless and fumeless mixtures equal to 75 per cent dynamite can be made at a cost of about 2 cents per pound. As regards safety, explosives containing liquid oxygen stand in a class by themselves in one particular, *i. e.*, in the fact that, should a shot be missed for any reason, the charge presently becomes inexplosive through volatilization. Of course this is merely the merit which accompanies the greatest defect of these explosives. They must be used within a few minutes of being compounded. Nevertheless this is by no means the absolutely prohibitive feature that might be expected, owing to two considerations, one the numerous gigantic individual blasts that are necessary on certain heavy construction works (the time required for the charge to evaporate being comparatively long in such cases) and the other the fact that the addition of the liquid oxygen to the combustible portion of the charge may be made the last thing before firing. I am rather firmly of the opinion that in the heaviest construction works of the future, especially where the so-called "coyote" shooting can be employed, liquid oxygen will play an important part.

This paper is intended to deal with accomplished facts in explosives development and there is no occasion at present to do more than refer briefly to the hopes of the nitroglycerine manufacturers that in synthetically prepared glycol may be found the solution of their bondage to the fluctuation of the corn and cotton seed crops. The production of glycerine depends considerably on the abundance or otherwise of pork and of cotton seed oil and the former depends largely on the corn supply. The stearine candle industry, another feeder to the high explosives maker, is not in a healthy condition, and altogether the situation of the dynamite manufacturers is not so completely free from anxiety in the matter of their glycerine supply as they might wish.

300 Cooper Street
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EXPERIMENTS WITH SMALL ANIMALS AND CARBON MONOXIDE[1]

By George A. Burrell and Frank M. Seibert

The usefulness of small animals in detecting vitiated air in mines is well established. The Bureau of Mines and others have much information on this subject, but in order to make this paper brief, accounts of their practical use or of accidents because they have not been used will not be given here. Time can be devoted, if so desired, to this phase of the subject in the discussion.

The Bureau has experimented with most of the more common small animals, such as canaries, guinea pigs, rabbits, chickens, dogs, mice and pigeons, and finds that canaries or mice are the most suitable for the work. Of the two the Bureau finds canaries to be the most sensitive. They were used in England before their acceptance in this country, presumably in places on the continent also. Their usefulness in husbanding the resources of breathing apparatus is of great importance.

An additional reason for the use of canaries lies in the fact that they are generally easily obtainable, and become pets of the men who have them. If handled intelligently in rescue operations, they seldom die as a result of their exposure to carbon monoxide.

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[1] Presented before the Coal Mining Institute of America, Pittsburgh, Pa., December 4 and 5, 1913. Published by permission of the Director of the Bureau of Mines.

In rather a brief manner, one of the objects of this paper is to give the results of experiments by the Bureau which have shown that they may be used repeatedly in rescue operations without danger of their being more susceptible to carbon monoxide poisoning after several or many exposures. This fact had not been determined experimentally hitherto, as far as the authors are aware. A second important point has to do with the relative behavior of men and small animals to carbon monoxide. Carbon monoxide was the gas experimented with because it is the constituent of after-damp most insidious in its action, most difficult to detect, and responsible for most of the deaths caused by mine explosions. Small animals, however, also feel distress sooner than men in atmospheres vitiated by other gases than carbon monoxide.

EFFECT OF REPEATED EXPOSURE TO CARBON MONOXIDE

Details of these experiments will be given later in a publication of the Bureau. They will only be outlined here. Canaries, mice and guinea pigs were repeatedly exposed to carbon monoxide under different conditions. In some experiments they were exposed to atmospheres that distress them in about two minutes. In the case of canaries 0.25 per cent was used in some experiments, and the animals were exposed 7 to 10 successive times. For instance, the animal was exposed to collapse, and then, when it had apparently recovered (7 to 12 minutes), it was exposed again and again, the object being to see if, after many exposures to a certain percentage of the gas, it would upon subsequent exposures show distress in a greater length of time, *i. e.*, become more or less acclimatized to the gas. No acclimatization effect was noticed. The same experiment was performed with mice and guinea pigs with the same result. Different percentages than 0.25 per cent were also used in the case of both canaries and mice. The experiments were also carried further to the extent that the same animals that had been exposed several or many times on one day were exposed several or many times the next day and on successive days.

Animals were also exposed to percentages that quickly distress them, and after the removal from the atmosphere and recovery were placed in atmospheres that ordinarily do not apparently affect fresh animals. This experiment was also reversed in the case that the animals were first placed in atmospheres that do not affect them, say 0.10 per cent in the case of canaries (for a long time, at least), and then they were exposed to atmospheres that ordinarily affect them quickly to see if results different from the ordinary could be obtained. In performing this work, the results of which can be briefly told, but which required considerable time for its performance, the conditions of recovery work with the aid of small animals was kept in view. In such work parties would usually advance until the animals showed distress. The animals would then in all probability be carried back to fresh air, and further advance, if such were made, would be accomplished with breathing apparatus. A general reconnaisance might be made with the animals to define the danger zone of the mine. In the latter event they might be exposed to proportions of carbon monoxide that would, in each case, cause collapse. Another possible contingency has to do with the use of the animals in a part of the mine where very small proportions of carbon monoxide exists, say 0.10 per cent, a proportion that does not seem to affect canaries or mice (as far as can be observed) in one or two hours' time, and then their use in a place where a larger percentage might be present. It is possible, too, that an animal which collapses at a certain place because of the proportion of carbon monoxide there, might, upon recovery, be used in an atmosphere containing a proportion that does not usually affect a fresh animal. Finally the same animal might be exposed over several successive days while a mine was being explored. It is believed that the experiments performed show that animals will not become acclimatized to carbon monoxide under the conditions surrounding recovery work in mines, and hence become less useful and even a source of danger. It might be mentioned that this question has been raised several times in discussing the use of small animals for detecting after-damp in mines.

It should be mentioned that two Canadian investigators, G. G. Nasmith[1] and D. A. S. Graham, found that the animals finally become acclimatized by continued exposure, *i. e.*, if a guinea pig is exposed for days and weeks to small percentages it can finally stand exposures that would otherwise kill it, but our tests have shown that in the case of small animals which are quickly removed to fresh air (after distress is shown) and then exposed again for a reasonable number of times, this acclimatization effect is not apparent. The two methods of experimentation are not parallel. It is pertinent to add that the effect Nasmith and Graham observed in guinea pigs, an increase in the red-blood cells, has been observed in men working around blast furnaces. Blast-furnace gas contains a high percentage of carbon monoxide.

EFFECTS ON THE DIFFERENT ANIMALS OF THE SAME PROPORTIONS OF CARBON MONOXIDE

The Bureau has performed many experiments in order to draw some conclusions regarding the effect on different animals of the same species of a given proportion of carbon monoxide. It was found that in general a given proportion of carbon monoxide affected different animals of the same species in about the same length of time, at least as far as the application of the results to the practical use of the animals in mines is concerned, but that once in a while an animal might behave markedly differently from what is expected. This is more true of mice than of canaries, yet even in the case of the latter several of them should be taken with an exploration party.

THE RELATIVE EFFECT OF SMALL AMOUNTS OF CARBON MONOXIDE ON MEN AND SMALL ANIMALS

In reading over accounts of rescue and recovery work in mines, one is impressed with the fact that some users of small animals have not been entirely satisfied with the behavior of mice and birds (especially mice) in that men have apparently felt distress before the animals became affected. The Bureau, as the result of many experiments made to determine the resistance of small animals to carbon monoxide poisoning, believes it has the data at hand which explains partly this dissatisfaction.

It was found, for instance, that almost all of the animals tried do not show sufficient distress in one hour's time with 0.10 per cent of carbon monoxide to make them valuable for detecting this percentage of the gas. In some cases the length of exposure was extended to three hours without any pronounced effects being observed. In one case only was a canary affected in so short a time as 12 minutes by 0.10 per cent of carbon monoxide. With another bird and the same percentage of carbon monoxide, distress was scarcely observable in 3 hours. Only a disposition to remain quiet was observed. Eight different canaries were used and six different mice. Only one mouse out of many was slightly affected in so short a time as 30 minutes with 0.10 per cent, but it was not overcome in 4 hours. Neither were chickens nor pigeons visibly distressed. With 0.15 per cent both canaries and mice began to be affected. With 0.15 per cent carbon monoxide canaries showed distress in from 5 to 30 minutes. A mouse showed slight distress at the end of an hour. With 0.20 per cent, canaries responded in from 2 to 5 minutes except in one case (35 minutes). Three mice responded in 12 minutes, and a fourth in 46 minutes. No blood tests were made, the object being to determine the usefulness of the animals for mining work where their behavior as apparent to the eye is the only guide. Haldane states that 0.06 per cent carbon monoxide is sufficient to produce distinct symptoms in mice.[2] The authors of this paper do not hesitate to say that because of his greater experience in experi-

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[1] "The Haemotology of Carbon Monoxide Poisoning," *Journal of Physiology*, **25** (1906), Nos. 1 and 2, 32–52.

[2] "The Relation of the Action of Carbonic Oxide to Oxygen Tension," J. S. Haldane, *Journal of Physiology*, **18** (1895), 201–217.

menting with small animals Dr. Haldane might detect outward symptoms in a mouse that would escape the authors' attention. On the other hand, the authors have had greater experience than many of those who might use small animals in mines. Further, in the laboratory, observations are better made than in the mine where the light may be poor. Dr. Haldane made many experiments with himself as the subject in determining the effect of carbon monoxide on men.[1] He found that 0.12 per cent causes a mouse to sprawl in 11 minutes. Haldane felt a slight tendency to palpitation in 33 minutes. In 90 minutes he had distinct dimness of vision and hearing and a slight tendency to stagger, besides abnormal panting when he stopped the experiment long enough to run up and down stairs. In two hours' time vision and hearing became markedly impaired and there was some confusion of mind. When the mouse was finally removed from the cage it could not move about. After 18 minutes from the time of stopping, Haldane had a distinct throbbing headache which did not last long.

With 0.045 per cent of carbon monoxide Haldane did not notice any symptoms in the 4 hours that the experiment was carried on, but on running upstairs there was unusual panting, slight palpitation, etc. A mouse was not distinctly affected. In defining the minimum harmful or poisonous percentage of carbon monoxide, Haldane states that 0.05 per cent in pure air is just sufficient to produce in time very slight symptoms in man, and the same percentage produces very slight symptoms in mice. He states that 0.20 per cent is very dangerous to man. With 0.05 per cent and thereabouts Haldane finds that the gas finally begins to affect men and the outward signs appear in mice.

Haldane's observations on mice are not entirely in accord with those of the authors of this paper. The reasons are probably, as already stated, differences in observation. The authors are convinced from their experiments that in a mine with poor light, and perhaps only hurried examination of the animals, and by persons more or less inexperienced in the actions of the animals, mice and canaries will not usually show distress pronounced enough to give good warning with 0.10 per cent or less of carbon monoxide. Haldane's work shows that this percentage may finally affect men—a headache in 40 or 50 minutes perhaps, or slight tendency to palpitations in less time. This condition will be a considerable time removed from actual distress or unsteadiness of movement. At the end of 20 minutes one of the authors of this paper had only a slight headache when he exposed himself to 0.25 per cent carbon monoxide (in air); later, however, he became very ill. Canaries collapsed in just a few minutes.

In connection with the above laboratory experiments the authors have made observations regarding the use of small animals in mines. One instance is noteworthy, as follows:

A mine fire occurred recently and a sample of mine gas was obtained that contained the following constituents:

	Per cent
CO_2	1.10
O_2	18.61
CO	0.12
CH_4	0.42
N_2	79.75
Total,	100.00

This sample was obtained in a place where exploration work was being conducted. Canaries carried with the party were not affected but two of the men finally complained of a bad headache. Later when they went to the surface they became ill. One was indisposed all evening.

These facts, although they appear damaging against the use of small animals for the purpose proposed, only militate in part against their usefulness. They still remain, in the authors' opinion, the best indicators of carbon monoxide that we have for exploring parties in mines. Canaries will give ample warning of percentages of carbon monoxide immediately dangerous to men. When the proportion of carbon monoxide is 0.15 per cent, canaries will show distress usually in from 5 to 12 minutes. With 0.20 per cent the distress is usually apparent in from 2 to 6 minutes. For distress to appear in men with these percentages requires much longer time, although in the case of some individuals the effects may, when they do disappear, last for hours. The authors have also determined this point experimentally, as have others. Men cannot stand the exposure to collapse from carbon monoxide like animals can. Canaries and mice after distress and collapse recover quickly if exposed to fresh air—only a matter of minutes usually. In the case of men exposed to collapse, recovery is often a matter of days.

In assigning reasons for the different effects produced on men and small animals by small quantities (say 0.10 per cent and under) of carbon monoxide, the authors of this paper would say that it is largely a question of observation. The blood of the animal is, of course, taking up the carbon monoxide, but only slowly and to the extent that even after a long time, one hour or more, the only effect observed in the animal may be a slight sluggishness or disinclination to move about. Men, on the other hand, especially when moving about or doing hard work, absorb much more oxygen and hence more carbon monoxide than when at rest, and may finally feel a slight or even a severe headache in the same gas mixture that is only slightly or not affecting the animals (as far as can be observed). The men may even finally become very sick. It is not believed that any pronounced acclimatization effect is produced in an animal on a short exposure which would account for the apparent resistance. It must be remembered that a man is in an excellent position to determine effects upon himself long before distress occurs, in the case of small percentages of carbon monoxide. Small animals may feel distress but not show it.

When the carbon monoxide content of an atmosphere is raised from 0.10 per cent to say 0.15 or 0.20 per cent, the susceptibility of a canary or mouse to the gas is markedly increased, as judged by the action of the animal; so much more so than in the case of men that a canary especially may show distress in 5 minutes, while a man may require 30 or more minutes. A man if he expose himself this long, however, may finally become very sick, and if for longer periods, may become dangerously so.

EFFECT OF CARBON MONOXIDE ON DIFFERENT MEN

The Bureau has compiled data from different sources to show the effects produced on different persons by carbon monoxide. The fact is clearly brought out that the gas may affect different persons in a different manner. Long-standing after-effects produced in people by severe poisoning, although apparently rare, are by no means unknown. It appears to be the evidence usually that recovery from exposure is complete but that in the case of some individuals long-standing after-effects may follow. These after-effects on different people cannot be connected absolutely with any degree of exposure, *i. e.*, one short exposure to large percentages, repeated exposures to large percentages as usually happens in the case of blast-furnace gas, or slow exposure to collapse with small percentages of the gas, as in the case of miners exposed to the smaller percentages that are found in mines following explosions. In the case of the same individual, the final blood saturation is what counts, of course. The point is that different people may withstand different degrees of blood saturation. In the case of blast-furnace men, the same men may be exposed to collapse or severe temporary sickness time and again. Usually, as far as can be observed from their behavior, they retain their normal condition, although, as has been pointed out by Thomas Oliver, severe after-effects may linger for two years.[1] This appears to be exceptional. An Illinois commission,

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[1] "The Action of Carbon Monoxide on Man," J. S. Haldane, *Jour. of Physiology*, 18 (1895), 430–462.

[1] Thomas Oliver, "Diseases of Occupation," p. 67.

appointed to inquire into conditions around steel plants, found it hard to separate effects on steel workers produced by bad living conditions and those produced on some of the men by carbon monoxide, although they were inclined to the view that carbon monoxide poisoning had considerable to do with the generally poor condition of some of the employees. The exact action of the gas in producing bad nervous disorders still remains somewhat obscure. Some do not believe the action so simple as to merely temporarily deprive the system of oxygen, although most of the good experimental evidence points to this view. An analogy has to do with men who work at high altitudes or suddenly ascend to extreme heights in balloons, where the oxygen tension is very low. Different individuals may also be affected differently at high altitudes. One must believe that in cases both of carbon monoxide poisoning and of oxygen deprivation by other causes, the idiosyncrasy of the individual plays an important part. Others have laid much stress on this point.

As regards acclimatization to the gas, it has been strikingly shown that guinea pigs may become immune. The compensation found in pigs has also been in part observed in men. The red-blood cells increase to compensate for those put out of action by the carbon monoxide. How long this may continue without pronounced distress on the part of men is important.

Repeated exposure to carbon monoxide may occur in the case of miners, in those who do the shot-firing. Blasting explosives always produce some carbon monoxide in coal mines. Men may return too quickly to the working face (before gases have disappeared), to examine their shot, and thus expose themselves to percentages, usually small, of the gas. Where large shots are fired, where the ventilation is poor, and where the working faces are too far ahead of the last breakthrough, contact by men with harmful percentages of carbon monoxide and other poisonous gases may follow. Miners at some mines frequently go home sick from powder smoke. The general effect of such exposure on them cannot be anything but bad.

In the conduct of exploration work, one sometimes hears it said that certain individuals of a party were able to withstand atmospheres that caused distress in other members of the same party. This may be true because some men are more affected than others by the same properties of the gas, but one or two other causes must be kept in mind. After-damp in different parts of a mine (in some places quite close together) will differ much in composition to the extent that at one place a very small and insignificant amount of carbon monoxide might be present, while at another place, close by, a harmful proportion might exist. One person of a party unknowingly might encounter the latter atmosphere while his comrades do not. Another reason usually less apparent to an exploring party has to do with the fact that the amount of carbon monoxide absorbed depends, of course, upon the air breathed. A man at rest may breathe 7 or 8 liters of air per minute. By even moderate exertion this can be increased to 3 or 4 times that quantity. It follows that if one or more members of an exploring party work harder than others they will become poisoned more quickly than the less active members.

SUMMARY

1. Small animals may be repeatedly used in exploration work without becoming less useful as indicators of carbon monoxide.

2. Of the more common small animals, canaries are best adapted for exploration work.

3. Men may feel distress, especially if they work hard, in the presence of small proportions of carbon monoxide (0.10 per cent or under), when animals at rest in their cages do not distinctly show it.

4. It is occasionally found that different animals of the same species may be differently affected by the same proportion of carbon monoxide; hence more than one animal should be used at a time.

The conclusions given are drawn from the authors' work on small animals and men, from J. S. Haldane's work on small animals and men, from the accounts of exploration work of dissatisfied users of small animals (especially mice), and some miscellaneous observations by the author on the use of small animals and general effects of carbon monoxide.

Bureau of Mines, Pittsburgh

CHEMICAL INDUSTRIES AND SCHOOLS

By Daniel M. Grosh

The writer through an address on the subject "What's the Matter with the American Chemist?" which appeared in This Journal, 5, 692, has been favored with the views and opinions of various correspondents. These communications were extremely diversive as to the reason why we cannot compete with foreign chemical producers, but all agree upon the one fact that Germany leads the world and controls the markets in chemical products.

The writer mentioned the chaotic condition of the dyestuff industry because at the time much newspaper space was being devoted to the agitation in that quarter, and, taking the situation in its entirety, this phase of the question is only one small link in the chain of chemical products.

The address evidently touched a responsive chord and caused some serious thinking and has brought to light some facts bearing on this subject which have hitherto remained obscured or vague. One correspondent in expressing his views on the question "Why cannot we make chemicals to supply our needs without importing them?" tersely answers "We can but we won't." The truth of this statement is greater than it appears at the first glance and seems to answer the question most effectively, but at the same time there pops up another "Why?"

In this as in all subjects much remains hidden that bears largely upon existing conditions and each influence is effective to a greater or less degree. It is the intention to discuss those influences which, according to the opinions of various interested correspondents, have been responsible for this country being left behind in the great race for supremacy in this industry.

The issue at stake, however, is not the reasons or results but the remedy. This means the hard cash of a prosperous industry, a commercial proposition. It is well to remember that every new industry created means just so many more mouths fed, so many more families maintained and so many more citizens preserved to usefulness and productiveness.

Closing our eyes to an unpleasant truth does not alter the situation and even though it hurts to admit it we must acknowledge that we have learned only the trade of producing chemical products instead of the science of chemistry. We had the same opportunities and greater advantages than Germany for the exploitation of the chemical industry but allowed them to slip through our hands and be eagerly grasped by the foreigner. In the early seventies, Germany was far below England and France in manufacturing, invention and foreign commerce. Overburdened with our productive lands and our natural wealths of raw materials, we have never been forced into the great fight for existence and many of our natural resources have passed from our control or remained undeveloped.

To speak of the chemical industry and not to mention the German syndicates would be omitting, perhaps, the main factor in the case. As every one knows, Germany possesses, to-day, the best developed chemical industry in the world and dominates the trade the world over. This syndicate of which we hear so much is something real and with enormous powers which it uses with a high hand. We have nothing to compare with it in our own land and its power is so great and so effectually does it control and regulate the market, that it can dump its supplies where it pleases and at prices to suit itself.

To this syndicate the German Government extends a helping hand at all times. It is Germany, first, last and all the time, and against the world. In the potash case a few years ago there was an actual partnership with the government to regulate the price of potash and together they control the supply of the world.

To what extent the individuality of the chemist contributes toward the general situation is to be judged by the reader. Foreign chemists are satisfied with a small salary—*here*, three times as much pay is demanded. Graduates are glad to seize the opportunity to get into a factory at little compensation to get a start and for the practical knowledge they will acquire. This presents a phase rather unfamiliar to our general views and shows they have either a belief in themselves and their future or a willingness to sacrifice themselves for their love of profession.

If a graduate is satisfied to work for a small sum, eager for a chance to do great work at a personal sacrifice, it certainly shows a high degree of patriotism or an intense love of profession. Ambition will generally make good in any capacity and prove its worth. While the wages paid abroad are very much lower, this condition cannot have much bearing, when the different standards of living and relative costs of same are impartially considered.

Germany is spending enormous amounts each year for its chemical development through its universities in which the instructors and chemical factories coöperate with very successful results. An individual or manufacturer up against a difficult problem has at call the finest advisory talent available as well as adequately equipped laboratories at his disposal. When such authorities as Prof. R. K. Duncan and his associates are striving their utmost to bring about a similar condition, practically absent in this country, it is most apparent that this spirit of coöperation has a high potential value. That there is a lack of such coöperation as exists abroad between the manufacturer and the chemist and also between the educational, financial and commercial interests, all will admit, but why should it continue if such coöperation is to the advantage of all concerned.

The writer has knowledge of cases where firms refused to take advantage of new processes devised by interested employees to reduce costs and improve the output. Superintendents resented any suggestions except those emanating from themselves and looked upon such as a reflection upon their abilities. Instances of this nature are by no means rare and especially a few years back when "ignorance was bliss," this phase of "destructive conservatism" may have contributed its share towards placing the chemical industry in its present state. Such a spirit certainly does not promote the efficiency and low manufacturing costs which are essential in industrial progress. The mental attitude of the worker is as important as scientific management and how much influence such incidents as the above have had upon the industry collectively depends upon the personal opinion of the reader.

Within the confines of Germany or France there is no such thing as a played-out farm. Land has been cultivated continuously year in and year out and to-day still shows a high degree of productiveness due to scientific application of fertilizers, which we are just beginning to get acquainted with. With the aid of the chemist, German farms are raising beets for sugar in competition with cane sugar and are producing beet sugar to the tune of 100 million dollars a year. Instead of sending their money out of the country for something they cannot produce, they keep it at home by discovering some substitute for the desired product. Again, the United States imports creosote for various purposes by the shiploads, produced from German coke ovens and permits the same by-product to go to waste at our own ovens. These two examples serve to show how we neglect our own resources and are simply a few out of many illustrations. It is not to be expected that we should appropriate all the means by which Germany has reached her present position. Times and conditions are constantly changing and the methods of twenty or thirty years ago could not be used to-day, but we can utilize those aids which our common sense tells us would be to our benefit and advantage.

We can develop our natural resources and make them productive. We can foster an intelligent effort to benefit and apply to industrial uses the energy and products of the individual investigator. We can establish laboratories where the problems of the manufacturer as well as the individual can be worked out. There can be coöperation between our industries and institutions of learning.

Let there be a campaign of education and enlightenment. It is surprising how little is known on this subject. Many persons well informed generally have but the slightest knowledge of existing conditions and even within the profession there is not the familiarity one would expect. We can look for no legislative assistance until the public is educated and as long as the truth is withheld and the gravity of the question is not impressed as a matter of public concern and welfare, there will be no progress.

Looking the situation squarely in the face and casting aside all prejudice any person intelligent and well informed can see what our future will be. To be honest in one's convictions does not mean pessimism or calamity howling. Let us learn the truth, rectify our mistakes and build anew. A campaign of education once inaugurated cannot fail to bear fruit. Will American industry heed the lesson contained in rich England's industrial eclipse, in poor Germany's steady rise?

5927 Walton Ave., Philadelphia

VENTILATION SYMPOSIUM

The New York Section of the American Chemical Society held a Symposium on Ventilation at The Chemists' Club, November 7, 1913. The various phases of this vital subject were discussed by qualified experts and their addresses are printed in full below. [Editor.]

PHYSIOLOGICAL PROBLEMS OF VENTILATION

By Frederic S. Lee[1]

Man is intimately dependent upon his environment. In civilization he lives under artificial conditions, and it is, therefore, necessary to employ artificial means in order to adapt his environment to his physiological needs. The air surrounding his body is one of his indispensable environmental factors, and when it is confined between walls the process of ventilation is required to keep the air in such condition that he is able to live within it in a physiological state. It cannot be too strongly emphasized that the problem of ventilation is fundamentally a physiological problem, and it must vary from time to time as the knowledge of man's physiological requirements becomes more exact. We know now much more fully than we knew a few years ago what qualities the air that he is to breathe ought to possess, and a few years hence our knowledge will doubtless be still more full. A few years ago ventilation was supposed to be a matter of maintaining the proper chemical purity of respirable air. It was only natural to draw this inference from the known fact that respiration renders the air chemically impure. The chemical compositions of inspired air and expired air are as follows:

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[1] Dalton Professor of Physiology in Columbia University.

	Inspired	Expired
Oxygen	20.94	16.4
Carbon dioxide	0.03	4.1
Nitrogen	78.09	78.09
Argon	0.94	0.94
Helium, krypton, neon, xenon, etc.	Traces	Traces

In considering the chemical vitiation of air by respiration it is obvious that the inert nitrogen, argon, helium, etc., may be neglected, and that attention should be focused upon the oxygen and the carbon dioxide. The necessity of oxygen in respiration has long been recognized, and it was long believed that its diminution, especially in the more extreme conditions, was a factor to be considered in ventilation. Against carbon dioxide the case seemed even stronger. It is increased more than one hundred times by the act of breathing; it was known to be poisonous to man; and its elimination was long believed to be the all-important requisite in adequate ventilation. The object of ventilation was thus to remove chemically impure air and introduce chemically pure air and plenty of it.

In recent years with the extension of human and animal experimentation the aspect of the subject has quite changed. It has now been shown that the oxygen of respirable air may be reduced to less than 17 per cent before its diminution becomes harmful. This proportion is too small even to support combustion. Hill says of a group of his students whom he confined in a small air-tight room: "We have watched them trying to light a cigarette (to relieve the monotony of the experiment) and, puzzled by their matches going out, borrowing others, only in vain. They had not sensed the percentage of the diminution of oxygen, which fell below seventeen." Except in extreme experimental conditions the amount of oxygen in crowded assemblies never falls below one-twentieth of its usual amount, *i. e.*, rarely below 20 per cent. Oxygen will, therefore, take care of itself and may probably be wholly left out of consideration in ventilating systems.

With the poisonous carbon dioxide, too, the case now seems not so very different. Within man's body carbon dioxide plays essential rôles. It is the stimulant which excites the nervous center of our respiratory mechanism and maintains its regular action, and a similar hormone influence has been recognized in other bodily functions. Moreover, the poisonous properties of carbon dioxide when in air have been exaggerated. Experimentation indicates that it does not become harmful to man until it accumulates to about one per cent or nearly forty times its usual amount. In crowded rooms it very rarely reaches even 0.4 per cent, or ten times its usual proportion in pure air and only one-quarter of its harmful amount. Like oxygen, therefore, it would appear that carbon dioxide may probably be eliminated from the problem of ventilation except under the most extreme and unusual conditions. It is still customary to use as the standard of suitable ventilation the amount of carbon dioxide permissible in the air of rooms. In the United States we are still very deficient in ventilation laws, but in England specific laws fix the quantity of this gas which may be permitted in the work rooms of certain industries. In view of the present status of physiological knowledge it would appear that some other standard than that of a fixed amount of carbon dioxide should be established.

Notwithstanding these recent changes in our ideas of the relation of oxygen and carbon dioxide to ventilation, I am not prepared to say without reservation that the continued exposure of an individual day after day and week after week to even a moderately diminished quantity of oxygen and a moderately increased quantity of carbon dioxide would be wholly without harm. But I am led to this reservation not by any existing positive physiological knowledge, but rather by the necessity of maintaining an open mind receptive to future possible discoveries—a mental attitude which ought always to characterize men of science.

There has long existed a belief, and even among scientific men, that expired air contains a peculiar organic and volatile constituent, probably of protein nature, which is toxic to human beings and other animals. Various attempts have been made to support this idea experimentally. The most of these experiments have consisted in condensing expired air and then injecting it into animals. Some of these experiments have seemed to result positively. The latest of these were performed by Rosenau and Amoss, in 1911, and the positive result was the production of an anaphylactic condition in a certain proportion of the experimental animals. One by one these successive supposed positive results have been balanced by equally significant negative results and have been explained otherwise than as indicative of the existence of the hypothetical substance; and now in this city Weisman and Lucas independently have repeated and extended the work of Rosenau and Amoss and have not been able to confirm their findings. In the light of present evidence, therefore, we cannot accept the belief that expired air contains an organic poison. Furthermore, the odor of air vitiated by human beings is no index of the presence of harmful ingredients.

It is pertinent here to refer to the case of ozone. Its powerful oxidizing properties and its intemperate advocacy by enthusiastic but unscientific persons have caused it to be hailed popularly as highly beneficial to the human body, not only in ordinary respiration but in the purification of the air of living rooms, and in the destruction of bacteria and other organic matter. In many offices and homes we find various forms of ozone machines, busily at work discharging into the atmosphere their peculiarly odoriferous product. Very recent investigations seem to make it clear that the supposed beneficial powers of ozone as a home companion are creations of the imagination. Two groups of American investigators, Jordan and Carlson, in Chicago, and Sawyer, Beckwith and Skolfield, in Berkeley, have independently carried out each a series of careful experiments[1] on the action of ozone on bacteria, animals and human beings. They find that ozone will indeed kill bacteria exposed in a room, but only when in such concentration that it will kill guinea pigs first. "There is no evidence for supposing that a quantity of ozone that can be tolerated by man has the least germicidal action." When present in any considerable quantity in the air ozone is irritating and probably corrosive to the lining membrane of the air passages of the nose, throat and lungs, causing the blood vessels of this membrane to be excessively dilated and to present the customary symptoms of "sore throat." It causes headache and drowsiness. The heart, at first accelerated, is later slowed and weakened, and the pressure of the blood in the arteries is unduly lowered. The case for ozone thus seems to narrow down to a supposed beneficial action in destroying or modifying unpleasant odors in the air of a room. When in not too great concentration such odors are, it is true, overcome, though it is quite probable that their disappearance is due, not to an actual destruction of the odoriferous substance, but partly to a replacement of the disagreeable odor by the odor of ozone and partly to fatigue or anesthesia of the olfactory membrane of the nose. It is very questionable whether this is wise, and Jordan and Carlson well say: "It seems to us that this is wrong in principle, and that ozone is being used and will be used as a crutch to bolster up poor ventilating systems. Ozone does not make pure air any more than strong spices make pure food." It thus seems probable that ozone as an adjunct to ventilation is destined to pass into oblivion.

Bacteria also may probably be eliminated as a factor to be considered in ordinary ventilation, for the idea is gradually making its way that the germs of infectious diseases are conveyed to the unfortunate individual almost wholly through some form of physical contact and that aerial infection occurs with extreme rarity. In exceptional cases air may be rendered un-

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[1] See also This Journal, 5, 882.

wholesome by the presence of poisonous gases. Instances of this are the leakage of illuminating gas from defective pipes and the production of poisonous fumes in certain industrial procedures. But it is now clear that sewer gas may be eliminated as a factor in our dangerous environment, for none of its gaseous constituents is markedly toxic and its bacterial content is so slight as to be negligible.

While it has thus been shown that it is not the chemical features of air and their relation to man which supply the physiological basis for the problem of ordinary ventilation, research has at the same time been demonstrating that two of the air's physical features appear to be the decisive factors. This idea seems to have been first suggested thirty years ago by Hermanns, and it has since constantly found increasing experimental support. Hence, in considering ventilation from the latest standpoint, we are obliged to turn from chemistry to physics. At the same time we turn also from the lungs to the skin. The physiological problems of ordinary ventilation have ceased to be chemical and pulmonary, and have become physical and cutaneous.

The average adult human body produces within itself and gives off to its environment during twenty-four hours, when at rest, 2400 calories of heat, and when engaged in vigorous physical labor more than twice this amount. Fully 95 per cent of this heat leaves the human furnace through the skin, partly by radiation and conduction, and partly by the evaporation of the water of perspiration. This loss cannot be regarded as one of nature's errors; on the contrary it is a physiological provision, carefully controlled by the nervous system, for the good of the organism. If this dismissal of heat from the body be prevented, heat will accumulate within—for its production never ceases throughout life—and deplorable consequences will follow. The bodily temperature will rise above the normal, and a febrile condition will result. There will be disturbances of metabolism, with the probable accumulation of abnormal and deleterious metabolic products; working power will be lessened; fatigue will come on early; and ultimately in extreme cases all the untoward phenomena of heat stroke will occur.

The normal loss of heat or, as the Germans call it, the "unwarming" of the body, may be interfered with by making the surrounding air too warm, thus preventing radiation and conduction; or by making the air too moist, thus preventing the evaporation of sweat; or most effectually by blocking both of these channels. This last-mentioned procedure is that which happens to human beings confined in improperly ventilated rooms. From their bodies the temperature of the air rises and the humidity of the air increases. As these events happen each body finds it not so easy as at first to rid itself of its superfluous heat, and this becomes increasingly more difficult. Heat-laden blood must be sent in larger quantity to dilated cutaneous arteries, flushing and warming the skin; sweat glands must be stimulated to visible activity; breathing must be deepened; and every method of which the body is physiologically capable is unconsciously brought into action to protect it. At first the sensations are merely those of general uneasiness, manifesting itself in restlessness; then progressively appear sleepiness, an oppressive sense of heat, headache, thirst, and still more severe sensations which, if relief is not obtained, may give place to the delirium of the Black Hole of Calcutta or the prison at Austerlitz—these sensations keeping pace with the development of the fever within and the other pathological events accompanying it.

Much experimentation has shown that these evil results of confinement in improperly ventilated rooms are caused not by the presence of toxic products of respiration, but by the heat and the humidity combined. Paul found that with human beings enclosed in a hot and humid experimental chamber the unpleasant symptoms began to appear within a few minutes and before there was time for the accumulation of supposed poisonous gases. When the air of the chamber was put into motion the temperature of the skin fell, the unpleasant symptoms disappeared very quickly, and the subject felt as if fresh air had been supplied. When the subject had been confined for a considerable time and the symptoms had become well developed, the breathing of pure air through a tube passing from the subject's face through the wall of the chamber to the outside brought no relief. When, on the other hand, an outsider with his body surrounded by fresh air breathed from a tube, the vitiated air of the chamber, no unpleasant symptoms appeared. Such facts make it clear that the symptoms are due to the action of the vitiated air, not on the lungs but on the skin. In one of Benedict's experiments a subject was confined for three days in a respiration calorimeter. During the second day the ventilation of the calorimeter was cut down so that the products of respiration were allowed to accumulate. During nearly the whole of this period of twenty-four hours carbon dioxide was present in a quantity averaging 2.2 per cent, or more than seventy times the usual amount. The humidity ranged between 54 and 66 per cent, while the temperature remained practically constant at the comfortable level of 20° C., or 68° F. The subject possessed his usual good health and on that experimental day was said to be "in unusually good spirits." Hill confined eight persons in a small, air-tight experimental chamber, containing approximately only three cubic meters of air. The oxygen fell from 20 to between 16 and 17 per cent, and the carbon dioxide increased from 0.04 to between 3 and 4 per cent, or nearly one hundred times its usual amount. The symptoms of the action of vitiated air soon appeared. Then three electric fans attached to the ceiling were started and, although the temperature of the air was between 80° and 85° F. and it was very moist, the simple movement of this wet, hot, stale air brought complete relief, for the simple reason that it whirled away the still hotter stationary air from the surface of the bodies and allowed them still to eliminate their internal heat.

These experiments and many others have proved beyond question that the chemical purity of air vitiated by the presence of human beings is a factor of minor importance in ventilation, and that the qualities to be avoided are an elevated temperature and an elevated amount of moisture. In our American cities we know too well that the chief danger of our torrid summer days is not the heat alone, but the combined heat and humidity; but few persons realize that it is precisely the same factors that are responsible at all seasons for the evil effects of the confined air of rooms. There is no doubt that the air of our American living rooms and many schoolrooms and other assembly chambers is kept too warm. A temperature of 70° F. is commonly recommended for living rooms, but a lower temperature with a moderate humidity is more healthful. The British authorities advise temperatures reaching as low as 60° F. Acclimatization undoubtedly has much to do with the matter.

No fixed standard percentage of humidity can be set, since the percentage of humidity is so closely related to temperature. Thus 100 per cent of humidity in air of 65° is equivalent to only 58 per cent at 75° and 33 per cent at 85°. A humidity of 60 per cent with air of 68° F. is rational.

If any single standard is to be chosen as the standard of healthful air, it is probably the temperature of the air as indicated by the wet-bulb thermometer, for this is a measure of heat and humidity combined. The British authorities are very positive about this. Thus, Haldane summarizes his observations in these words:

"These experiments proved that in very warm air it is the temperature indicated by the wet-bulb thermometer.......... which determines the ill-effects produced. With a wet-bulb temperature exceeding 88° to 90° F. [= 31° to 32° C.] in fairly still air the body temperature begins to rise, even in the case of persons stripped to the waist and doing no work; and when once started this rise continues until symptoms of heat stroke arise, unless the person leaves the warm air. In the case of persons doing muscular work, the rise of body temperature is much more rapid and begins at a much lower wet-bulb temperature. It will, for instance, begin (in persons stripped to the waist) at a wet-bulb temperature of about 80° F. [= 26.7° C.] in still air with moderately hard muscular work, so that hard and continuous work is impracticable at wet-bulb temperatures of over 80° in still air. There is no doubt that when ordinary clothes are worn, serious rise of body temperature occurs at a still lower wet-bulb temperature. Soldiers marching in uniform are, for instance, liable to heat stroke at wet-bulb temperatures of under 70° F. [= 21° C.]."

Thus, while the problem of ventilation seems clearly to resolve itself into the problem of supplying to the individual moving air of such a temperature and such a content in aqueous vapor as to enable him to maintain his body in its best physiological condition, there still remain many physiological problems related to ventilation which press for solution. At what temperatures and what degrees of moisture do the really evil effects of bad air begin to appear? In what ways other than the rise of bodily temperature and the obvious symptoms do these evil effects manifest themselves? Here there are many possibilities: alterations of respiratory exchange, of relations of the oxygen to the haemoglobin of the blood, of the action of the heart, of the pressure of the blood in the arteries, of the course of fatigue, of the working power of the brain. It must be believed that the normal course of the body's metabolism is altered, but no one knows with any degree of exactness what the alterations are. Do a high temperature and a high humidity bear any relation to bacterial infection? What are the differences between temporary and prolonged exposure to these unfavorable conditions? Most of the experiments heretofore conducted have been of short duration, and few have extended for so long a period as even a whole working day. Still fewer have related to the exposure, day after day, for weeks or months, to an atmosphere that is only slightly unfavorable; yet it is probable that the evil effects of such an environment are cumulative. How are the effects of a high temperature and a high humidity altered by performing physical or mental work? At what temperatures and humidities can physical work and can mental work best be performed—in other words, under what conditions of ventilation can the highest physiological efficiency of the individual be secured? Ought these conditions to be varied, and if so in what way, according to the occupation of the individual concerned? Should, for example, the home, the schoolroom, the hospital, and the work shop have each its own ventilation standard and in what terms should these standards be expressed? These are some of the physiological questions to be answered by the investigation of the future. What we already know about ventilation and what we hope to know in the future, combine to make it clear, I trust, that, as was stated in my introduction, the problem of ventilation is fundamentally a physiological problem.

COLLEGE OF PHYSICIANS AND SURGEONS
NEW YORK CITY

MECHANICAL PROBLEMS OF VENTILATION

By D. D. KIMBALL

It is not my understanding that the subject assigned me refers to the details of the problem of working out a design for the ventilation of any building for any use, for such problems have become those of details only.

So far as this subject refers to the present wide-spread atmosphere of investigation into the general problem of ventilation it might almost be said that there are no mechanical problems unsolved in the field of ventilation; which is to say, the engineer can provide any chemical or physical condition of the atmosphere of an enclosed space which may be required. The composition of the air may be maintained with any reasonable proportions of oxygen and CO_2 (and ozone too, if desired) and the air may be kept freer of dust and bacteria than the outside air. It may be maintained at any temperature or any degree of relative humidity, and it may be given any degree of movement or diffusion desired. Odors and dust of any kind and of any amount can be removed.

These are matters fully understood by the engineer, and practice and formulae are at hand for guidance along correct lines.

The chemical and physical properties of the air may be varied at will and within short periods of time. And all of this may be accomplished by the artificial ventilating system. It cannot be accomplished by natural ventilation.

But nevertheless, someone will rise to insist that these things are not accomplished and that, therefore, these statements must be those of theory and not those of accomplished fact. And on the surface it appears as though such a person would not be far from right.

Therefore, let us briefly consider the reason or reasons. It will not be contended that there are not a great many ventilating systems in use which are justly the subject of criticism, even serious criticism, nor that there are relatively few systems in use for which entire satisfaction may be claimed.

But again, let it be stated that this condition results, not because of the mechanical problems involved but for other reasons, serious and fundamental.

There is now no agreement as to which constitutes proper ventilation. Information is seriously lacking as to both the chemical and physical properties of the air which are most desirable. There are many chemical and physical phases of this problem which are of undoubted importance, such as oxygen, carbon dioxide, ozone, temperature, humidity, air movement, dust and bacteria, but in the case of no one of these elements is there entire accord among the Physiologists or medical men as to the effect of different conditions, except in so far as the trend of recent opinion seems to indicate that the physical, rather than the chemical, conditions of the air are of the greater importance, which is a reversal of earlier opinions. That is, temperature, humidity and movement of the air, and its freedom from dust, bacteria and odor are the first essentials of ventilation. Therefore, let the physiologist and medical men determine, by a continuance of the splendid studies and experimentation now going on, what are the most desirable atmospheric conditions. The engineer may then be counted upon to provide such conditions.

But decisions on these important matters must be well founded and may not be based upon insufficient investigations and inconclusive tests as have been so many of the recently announced views as, for instance, the oft reiterated pronouncements in favor of window ventilation. In the tests of this important phase of the ventilation problem, as recorded to date, the subjects have been in small classes under the care of specially selected teachers and nurses, with special diets, short study periods, exercise and rest periods, investigations and instructions regarding home conditions and with other details, all at variance with regular school practices, all of which doubtless materially affect the result, and yet the entire credit is given to the effect of the window ventilation. No consideration is given to the fact that proper window ventilation may be had upon but one or two sides of the building, and then only on the sides of the building which are favorably exposed, nor is any mention made of the enormous increase in the cost of maintaining the school system if such a system of school administration were applied to an entire city, such as New York.

In this reference to window, or natural, ventilation there is no intention to decry its use within proper limitations, nor as an adjunct to the artificial ventilation system, which leads to the remark that a properly designed system of ventilation is not put "out of balance" by the opening of a window, the popular impression to the contrary notwithstanding.

Therefore, let the physiologists and medical men but come to an agreement as to the optimum atmospheric conditions and the engineer may be depended upon to produce just those conditions, IF, and herein lies the real problem of mechanical ventilation from the standpoint of the engineer, IF but a reasonable appropriation is made for the design and installation of the heating and ventilating system, and for its operation.

In the first place, not more than one plant in ten is designed, or laid out, by a consulting engineer. There may be, unfortunately, some practising engineers incapable of designing a system to meet modern requirements, but there are plenty of competent engineers. If a continuance of the unfortunate experiences of the past is to be avoided the owner must be made to realize that the design of a heating and ventilating system is no part of a plumber's work or an architect's work or training, for unfortunately some architects do not yet realize this fact and many architects prefer to entrust the design of the heating and ventilating plant to a friendly and willing contractor rather than to themselves pay the engineer's fee or to ask the owner to pay it. Result—the contractor lays out the work for his own benefit, is indeed glad to do so for the advantage which he may thus obtain over other bidders, the owner is without the expert services which he should have, and in the end he pays much more than enough extra for his plant and its operation than would have been required to pay directly for engineering services.

It is this class of engineering, also, which produces the most failures in ventilation work, the blame for which the engineer carries.

The cost of the best engineering services for the design and supervision of the heating and ventilating plant will vary from one-half to three-quarters of one per cent of the cost of the building.

A first-class engineer will produce savings in cost of installation and operation vastly exceeding this, and yet, but relatively few owners avail themselves of such services, while the wail against the inefficiency of the ventilating system goes on.

In the second place, in the case of nearly every building, the appropriation for the installation of the heating and ventilating system is reduced to the very minimum. Take, for instance, a school building. Usually a certain amount is appropriated for the building, then the committee selects its architect. If by competition, each architect strives to outdo the others in the size or ornamentation of the building which he offers to build for the amount appropriated. In any case the architect is usually confronted with the requirements of the committee, which requirements are from ten to twenty-five per cent in excess of what may be reasonably expected for the sum appropriated. And then begins the process of trimming, and the heating and ventilating plant, being the biggest single item of equipment, invariably comes in for the most attention and with the worst results. And this, too, despite the fact that the ventilating plant is really the lungs of the building and counts most for the comfort and efficiency of the building and its occupants. But, of course, there must be so many rooms, just so many gargoyles, and just so much marble. For these things are seen and read of all men. And thus the committee can point with pride to the size and beauty of its building and compare it with what a neighboring city secured for a similar sum.

Only recently an instance occurred where an expenditure of $1,000 additional in the installation of the ventilating plant would have saved twice this sum in the annual operating costs but this could not be permitted because the money was needed by the architect for additional space in, or ornamentation of, the building.

The air washer, a most desirable adjunct to the school ventilating system, desirable because it eliminates dust, bacteria and odors and makes possible any degree of humidification, costing but approximately five per cent of the cost of the heating and ventilating plant, is rarely found in newly built school buildings, and solely because the school, or building, committee does not provide the means, or the architect, being forced to satisfy the committee as to the size or appearance of the building, cannot spare the money.

One of the most frequent complaints offered against the artificial ventilating system is that air of the same temperature is supplied to all of the rooms of the building, regardless of their exposure to sun and wind. Often a room on the sunny sheltered side of a building should have its entering air supplied at a temperature of from five to ten degrees less than the temperature of the air entering a room on the side of the building which is in the shade and exposed to a severe wind. But the common ventilating duct supplies the same air at the same temperature to all rooms. And this system is usually enforced because an extra expenditure of two to four per cent of the cost of the heating and ventilating system may not be permitted for the installation of a double duct system or an individual duct system, by means of which the temperature of the air may be regulated for each room according to its needs.

In the single, or common, duct system one duct leaves the heating chamber and branches to the vertical flue to each room. The double duct system has a second duct, carrying cooler air, directly under the above mentioned duct, also branching to the vertical flue to each room. Mixing dampers are provided at the base of each flue by means of which the mixture of warm and cool air entering the flue, and thus the room, is regulated by a thermostat in the room, according to its individual needs. In the case of the individual duct system, the most desirable but the most expensive, the duct for each room is carried back separately from the base of the flue to the heating chamber, which is, in this case, divided into upper and lower chambers, the air in the upper chamber having passed through all of the heating coils, and the air in the lower chamber having passed through but a portion of the heating coils. Connections are made from both chambers to each individual duct, with dampers in both connections arranged to operate in conjunction with each other, as controlled by the thermostat in the room, thus giving to each room air of a temperature suited to its needs, and without reference to the needs of any other room, either as to temperature or volume.

In the third place the difficulty of obtaining sufficient space for the installation of necessary apparatus and in obtaining suitable locations for ducts, flues, air openings, heating units and other details of the plant, places serious limitations upon the efficiency of the ventilating system, for diffusion of air and the resulting air movement are most important. The co-operation of the owner, architect and engineer are essential to the best results in this matter.

A further problem has to do with the standard of the janitorial service usually found in charge of the operation of heating and ventilating plants. Many well installed plants are rendered wholly inefficient by unskilled attention, and this despite the fact that the employment of a better class of operating engineers would result in a fuel saving more than sufficient to cover the extra cost of first-class and experienced men.

What has been said of the ventilation of schools applies with equal force to hospitals, auditoriums, stores, factories and all other types of buildings.

In conclusion be it said that given authoritative standards, the employment of capable consulting engineers, a proper appropriation for the installation of the heating and ventilating system, a reasonable freedom to the engineer in the working out and in the application of his design, and skillful operation, and the engineer's problems in mechanical ventilation will have been overcome.

Without the consummation of these ends the splendid efforts now being made to solve the chemical, physical, physiological, psychological, efficiency and comfort problems of ventilation will have been wasted.

15 West 38th Street, New York City

INVESTIGATION OF SCHOOL AIR IN NEW YORK CITY

By Charles Baskerville

The Public School System of Greater New York has to do with over 700,000 children requiring the services of about 18,000 teachers with an annual expenditure of approximately $40,000,000. The Board of Estimate and Apportionment approves all appropriations, which to be available must subsequently be passed upon by the Board of Aldermen. A special Committee on School Inquiry was appointed by the Board of Estimate and Apportionment to look into the problem of efficiency of the entire school system, involving the child, its instruction, and physical environment.

The Committee desiring to utilize the equipment and services of some of the staff of the College of the City invited me to undertake the study of the air of the New York City Schools. The invitation was accepted after I had succeeded in securing the coöperation of my colleague, Professor C.-E. A. Winslow, who subsequently was selected as chairman of the New York State Commission on Ventilation.

Our work constituted a part of the investigation assigned to Mr. Chas. G. Armstrong, the engineer to the School Inquiry Committee.

A preliminary investigation was made during the spring of 1912 after the ventilating plants in those schools having them had been shut down. For this work $750 was allowed. The work was continued, on our recommendation, in the fall of 1912 and winter of 1913, when the various ventilating systems were in operation, with a further expenditure of about $7,500. Neither Professor Winslow nor I accepted compensation for our services in connection with the investigation. The money was spent for the services of assistants and special apparatus. Space admits only a very brief summary of our work, the full report of which is now in press by order of the School Inquiry Committee referred to.

Our problem was to determine the quality of New York air and if possible express an opinion upon the efficiency of the several systems of ventilation in operation in the schools, which might serve as a guide in making recommendations looking toward the re-construction of some of the school buildings, or, better operation of the systems already installed, and to advise as to future construction. We were able to meet these demands in part only, some reasons for which will be clear in what Professor Winslow will say in the last paper to be presented this evening. Other reasons are presented herewith.

The systems studied were (1), window system (designated the "open window" method by the lay press); (2), the natural system, where ducts were provided, but no mechanical means for insuring a flow of air in a desired direction or regulating the speed of the flow; (3), mechanical ventilation by means of fans with heating coils in the main duct; and (4), the last mentioned provided further with a washer, which also acted as a humidifier. In some, in fact practically all, schools investigated, where mechanical ventilation was the method used, the air was taken in at or near the street level and not filtered, except in so far as in special cases, we may regard passing through a spray of water as filtration, which it undoubtedly is. In this connection, however, it is important to note that after it became known that we had begun the preliminary investigation—or perhaps it was coincident with our beginning—the Board of Education appointed a committee headed by Hon. John Martin, to study the matter of ventilation in the schools, which committee made a very common sense report, whereupon the Superintendent of Schools, Dr. Maxwell, not only authorized, but ordered, the teachers in the schools to open the windows in whatever school they might be, at any time they deemed it desirable, it mattered not what system was in operation or how efficient it might be operating, thus placing another duty upon the teacher already overloaded with responsibility. Our field squads encountered these and many other conditions in their work. Acting under orders they made their observations of existing conditions as they found them. Of necessity, the comparative value of our investigation from a refined point of view was materially lessened. However, what we did learn proved of no little value as will become apparent to one who studies the report.

Two fundamental facts presented themselves to us at the outset; first, the quality of the air of the city itself, and second, the quality of the air in different localities of the city.

When it is considered that the children are in school 5/24 of a day for 5 days in a week for 8 months, that is to say, about 1000 hours of the total 8760 hours of the year, approximately 3/24 of their existence, while the remaining 21/24 of their time is spent in the streets, where the air is superior in certain ways and far inferior in others, and in their homes, where different features are better, but others worse, it becomes a matter of no small moment to recommend the expenditure of many millions of dollars for the installation of elaborate systems of ventilation involving the cost of maintaining them in operation when the heating plants are not going, as desirable as they may be, for the actual benefit derived.

The examination of all the 600 schools in New York was obviously out of the question, so under the advice of Mr. Armstrong, we selected 32 typical examples, ranging from modern and well managed fan-ventilated schools to older buildings in congested tenement districts, ventilated without fans, and including buildings of various sizes from one of the largest high schools to a four-room country school in Richmond Borough.

Ten of these schools were studied intensively, being visited once a week between December 2, 1912 and February 14, 1913, while the other twenty-two were visited on one or more occasions between February 14 and March 15, 1913. The latter group included some night schools.

The work was organized under three major heads, *viz.:*

I. A study of the physical and chemical condition of the air.
II. A study of the air distribution within rooms.
III. A physiological study of "crowd poison."

I. Physical and Chemical Condition of the Air—Those factors known to possess more or less physiological significance only were considered. They were (*a*) Temperature, (*b*) Relative Humidity, (*c*) Carbon Dioxide, (*d*) Dust, and (*e*) Bacteria.

(*a*) *Temperature*—Over 1800 determinations were made, besides some 340 daily thermograph records obtained with 12 Tycos instruments located for various lengths of time, in different schools. The general results obtained by the sling psychrometer are shown in Fig. 1. The thermograph records will be referred to under "operation."

The data are expressed in the form of distribution curves, the abscissae representing the observed values in each case and the ordinates the percentage of all observations falling within the limits of values indicated below. It is evident that these records as a whole indicate very good conditions. The temperature curve centers closely, as it should, about +68° F. On the whole, this result must be considered highly creditable and an indication that the children of the New York schools for the most part enjoy good atmospheric conditions, free from objectionable overheating. An examination of particular schools, however, shows that this general curve covers up markedly different conditions in individual cases.

(*b*) *Relative humidity* was recorded with over 1800 observations made with the standard United States Weather Bureau sling psychrometer, swung through an angle of 180°.

The general distribution of results in regard to relative humidity is shown in the fourth curve of Fig. 1.

WIDE HUMIDITY RANGE

The range of relative humidity is seen to be a wide one. Sixty per cent of all observations, however, fall between 20 per cent and 40 per cent of saturation and the general average for all schools is 35 per cent, indicating a distinctly dry atmosphere. We found a close correlation between outdoor temperature and indoor temperature and indoor relative humidity, closer if anything in the naturally-ventilated than in the artificially-ventilated schools. This is an important point, in view of the criticism often leveled at the supposedly abnormal air of the fan-ventilated schools. It does not make the least difference whether air is heated in the ducts or in the rooms, the same rise in temperature produces the same drying effect.

The only way to avoid dry air in the schoolroom with certainty is by means of fan ventilation, combined with artificial humidification.

(*c*) *Carbon dioxide* was determined (nearly 800 determinations) with an improved Petterson-Palmquist portable apparatus. It is recognized that a knowledge of the CO_2 content of the air is of comparatively little value beyond measuring the rate of exchange, but we secured valuable data especially in connection with the night schools.

Our results in regard to carbon dioxide are summarized in the lowest graph of Fig. 1.

The general average value for all schools was 9.1 parts per 10,000. Sixty-six per cent of the observations fell below 8.5 parts, which may be considered a very satisfactory result on any standard. Twenty-nine per cent of the tests showed between 8.5 and 12.5 parts, which would have been considered high on the older standards established when carbon dioxide was held to be a measure of some mysterious poisonous matter in the air.

There remain 6 per cent of the tests, however, showing over 12.5 parts which are clearly excessive. These were associated with overcrowding and deficient air supply in individual rooms.

Supplementary observations made in four schools during evening sessions (when there is no artificial ventilation) showed some very high carbon dioxide values ranging, in one case with gas burning, up to 26.0 parts.

This is a special problem which deserves more attention than it receives in many cities.

(*d*) *Dust Particles*—Nearly 700 samples were collected by filtration through sugar with an apparatus for measuring volume by time, especially devised for us by Wallace & Tiernan (described on p. 238). After the sugar was dissolved, the dust particles were examined in an aliquot part under the microscope (2/3 in. objective), general character noted, and counted (the standard method).

The general distribution of dust counts is shown in the second graph of Fig. 1. The largest number of samples showed between 200,000 and 400,000 particles per cubic foot. The general average for all schools was 601,000 particles and 20 per cent of the samples showed 800,000 or more, with a few values ranging up to 2,000,000 and over.

The sanitary significance of these results is probably not great. Dust particles constitute a serious menace to health in industrial establishments, grinding shops, granite cutting sheds and the like, since the hard metallic or mineral particles which are found under such conditions injure the lung tissue and often form a controlling cause in the development of industrial tuberculosis. There is no evidence, however, to show that such particles as occur in ordinary schoolroom air have any such significance. The particles which we found were for the most part minute and chiefly organic in nature. In the counting cell they separated into two layers, the greater number, floating on the surface, being barely visible under the microscope and consisting in large part of mold spores; while less numerous particles settling on the bottom included larger shreds of vegetable fiber and inorganic matter.

(*e*) *Bacteria*—About 700 samples were collected by filtration through sterile sand. The sand was washed with sterile water and the bacteria plated on litmus lactose-agar, the general method recommended by the Committee of the Laboratory Section of the American Public Health Association on Standard Methods for the Examination of Air. The term "bacteria" included yeast and molds as well; all microbes, in fact, which will form visible colonies on litmus-lactose agar in five days at room temperature. The most frequent result was 25 microbes or less per cubic foot, but the high results pulled the general average up to 96. However, 68 per cent of the samples showed counts of 100 or less and only 9 per cent over 200.

These counts include all sorts of organisms from all sorts of sources, which are able to withstand drying long enough to be lifted up and blown about in the air. Most of them, of course, are of no sanitary significance, and the values, averaging under 100 per cubic foot and in most samples much less, must be considered satisfactory by comparison with the results reported by Miquel (150 bacteria per cubic foot in the air of Paris), by Tenon (40–60 bacteria per cubic foot in quiet hospital air), by Hesse (60 bacteria per cubic foot in a classroom before the students arrived, raised to 430 during the hour, and 1,000 just after the class had left), and by Soper (140 bacteria per cubic foot at the remote end of the Fulton Street Subway station, New York City).

BACTERIA OF HUMAN ORIGIN

In order to obtain an estimate of the bacteria of human origin which might at times include pathogenic forms, we made all our plates on litmus lactose-agar, as noted above, and isolated all red colonies which appeared on the plates.

It is well established that acid-forming streptococci are among the most abundant forms in the human mouth, while they are absent from sources which have not recently been exposed to human or animal pollution. We have found the number of these organisms in preliminary experiments one and a half years ago to be quite small. We then found among 30,000 colonies isolated from 750 plates, exposed in schools with window ventilation, only ten mouth streptococci.

In the present study, in the examination of a total of 868 cu. ft. of air, we found 260 mouth streptococci, or thirty for every 100 cu. ft. of air. The average number of mouth streptococci for the individual schools ranged for the most part between ten and thirty-five per 100 cu. ft. In one crowded school in a poor district it rose to 75 per 100 cu. ft., and in a school in a good semi-suburban district, no streptococci were found in 41 cu. ft. of air. The general average of thirty mouth streptococci per 100 cu. ft. gives a ratio of about one of these forms to 300 total bacteria.

A child breathes less than 100 cu. ft. of air during an average school period and these mouth streptococci must, of course, be far more abundant than pathogenic forms. At a rate of twenty to twenty-five mouth streptococci per day the chance of ingesting pathogenic bacteria from the air is seen to be a slender one.

II. A Study of the Air Distribution within Rooms—This involved some 500 anemometer readings, some 2000 temperature determinations in various parts of the many schoolrooms

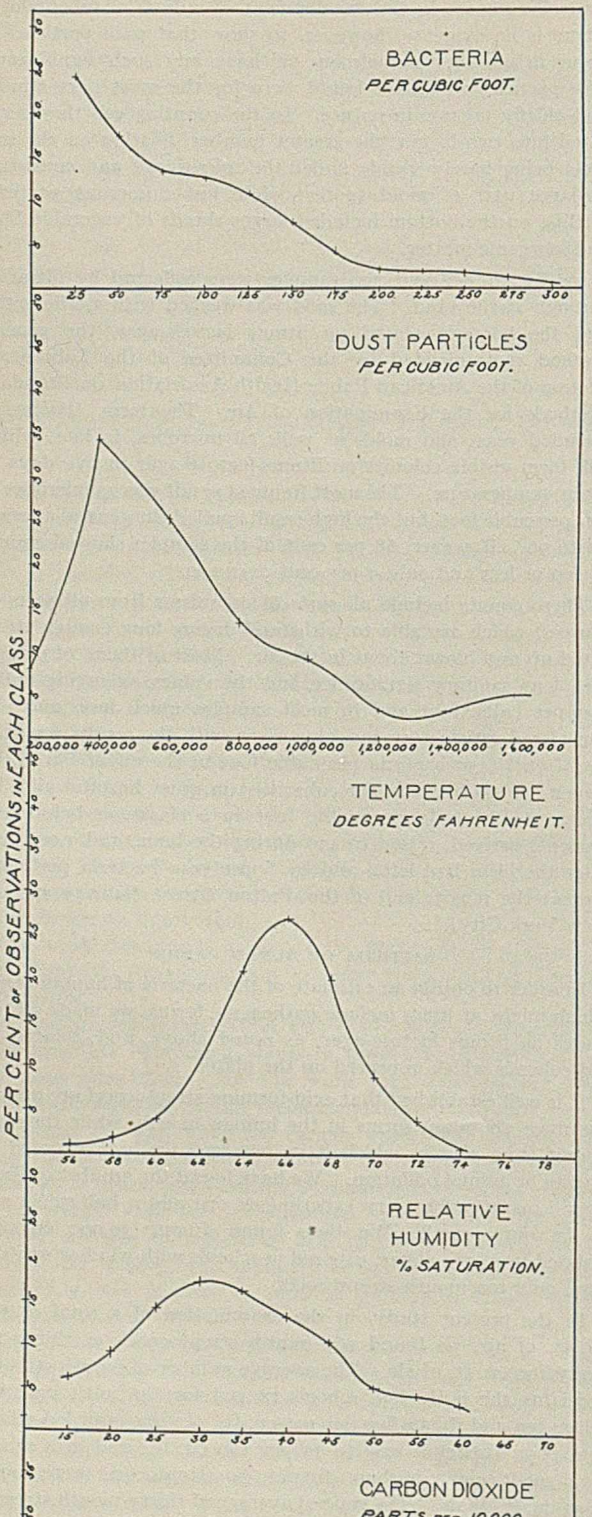

Fig. I—General Distribution of Results for all Schools Studied

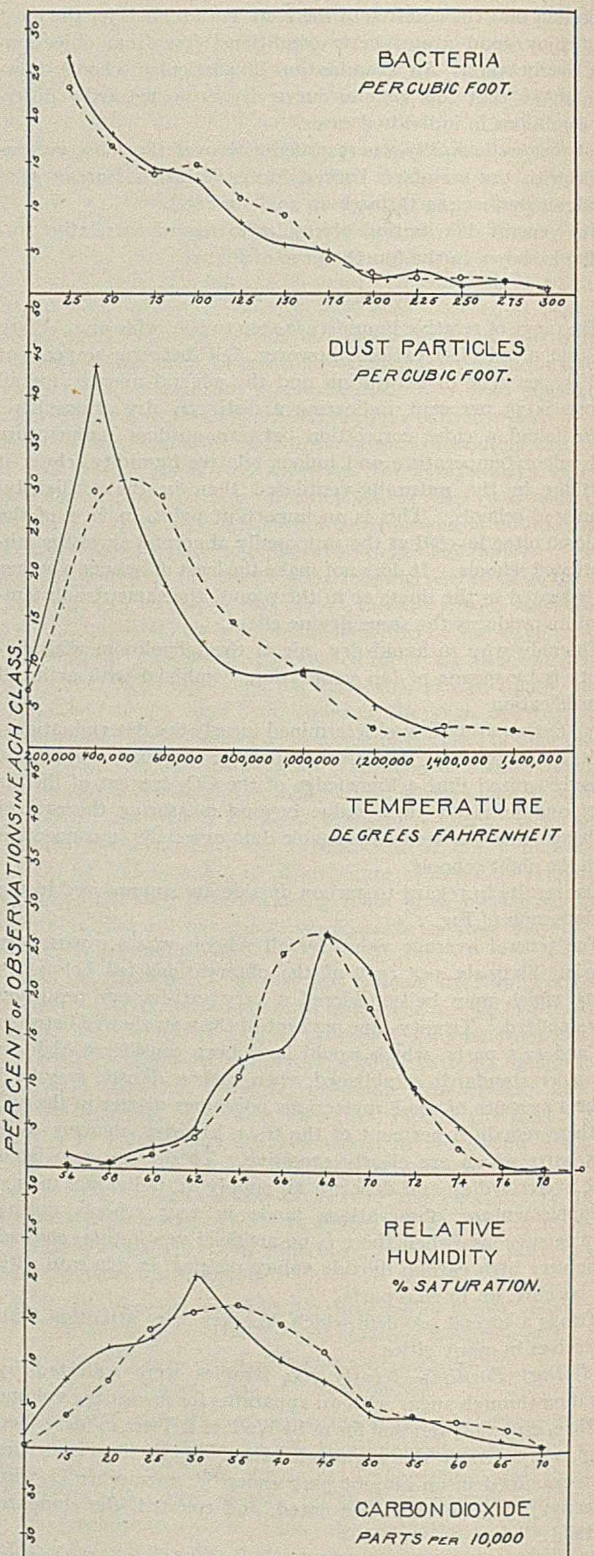

Fig. II—Distribution of Results in Ventilated Schools studied. The data obtained gave some interesting facts as to how the mechanics of ventilation work out in practice.

Inlet and outlet velocities were studied with the anemometer in 50 rooms, 25 in one of the best fan-ventilated schools (33 Bronx), 16 in four fan-ventilated schools where high carbon dioxide values had been found and 9 in four schools ventilated without fans. The amount of air supply in the fan-ventilated schools showed that in School 33 the amount was more than ample, while in the poorer school it was inadequate. For the most part we found a good plenum condition in all the fan-ventilated rooms. The very high ratios were usually in rooms with doors or windows open.

The results obtained in the naturally-ventilated rooms are not very significant, since doors and windows were freely opened. It is of interest to note, however, that in one school we found inlet velocities of 200 and 300 lin. ft. per minute without fans, maintained by unusually high temperatures of inlet air.

The circulation of air within the rooms themselves we studied by the use of smoking joss sticks and by an elaborate series of local temperature measurements. The results obtained by the use of the joss sticks in about 70 rooms were very hard to correlate. In about half of the fan-ventilated rooms there were clean-cut currents which could be traced across the upper part of the room, down the side wall opposite and back along the floor to the outlet. In an equal number of cases, however, the currents were indefinite and broken and in a few cases no currents at all could be discerned. In the rooms without fans the currents were usually very erratic, although in one or two cases a definite circulation was produced by windows open at top and bottom. In general the naturally ventilated rooms were much more subject to local drafts than were those ventilated by fans.

The local temperature observations were on the whole more valuable as throwing light on air circulation. In 24 rooms in fan-ventilated schools we found an average increase in temperature between inlet and outlet of 4.3° F.

The outlet temperature corresponds very closely to the general room average. This indicates that the outgoing air is a pretty fair sample of that in the room and that its temperature may be taken as a fair measure of that of the room as a whole.

The difference between bottom (3 ft. above floor) temperature and top (12 ft. above floor) temperatures was inconsiderable, and more variable than might have been expected. Of twenty-six rooms in which both were determined, just half showed a higher temperature at the top than at the bottom, while in the rest the upper air was cooler. The top excesses were higher than the bottom excesses, however, averaging over 2.0° instead of under 1.0°.

The slight extent of the differences observed is probably due to the fact that, on the one hand, cool air was being blown in at the top of the room while, on the other hand, the air, as it was warmed in the room, tended naturally to rise. This condition must interfere to some extent with normal air circulation and offers a certain argument in favor of upward as opposed to the usual downward ventilation.

Finally, the range between the maximum and minimum individual temperatures observed in the room is significant as a measure of general air circulation. The differences ranged for individual rooms between 1.7° and 12.0°, and averaged 5.8°, showing on the whole a fairly good mixture of the air. These observations were all made in fan-ventilated rooms.

In rooms ventilated without fans, conditions were more variable. Among eighteen rooms without fan-ventilation (that is, without a current of cool air blown in near the top) all but one showed a higher ceiling temperature, the excess in two cases being over 11.0°, and averaging 5.8°.

Another marked difference between the fan-ventilated and the artificially-ventilated rooms lies in the evenness of temperatures at different points. The range of difference between maximum and minimum room temperatures for the fan-ventilated rooms as noted above, was from 1.7° to 12.0°, and the average 5.8° For thirty-eight naturally-ventilated rooms, it ranged from 1.2° to 20.2°, and averaged 7.9°. Obviously, the air circulation is rather defective when such conditions exist.

It may be of interest to note that in five of the naturally-ventilated rooms, all in one building, the temperature of the incoming air was respectively, 83°, 86°, 90°, 98°, and 125° F. In the latter case one of our thermometers (registering to 130°) was burst by the heat of the inlet air the first time the temperature was taken.

COMPARISON OF NATURALLY- AND ARTIFICIALLY-VENTILATED SCHOOLS

For the purpose of estimating the value of fan-ventilation, as actually operated in New York schools, curves were plotted for all the schools classified on this basis and this curve is reproduced in Fig. II. Of course, it must be understood that by natural ventilation is meant simply that fans were not running. In almost all cases there were ducts and often heating coils were within them and air was undoubtedly passing through them. So, on the other hand, where fans were in operation, windows were often open and outside air passing in or out through them. The distinction is made solely on the fact that fans were or were not in operation in connection with the particular room in which each test was made.

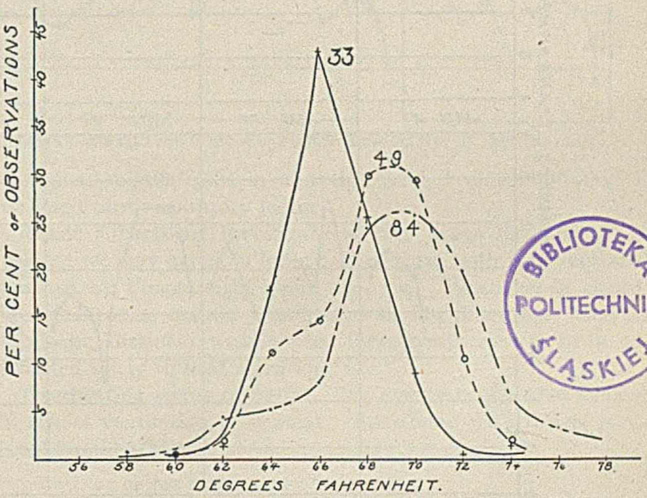

Fig. III—Temperature Curves, Public Schools Nos. 33, 49, 84
33—Good Fan Ventilation 49—Naturally-Ventilated
84—Badly Operated Fan Ventilation

The general results for the two classes of schools are on the whole remarkably alike. The fan-ventilated schools show more dust, more humidity more carbon dioxide and a somewhat more equable temperature; but none of the differences is very great or very significant.

In dust and carbon dioxide, the fan-ventilated schools appear slightly inferior to the others. In humidity they are better (if dry air be a disadvantage). In temperature they are also somewhat better, showing less observations over 72°.

So far as temperature is concerned, however, it should be noted that the curve for the fan-ventilated class conceals wide variations between the individual schools included in it. Of our ten schools more thoroughly studied, it is noteworthy that the four really good records (from the standpoint of temperature) were in fan-ventilated schools. The three wholly or partly naturally-ventilated schools are mediocre or poor; and two fan-ventilated schools are worst of all.

In Fig. III are shown typical curves for these three classes. Either almost perfect conditions or very poor conditions may be obtained with fan-ventilation according to the care and intelligence of the janitor in charge.

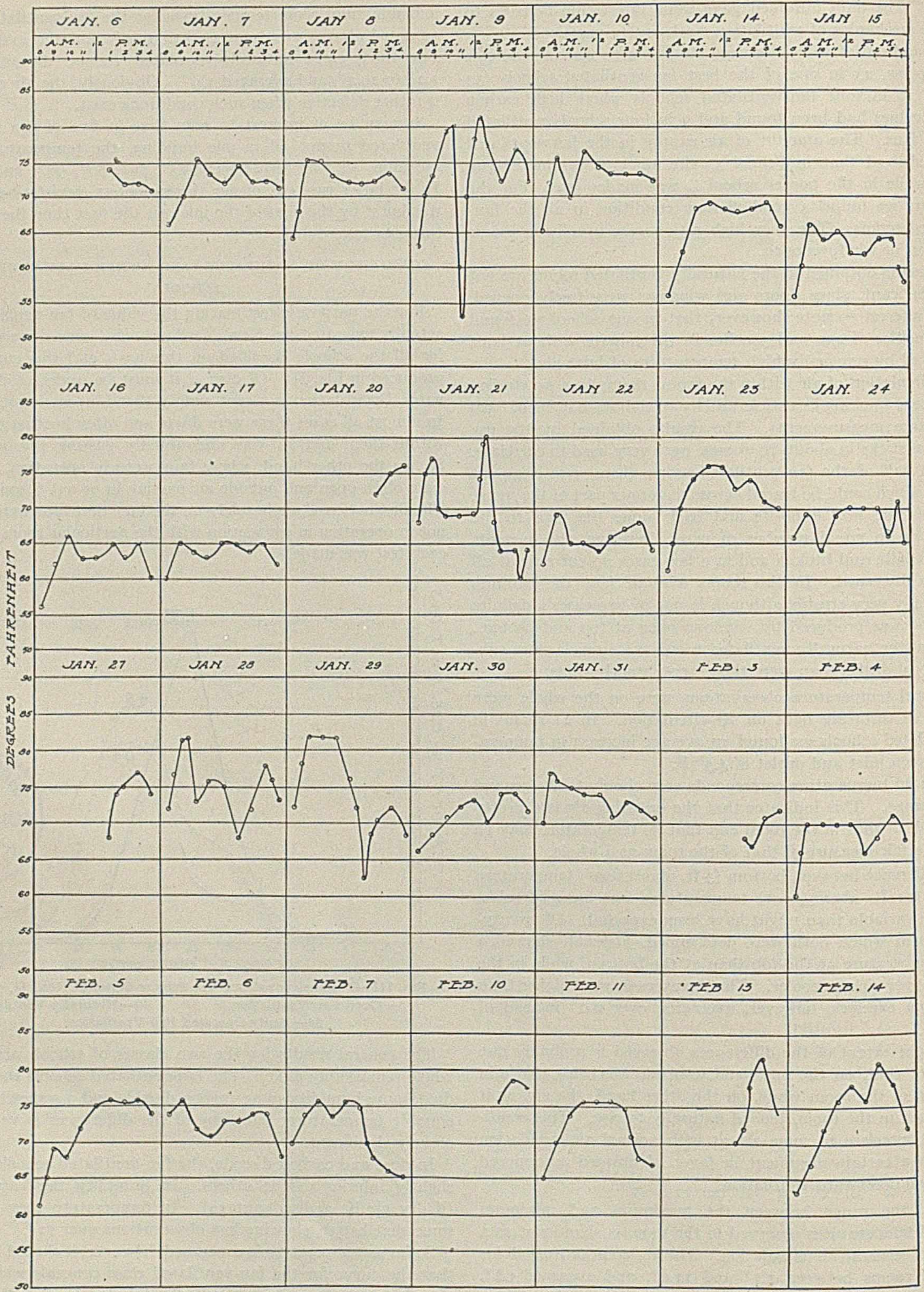

Fig. IV—Automatic Temperature Records in a Badly-operated Fan-ventilated School—Public School No. 1, Queens

On the whole it can be said that, comparing the actual condition of rooms ventilated with and without fans, New York was not deriving any material advantage from its fan-ventilation last winter as actually operated.

THE OPERATION OF A VENTILATION SYSTEM

A system of ventilation inherently not the best may give good results by good operation, and an excellent system may give poor results by poor or unintelligent operation. This folliful statement was vividly illustrated in our investigation. We found certain schools of either type which had an ample air supply and uniformly low carbon dioxide values. We found other schools, of both types, in which the supply of air was inadequate and carbon dioxide figures consequently high. In the case of fan-ventilated schools this usually meant low inlet velocities (sometimes inadequate inlet areas) or overcrowding, while in the naturally-ventilated schools it meant either overcrowding or neglect to open windows.

The most striking results of careless operation were shown, however, in the matter of overheating. In the case of the naturally-ventilated schools the coöperation of both janitors and teachers is required in order to secure good results, and, where so many persons are concerned, it is practically impossible to reach a maximum of efficiency. Such results as that indicated in Fig. III for School 33 could scarcely be attained where window ventilation plays any large part.

In fan-ventilated schools, on the other hand, the whole responsibility rests (or should rest) with the janitor, and either very good or very bad results may be attained, according to his intelligence and responsibility. The continuous records obtained by our recording thermographs brought out the importance of the operating factor with startling clearness, and four of our curves are reproduced herewith to illustrate the variation which occurred (Figs. IV and V).

In order to remedy this condition we urged that a thermograph of some improved type be installed in each school building and that the records obtained be carefully inspected and made the basis for an efficient control of ventilating systems and janitorial service and we recommended that these records be supplemented by periodical studies of temperature and volume of air at the room inlets.

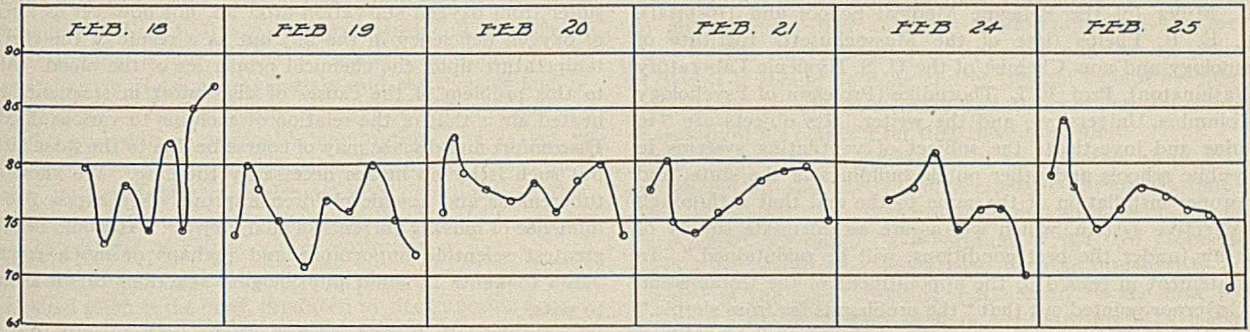

FIG. V—AUTOMATIC TEMPERATURE RECORDS IN A BADLY-OPERATED NATURALLY-VENTILATED SCHOOL—PUBLIC SCHOOL NO. 25, MANHATTAN

CRITERIA FOR SCHOOL-ROOM AIR

The chief value of these investigations lies perhaps in their possible use as a basis for comparative studies in the schools of other cities, which are greatly needed, if scientific records are to take the place of opinion in the field of school ventilation.

The results obtained in regard to dust and bacteria seem to indicate that, so far as these suspended matters are concerned, the air of the New York schools is in a satisfactory condition, without any special measures of protection, provided we regard the air of New York as good. Personally, I know the air in New York City is better than in some cities, it is also worse than in some other cities. The topographic conditions are an important factor. The general air conditions can and should be improved, for example by more extended washing down of the streets. I have not ceased in my hopes furthermore to see the city wash down its streets at suitable intervals with proper disinfecting solutions.

So far as carbon dioxide is concerned, our results indicate that it is comparatively easy, either with or without the use of fans, to keep the air in a schoolroom so changed that its carbon dioxide will average well under 10 parts per 10,000 and will rarely exceed 12 parts. This test furnishes an excellent measure of air change and under ordinary conditions such an air change is essential in order to remove odors and preserve a freshness agreeable to the senses. Where air is recirculated, however, with washing or chemical treatment to remove odors, the carbon dioxide standard may have to be relaxed still further, although it will always be of value as an index of what is going on in the way of air dilution.

III. A Physiological Study of "Crowd Poison"—In view of the claim of Rosenau and Amoss that specific proteid compounds of human origin can be detected in respired air by the delicate physiological reaction of anaphylaxis, we devoted considerable attention to this point. Dr. D. R. Lucas, who conducted this part of the investigation, was able to demonstrate easily the presence of such specific proteid substances in the saliva under carefully controlled conditions, but was unable to detect them in material condensed from the breath or in air heavily contaminated by the respiration and exhalation of dogs and human beings. We were forced to conclude that "there is at present considerable uncertainty as to the presence of such specific proteid substances in demonstrable amounts in respired air and that there is absolutely no evidence of the presence of any organic substances of a deleterious nature in such air."

Similar experiments carried out simultaneously and independently by Dr. Charles Weisman at Columbia University and published as a Doctor's Dissertation have led to the even more definite conclusion that "the results of these experiments disprove the statements of Rosenau and Amoss that the breath contains 'volatile' protein and that such 'volatile' protein is an important respiratory factor."

While subsequent investigations may prove it different, at present we may agree, in large part at least, with the conclusion reached by Flügge eight years ago, *viz.*, "Whenever in closed, crowded rooms certain impairment of health ensues, such as headache, dizziness, nausea, etc., these symptoms are to be attributed solely to heat retention."

Overheating seems to be the chief evil to be guarded against in school ventilation at present. Associated with this is regulated humidification.

COLLEGE OF THE CITY OF NEW YORK

THE NEW YORK STATE COMMISSION ON VENTILATION AND ITS PROBLEMS

By C.-E. A. WINSLOW[1]

Rudolph Hering has well said, in his recent address as President of the American Public Health Association, that the subject "of supplying suitable air to enclosed spaces, of heating, ventilating and removing foul air, is one which as yet is not sufficiently well understood in detail, and on which there are still opposing opinions. In fact, of all of the branches of sanitary engineering at the present time it needs most investigation and most study." In the last few years, however, a new and encouraging interest has been manifested in the study of ventilation problems. Among the various signs of this awakening none is perhaps more significant than the creation of the New York State Commission on Ventilation to undertake a broad and fundamental study of the physiological and mechanical problems which underlie the art of air conditioning. For the first time, in this country, at least, a sum of money is to be applied toward the solution of these problems which, though small in comparison with the magnitude of the task, is large enough to give

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[1] Chairman, New York State Commission on Ventilation.

hope of substantial results. The Hodgkins Fund of the Smithsonian Institution has made possible the publication of a number of individual researches on the relation of the atmosphere to health which have become classics. College and health departments and committees from many societies have made important contributions to the subject. There has not before, however, been any body which could attack the whole problem under such favorable circumstances as can the New York State Commission on Ventilation.

This Commission was made possible by the assignment to its use of the sum of $50,000 out of a munificent gift made for various social investigations by Mrs. Elizabeth Milbank Anderson to the New York Association for Improving the Condition of the Poor (Mr. J. A. Kingsbury, *Director*). The Commission was made an official State Commission by appointment of the Governor on June 25, 1913. Its members, who serve without pay, are Mr. D. D. Kimball (Ventilating Engineer), Prof. F. S. Lee (Professor of Physiology in Columbia University), Dr. J. A. Miller (of the Bellevue Medical School and Hospital), Prof. E. B. Phelps (late of the Massachusetts Institute of Technology and now Chemist of the U. S. Hygienic Laboratory in Washington), Prof. E. L. Thorndike (Professor of Psychology in Columbia University), and the writer. Its objects are "to examine and investigate the subject of ventilating systems in the public schools and other public buildings of the state, and the proper installation of the same to the end that a thorough and effective system, which will assure an adequate supply of fresh air, under the best conditions, will be maintained." In his statement in regard to the appointment of the Commission the Governor pointed out that "the problem is far from simple." He continued, "It is much more than an engineering problem, for the best scientific experts have not determined what conditions should be met by the engineers. Even the most fundamental facts which must lie at the basis of any efforts to ventilate our school buildings, have not been scientifically determined by any experiments which have been made thus far. It is not known, for example, and cannot be known without more adequate experiments than have been possible up to this time, what temperature should be maintained in public school buildings. Indeed, it has not even been proven whether a constant temperature or a varying temperature is more beneficial. We do not know scientifically what degree of humidity should be maintained in our schoolrooms.

"I am informed, also, that it has not been proven what amount of carbon dioxide in the air is possible before the air becomes detrimental to health. In other words, there is no scientific proof for some of the most fundamental factors involved in the problem of ventilation. On the other hand, I have been assured that if careful scientific studies were made with the express purpose of measuring some of the unknown factors, such studies could be reasonably expected to put us in possession of data which would enable the scientist to tell us with some degree of accuracy what those fundamental conditions are which should be maintained in schoolrooms if they are to be beneficial to the health of children."

Other speakers have so ably presented the positive results of previous studies of ventilation problems during the last ten years that I need not dwell upon what has already been achieved. We may take it as established that changes in the oxygen or carbon dioxide content of the vitiated air of rooms never remotely approach the limits at which harmful physiological effects can be produced. We may safely assume that specific organic poisons are absent from breathed air since all recent experiments along this line have yielded negative results. We may conclude with reasonable certainty that the symptoms of discomfort in a badly ventilated place are due to the physical condition of the air in respect to temperature, humidity and movement, and not to any chemical properties whatever. All this represents solid and important progress. I wish to-night, however, rather to call your attention to the lacunae in our knowledge, which this new Commission is to try in some small measure to fill in.

In the first place, since as scientific men we must ask not only what happens under a given set of circumstances but how and perhaps why it happens, we need to know much more than we now do as to the mechanism of the bad effects produced by atmospheric heat and moisture. Through what means is the difficulty in giving off bodily heat translated into the sense of discomfort, the headache, the drowsiness and the other symptoms experienced in a warm room? There are many suggestive possibilities. One of the most striking recent hints is the observation of the English physiologist Barcroft that under the influence of external heat the dissociation curve of the hemoglobin is so altered, presumably as a result of decreased alkalinity, that oxygen is less rapidly absorbed. If this result is confirmed it may be that in a badly ventilated room we really suffer from oxygen starvation after all, not however as a result of oxygen deficiency in the air, but as a result of the effect of temperature upon the chemical properties of the blood. Allied to this problem of the causes of discomfort in stagnant, overheated air is that of the relation of such air to various diseases. Discomfort and disease may of course be due to the same factors but such is by no means necessarily the case. We know that tuberculous and anemic children improve when exposed to the influence of moving currents of cold, dry air. It would be of the greatest scientific importance and perhaps of much practical value to know by what physiological reactions this is brought to pass.

The upper limit beyond which our room temperatures should never be allowed to go is clearly indicated by the experiments to which reference has been made and it seems certain that except for old people it should be fixed at least as low as 70°. As to the lower limit, however, we are far more in doubt. In this country we are apt to consider 65° quite cool enough, while in England, rooms are usually kept 5° lower. It is maintained by some advocates of open-air schools that the unheated air of winter ranging from 50° to 0° is more desirable than either. It seems probable that the problem is complicated by the existence of a "danger zone" of temperature, low enough to cause a dangerous chill, but not low enough to stimulate the defensive reactions with which the body defends itself against more severe cold. It is certainly complicated by a considerable power of gradual acclimatization, by which the defensive mechanisms adapt themselves to a higher or lower air temperature in the course of days or weeks. It would seem, however, that there must be a certain range of temperature which is most favorable to maximum efficiency with a minimum expenditure of bodily energy. On the basis of the fundamental human instinct for keeping warm in winter I doubt very much whether this range will correspond with the chance variations of the winter temperature in a northern climate; but I am quite open to further light upon the subject.

We must distinguish between favorable conditions of normal air temperature and the possible value of sudden brief variations therefrom. It is maintained with good reason that any uniform temperature maintained for long periods may be distinctly harmful by lowering the tone of the heat regulating mechanism and by robbing the body of valuable nervous stimuli. The good effects of cold baths are well recognized and "cold air baths" may be equally beneficial. Closely allied to the question of variations in temperature is that of air movement. At temperatures over 70° F. strong air currents which may carry off the excess heat in the aerial blanket surrounding the body are essential to comfort. Even at low temperatures air currents certainly exert a pleasant and wholesome stimulating effect within certain limits. What these limits may be, however, we do not clearly know, and we do not understand the exact nature of the bad effects produced by chilling of the body surface, particularly of the local chilling caused by what is commonly termed a draft. The value of moving air under certain circumstances is unquestioned; but so is the harmfulness of "drafts." Where the threshold lies between the two, and why it lies there, is what we need to determine.

The problem of humidity is almost as complicated as that of temperature. We know a good deal of the upper limits of high temperature combined with high humidity. We know that low humidity combined with low temperature produces grave chilling effects but where the permissible upper limit of humidity lies at a given low temperature has not been carefully worked out. As to the supposed harmful effects of low humidity combined with high or moderate temperature we are almost wholly in the realm of conjecture. We are told that schoolroom air is drier than the desert of Sahara; and as Professor Baskerville has pointed out, the air in the New York schoolrooms is certainly pretty dry. Dry hot climates, like that of Egypt are, however, sought out for their health-giving properties and the claims that the dry air of our rooms in winter overstimulates the cutaneous nerves causing nervousness and restlessness and injures the respiratory membrane so as to promote nose and throat disease, while a reasonable assumption, has as yet no firm basis of experimental observation. So far as I am aware, there are no sound data by which we may determine whether, with a temperature of 70° C., the humidity should be 25 per cent or 50 per cent or 75 per cent of saturation.

One of the first things that strikes an observer on entering an unventilated room is the odor, produced by decomposing organic matter in the mouths, on the bodies, and on the clothing of the occupants. Highly offensive to one coming in from a purer outside air, these products are usually imperceptible to those who have been in the room while they have been accumulating and whose olfactory nerves have been gradually accustomed to them. It is of course possible that even when unperceived these bodies may exert some subtle, harmful influence, but there is not the slightest evidence that such is the case. In any event it seems reasonable to demand for decency's sake that the air of occupied rooms should not be malodorous. It is somewhat an open question, however, how far such conditions should be met by ventilation and how far by a rise in general standards of personal cleanliness.

In regard to the dust content of the atmosphere, the serious danger from comparatively large particles of mineral matter such as are produced in stone-cutting, needle grinding and the like, is well established both by animal experimentation and by statistical study of the incidence of tuberculosis in the dusty trades. Whether the very minute dust particles, largely of organic nature, which to the number of a million or so per cubic foot may be found in ordinary schoolroom air have any such significance at all is another question, to which we have at present no answer. The chief argument for the use of air washers is in most cases the possibility of freeing the atmosphere from such dust particles. We know that where delicate physical instruments are in question, it is essential to wash ordinary city air. The respiratory passages are, however, equipped with an excellent mechanism for self-cleansing and it is altogether possible that the ordinary dust content of the atmosphere is a negligible factor. I do not believe that we have at present any valid reason for advocating the washing of normal city air on sanitary grounds.

With regard to the bacteria in air, evidence is reasonably clear that they have no serious sanitary significance. Local pollution takes place by the discharge of mouth spray immediately in front of an infected person; but such spray quickly falls to the ground and does not in any sense constitute general aerial pollution. The experience of modern hospitals in which various diseases are treated in the same open ward without cross infection, provided only direct transfer by nurses and other attendants be avoided, is reasonably conclusive on this point. The heavier dust particles deposited on surfaces do contain considerable numbers of mouth cocci and some tubercle bacilli, however; and the possibility that an appreciable danger might exist from dust stirred up in clouds as by gymnastic exercises in a dirty schoolroom seems to be well worthy of further study.

These questions to which I have briefly referred are all concerned with the physiological problem of precisely what air conditions are most favorable to the human organism. The mechanical problem of how to maintain a given set of air conditions is far better understood. Many existing ventilating plants yield unsatisfactory results, it is true, but there are three good reasons for this, none of which are related to any shortcomings in the art of the ventilating engineer. In the first place, until recently he has been told by the hygienist that the prime object of ventilation was to remove noxious gases rather than to regulate air temperature and humidity, so that he has naturally laid stress on air volume rather than air conditioning. In the second place he has rarely been given appropriations to do his work as he felt it should be done and in the third place he has still more rarely been able to count on an intelligent and conscientious operation of his plants after they have been built.

The first of these difficulties is now cleared away by the recognition on the part of all competent authorities that the chief aim of ventilation is to provide a moving current of cool air. This necessarily implies a separation of the two processes of heating and ventilation which have been so disastrously intermingled in the past. Cooling, not heating, is the task which should be closely associated with ventilating and a constant supply of cool air to remove the heat produced by human metabolism and by the combustion of illuminants is the fundamental end to be attained. It is interesting to note that Rietschel in the last edition of his standard work on ventilation bases his calculations of air volume primarily on heat removal, and on carbon dioxide dilution only secondarily and in certain specified cases. The substitution of this clear and definite aim for the old idea of mere air dilution will go far to make ventilating practice purposeful and efficient.

There are, however, still many purely mechanical problems which require further elucidation. Taking first natural ventilation or air interchange through walls, cracks, chimneys, windows and the like there is need for further data than we now possess as to the amount of leakage through walls under varying conditions of temperature and external wind movement. There is need of more exact knowledge as to the amount of ventilation through chimneys and ducts and windows with similar variables in weather conditions and as to the resulting circulation of air within the rooms.

The question of the adequacy of such natural ventilation by the admission of untempered air and the necessity or desirability of artificial or fan-ventilation is one of the most vigorously debated points in contemporaneous discussions. It is clear that with one or two persons in a large room window ventilation is adequate and sufficient. As soon as the factor of crowding comes in, however, difficulties begin to appear. In hospital wards the consensus of opinion seems to be in favor of natural ventilation. The patients have a comparatively ample air space. They are warmly covered and are doing no manual work. The windows are, or may be, under the constant control of skilled attendants. In a schoolroom these favorable factors are all wanting and in very cold weather it is usually found to be quite impossible by window ventilation to maintain properly cool conditions at the interior side without chilling those nearest the windows. In the ordinary factory workroom conditions for natural ventilation are even more unfavorable. It seems to me probable that in most schools and factories artificial ventilation with tempered air (either warmed at its point of admission to the room or warmed at a central point and blown in by fans) is generally essential to good atmospheric conditions. The limits of occupancy and of outside weather conditions within which such artificial ventilation is needed deserve careful study, however. If it is possible in a room of a given type, perhaps by the use of special window ventilators to insure good diffusion and to maintain good air conditions without fan ventilation during the greater part of the year it might be reasonably maintained that the expense of artificial ventilation was hardly justified, for the removal of atmospheric odors on a few extreme winter days when the worst evils of bad ventilation could be eliminated by avoiding overheating and on the windless days of moderate temperature when window ventilation is inadequate to remove the heat produced within the rooms. I am inclined to believe that the number of days of the latter class in schoolrooms open to winds on only one or two sides is likely to be large, and that the difficulty in securing proper supervision of window ventilation is sure to limit its practical value very seriously. The whole matter, however, is worthy of open-minded investigation.

Intimately connected with this question of the limits within which artificial ventilation is necessary—and fundamental in artificial ventilation itself—is the problem of the necessary volume of air to be supplied under various conditions. On the older conception of carbon dioxide dilution it was easy to derive constants of air supply. To-day we must calculate our necessary volumes of air on the basis of heat removal. Assuming no heat loss through walls and ceilings and assuming that incoming air must not be below 60° nor outgoing air above 70°, 2000 cubic feet of air per hour will be required to take up the heat produced by a single person and 1500 cubic feet will be required to take up the heat of a single gas burner. The first figure happens to be almost exactly that deduced on the theory of carbon dioxide dilution. The amount of heat loss through walls and ceiling will modify this constant to an almost infinite degree with variations in building construction and weather conditions. Professor Bass in his experiments at Minneapolis has found it possible to reduce the air supply to a fraction of this amount without objectionable results.

Perhaps the most important mechanical problems of ventilation are those which relate to the distribution of air between different rooms and the circulation of air within the rooms themselves. German and English experiments on duct construction should be verified and extended. The mistaken claim that a ventilation system cannot be designed which will not be unbalanced by opening windows in some rooms and not in others must be set at rest. In regard to the circulation of air within the rooms there are even more difficulties. Too often a room has been treated as a box to which as a unit it was only necessary to supply a given amount of air. What happened to the air thus supplied, and how far it maintained good conditions in various parts of the room, was left to chance or to the working out of a few crudely generalized principles. I am quite convinced that in most existing installations the number of inlets and outlets is too small to ensure at all times a reasonably good distribution of air. Prof. Bass's results, to which reference has been made, were accomplished by supplying air through individual inlets at each desk. This is an extreme case but we need to know with some exactness the proper mean between this condition and the usual single inlet and outlet. In connection with this question is the mooted problem of upward *vs.* downward ventilation. My own personal feeling is that it will frequently be best to take advantage of the natural upward tendency of air which is being warmed by supplying cool fresh air below and removing the warmed air above as is done in some of the most successful ventilating systems now in use in auditoria and factories. The objection felt to drafts of cool air is the limiting factor in this system, however, and we must not rest on abstract generalizations but on careful studies of the variables involved in practical operation.

The most important contributions to the art of ventilation in recent years have certainly been the experiments on recirculation of air at Minneapolis and at Springfield, Mass. If it is possible, as the theory of the newer ventilation would suggest, and as these studies seem to indicate, to use the same air over and over again, merely adjusting its temperature and humidity and washing or ozonizing to eliminate odors, the cost of operating a ventilating system may be cut from one-third to one-half and the whole practice of ventilation will be revolutionized.

Finally, there are many minor mechanical problems which require further study. The efficiency of various types of air washers should be carefully compared as has recently been done in certain installations by Professor Whipple of Harvard University. The use of ozone machines as an alternative to air washers for deodorizing deserves further consideration, although physiological investigations, both in this country and in Germany, throw serious doubt upon the advisability of this procedure. The distillation of objectionable gases from dust on heating surfaces is an interesting and important question; and there are many more to which I cannot even allude in this hasty review.

More than enough has been said, to indicate the need for light upon many of the physiological and mechanical problems which underlie the art of ventilation, and to illustrate the fact that the New York State Commission on Ventilation has quite enough to occupy its energies. We are only at the threshold of our work and have at this time only questions to ask and no answers to give. Our staff is now practically organized, however, with Mr. G. T. Palmer as Chief of the Investigating Staff and Mr. Joseph Herzstein as Secretary and we shall begin actual work before the end of the month. Through the courtesy of the Board of Trustees of the College of the City of New York two experimental rooms have been equipped in the Biological Laboratories of the College in which any desired conditions may be maintained. Here it is hoped that the fundamental physiological problems may be so worked out as to determine with reasonable definiteness what atmospheric conditions in regard to temperature, humidity, air movement and the like are most favorable to human health and efficiency. Special studies will also be made here in regard to the distribution of dust particles and bacteria in the air and the physiological effects of dusty air in promoting tuberculosis.

Through the courtesy of the Board of Education of the City of New York experimental schoolrooms are included in the plans for one of the new buildings to be completed in 1914 in which air of any desired condition can be admitted and withdrawn from any point. In these rooms the favorable air conditions determined in the City College experiments may be tested out on a practical scale and detailed studies may be made in regard to air circulation. The latter should be supplemented by special experiments on the mechanical problems of air flow and air circulation, and by tests of various mechanical devices used in ventilation, such as air washers and the like.

Coöperative investigations have been arranged for, under grants from the Commission, which will bring to it the advantage of much previous experience obtained by the leading students of ventilation problems in this country. These will include studies of certain fundamental physical problems of heat and moisture loss at the Massachusetts Institute of Technology (under Professor Phelps), observations on the results of the use of recirculated air in the International Y. M. C. A. College Gymnasium at Springfield, Mass. (under Dr. J. H. McCurdy), investigations of the physiological and psychological results of recirculated air supplied from individual inlets in a schoolroom in Minneapolis (by Prof. Bass), and records of efficiency of factory operatives under various atmospheric conditions (by Dr. Hollis Godfrey).

The task before us is a large and important one which we approach with a keen sense of responsibility. There are three factors and only three which universally affect the life processes of living beings from one end of the biological scale to the other. These are the physical and chemical conditions of the enveloping medium, food supply and predacious or parasitic enemies. The first of these factors, in the case of land animals, is solely a question of air conditioning or ventilation. I cannot doubt that when the ideal air conditions and the practical methods of securing them have been worked out with reasonable completeness it will mean an incalculable gain in human health and efficiency.

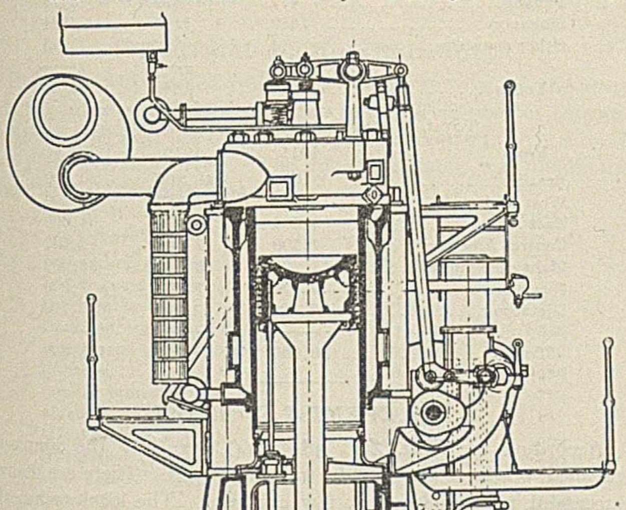
College of the City of New York

CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

THE MOTOR SHIP "FIONIA"

The Engineer, **117** (1914), 40, has recently published an account of the large passenger and freight vessel "Fionia" and her power plant. The "Fionia" was built by Burmeister and Wain, of Copenhagen, for the East Asiatic Co., to be used on the Bangkok route and is the ninth vessel of her kind that they have launched. She is 395 feet over all and driven by two six-cylinder 2000 h. p. Diesel internal combustion engines. The diameter of the cylinders is 740 mm., stroke 1100 mm., and the speed is 100 r. p. m. Each cylinder is mounted on two columns and the columns are coupled together at the upper part on the sides by cast iron plates to give fore and aft steadiness; the guides are made fast to the columns in the ordinary way. The bed plate is like that of an ordinary steam engine with open pits, but a steel tray is fitted underneath its whole length, and this with the light steel plate removable doors fitted between the lower parts of the columns allows forced lubrication to be used. A diaphragm piece is fitted across the top of the columns through which the piston rods pass in a light gland, and this prevents any oil which may come down from the pistons becoming mixed with the lighter oil in the crank pit.



Vertical Section of Main Engine

The cylinder jackets are cast together in blocks of three and bolted to the columns in the ordinary way.

The cross-heads, connecting rods and pistons follow ordinary steam practice, the piston rod being deeply spigoted into the piston, to which it is bolted by a number of light bolts. In the "Fionia" it was necessary to give up the very nice piston cooling arrangement previously used on the "Lelandia," in which the oil was forced through the shaft up the connecting- and piston-rods and into the piston, whence it was passed down on to the guides where it was cooled to a certain extent. In the case of the new "Fionia," however, it was thought that the volume of oil necessary to cool a 740 mm. piston would present difficulties in recooling, so recourse was had to sea water which is admitted to the pistons by ordinary telescopic tubes.

Reavell air compressors are fitted on the main shaft for supplying injection air, and are supplemented by 200 h. p. Diesel compressors. Two more 200 h. p. four-stroke Diesel engines running at 225 r. p. m. are fitted for auxiliary purposes; one provides current for the auxiliary machinery, steering gear, lighting, etc., while the other acts as a stand-by. In addition to these, there is a crude oil motor simply for the purpose of lighting the ship when in port, where none of the other auxiliaries are required.

BOILER EXPLOSIONS IN CHEMICAL INDUSTRIES IN GERMANY IN 1912

Eleven boiler explosions, exclusive of military, naval and locomotive boilers, occurred in Germany in 1912; of these, seven occurred in chemical or related industries. The *Chemiker-Zeitung*, **37** (1913), 1456, analyzes each of these cases, giving the attendant circumstances, character of the feed water, type of boiler, probable cause of the accident, etc., and these facts may be summed up as follows: All seven boilers were horizontal; in two cases the accidents were due to the water being allowed to run low through carelessness; in the other cases the accidents were caused by weakness resulting in the opening of seams, aided in one case by local overheating due to incomplete removal of boiler scale. In the seven explosions eight persons were killed, one accident only not proving fatal.

BENZOL IN GERMANY

In connection with the liquid fuel campaign it is interesting to learn from the *Jour. of Gas Lighting and Water Supply*, **124**, (1913) 1004, that there are now upwards of seventy German makers of benzol represented in the German Benzol Association. An important thing from the motorists' point of view is that these firms all produce benzol of uniform quality. Distribution of the benzol is performed by some 1100 sale depots scattered through Germany. The price at which the benzol is sold is fixed, and averages 40 per cent lower than the price of petrol. This being true, the latter can not surely maintain its present price much longer, in view of the favorable experiences with benzol for motor use. It is stated that the associated firms referred to have this year produced 140,000,000 kg. of benzol, the entire quantity being obtained from German coal. The coke ovens are responsible for the greater part, and there are signs of further quantitative progress in the production of coke, which will in time supplement the supply of benzol.

DOUBLE SCISSORS CROSSING IN ROLLED MANGANESE STEEL

There has recently been constructed at the works of Edgar Allen & Co., Ltd., Sheffield, England [*The Engineer*, 117 (1914), 78] for the Buenos Ayres Great Southern Railway, a layout with remarkable features. It is a double scissors cross-over built up entirely of rolled manganese steel rails, and is claimed to be the largest and most intricate junction ever constructed of this material. The entire layout weighs upwards of 100 tons and is about 145 yards long.

The application of rolled manganese steel to railway work is a development of the use to which this material has been put in the tramway world. Although the initial cost of manganese rolled-steel rails is much higher than that of ordinary steel, the life of the former is much greater than that of the latter, so that the expense and trouble of frequent replacements are avoided. Manganese steel is so tough that it may be bent double while cold without fracture, and yet is so hard that it effectually resists cutting by tools, while its resistance to abrasive wear is remarkably high. Rails of this material have been subjected to very severe tests on one of the London electric railways, and the results under the most trying conditions have shown that the durability is far greater than that of other kinds of rails previously used in similar situations.

The layout comprises eight sets of 18 ft. switches, four sets of 12 ft. slip switches, twenty acute crossings and closure rails, forming eight turnouts and eight diamonds, two of which have slip roads; the whole when connected with the closure rails forms a complete double scissors cross-over.

ANCIENT NORSE IRON NAILS

A report in *Chem. Ztg.*, 37 (1913), 1599 of the Polyteknisk Forenings Kemikergruppe, Kristiana, on chemical methods adapted to preserving wood antiquities, makes the following statement about nails in a Viking ship: "While the original old iron nails with which the wooden parts of the ship are held together have remained bright and untarnished, several new ones which had to be used in assembling the vessel have already rusted. The cause of the great durability of the old iron, proof of which is also given by the fully preserved anchor, will be investigated by a special commission."

In connection with this investigation, C. Hugo reports in *Chem. Ztg., Chem.-Tech. Rep.*, 37 (1914), 13 that a great iron kettle from the Norwegian iron works at Lesjeskogen, which were in operation between the years 1652 and 1812, was used by him and others in that place in 1886 and following years as a wash kettle, and although it stood in the open and was often left full of water, it remained completely free from rust as did the clothes washed in it. There are probably still in Romsdalen large quantities of the ore used in these works. [*Teknisk. Ugeblad*, 1913, No. 20, p. 200.]

RUBBER STATISTICS

The *Chemiker Zeitung*, 38 (1914), 96 gives some interesting statistics of rubber production on the Island of Java and outlying possessions; after a summing up of the general situation, the following figures appear, the amounts being given in metric tons:

TOTAL EXPORTS OF RUBBER FROM JAVA

To	1910	1911	1912
Holland	39	181	794
England	8	99	433
Belgium	13	15	63
Remainder of Europe	6	6	10
United States	1	22	9
Singapore	3	25	3
Other countries	1	12	10
Totals	71	360	1322

EXPORTS OF RUBBER FROM THE OUTLYING POSSESSIONS

To	1910	1911	1912
Holland	45	63	260
England	17	22	108
France	..	9	..
Belgium	70	21	91
Germany	185	56	15
Penang	471	479	1176
Singapore	1859	1195	1074
Other countries	4	2	13
Totals	2651	1847	2737

TOTAL WORLD PRODUCTION OF RUBBER

From	1911	1912	1913
Brazil	39,000	40,500	40,000
West Africa	15,000	13,800	13,800
East Africa	5,300	4,000	4,000
Central America	2,500	2,500	2,500
Plantation rubber	14,200	28,500	38,000
Guayule	9,200	7,000	7,000
Djelutong	2,800	2,700	2,700
Totals	88,000	99,000	108,000

THE CHEMIST IN BRAZIL

According to *Chem. Ztg.*, 38 (1914), 57, only the simplest chemical products are manufactured in Brazil. There are many successful pharmacists but few chemists. The local technical schools are only beginning to teach chemistry and the Brazilians know almost nothing of professional chemists. The chemist is generally expected to know all trades and arts. Wages are fairly high but are consumed by high living expenses, doctor's bills, etc. The climate is unhealthy and dangerous to many: sanitary conditions are generally poor.

Chemists are urged to investigate the financial standing of firms offering positions and to insist on written contracts, as well as a guarantee or salary paid in advance. These precautions are necessary on account of the uncertain legal conditions in Brazil. Many chemists have gone to Brazil only to find their company already dissolved or bankrupt. Yet Brazilians are very generous when successful and in many instances have been known to give bonuses far in excess of regular salaries.

A knowledge of Portuguese is necessary, though the educated population speaks French. German is used a little in the South but is nowhere popular.

Sulfuric acid is manufactured at Sao Paulo, by the chamber process, from North American sulfur but competition is very severe on account of the cheapness of the imported acid.

The brewery industry is chiefly in the hands of Germans. The light products are most successful, but the price is high—18 to 20 cents per pint.

The large quantities of banana leaves, palms, etc., available would support a first-class industry in cellulose products but none exists as yet. Textiles are chiefly cotton and though the industry flourishes there are still many technical difficulties to be overcome. Glass and matches are made in many sections of the country. The brick and artificial stone industries are developed to some extent, but very little is done in the earthen-ware line though kaolin deposits are abundant. [The rubber industry was discussed in *Chem. Ztg.*, **35**, 1303 (1911).]

The iron industry is quite undeveloped. The ore is very pure, rich, and easily smelted but a suitable fuel is lacking. It is reported that an English firm has a concession to build several blast furnaces. Coal for gasworks, railroads, etc., is imported chiefly from England and charcoal is made by the peasants for their own use. There is one modern charcoal kiln near Rio de Janiero and another near Sao Paulo.

Rich manganese ores are abundant but a market is lacking, as is the case with other possible products. The government is beginning a survey of its mineral resources. Oil and coal of very poor quality occur in quantities in the state of Sao Paulo and elsewhere. Almost all the necessary minerals for a solidly founded series of chemical industries are to be found in Brazil: only the necessary capital and spirit of enterprise are lacking. Much in these lines is looked for from North America and England, from whence financiers and large companies have begun a systematic campaign for concessions.

INDUSTRIAL ACCIDENTS IN 1913

Information collected from all available sources by the Prudential Insurance Company shows the total number of persons killed in American industries in 1913 to be about 23,000 in a total of 38,000,000 employed. The following table was made up from available information:

Occupations	Number employed	Fatal accidents
Agricultural pursuits	12,000,000	4,200
Building and construction	1,500,000	1,875
Coal mining	750,000	2,625
Draymen, teamsters, etc.	686,000	686
Electricians (light and power)	68,000	153
Fisheries	150,000	450
Lumber industry	531,000	797
Manufacturing (general)	7,277,000	1,819
Metal mining	170,000	680
Navigation	150,000	450
U. S. Navy	62,000	115
Quarrying	150,000	255
Railroad employees	1,750,000	4,200
U. S. Army	73,000	109
Street railway employees	320,000	320
Telephone and telegraph (including linemen)	245,000	123
Watchmen, policemen, firemen	200,000	150
All other occupied males	4,678,000	3,508
Total males	30,760,000	22,515
All occupied females	7,200,000	540
Grand total	37,960,000	23,055

The probable number of serious injuries, causing more or less prolonged absence from work, was estimated at 300,000.

PROCESSES FOR FIREPROOFING WOOD

Consul-General John L. Griffiths, London, England, states that considerable attention has been given in the United Kingdom to the best method for fireproofing wood, especially in connection with railroad construction. The following process, it is claimed, has received the favorable consideration of the British Admiralty: The wood is placed in large iron cylinders having hermetically sealed doors. The wood is steamed, and under vacuum the air and moisture in the pores of the wood are removed and the sap vaporized. The fireproofing solution is then run into the cylinders, and under pressure forced throughout the pores and fibers. Subsequently the water in the solution is evaporated in drying kilns, and the chemicals, in minute crystal form, are left embedded in the wood. When heat is applied, these crystals expand to many times their original size, forming a glassy coating to the fibers of the wood which excludes the oxygen in the air. In time the heat causes the crystals to collapse, but further crystals in the wood immediately expand, and the same process of resistance against fire continues. The chemicals used are antiseptic and preservative, consisting chiefly of phosphate of ammonia. As a result of the treatment, the life of the wood is also lengthened, for the cause of decay (sap water) is eliminated. This process is claimed to be especially satisfactory, inasmuch as the material treated is not saturated with a solution of salt, nor are such chemicals used as tungstate of soda, sulfate of ammonia, sulfate of alumina, alum, etc., which invariably cause discoloration of the wood, corrosion of metals, destruction of fibers, and prevent satisfactory painting or polishing. After this treatment, the wood can be worked, nailed, glued, painted, polished, etc., as though it had not been subjected to any special process. All kinds of timber can be treated, including oak, teak, deal, pine, mahogany, walnut, beech, birch, ash, maple, whitewood, pitch, pine, larch, etc.

The first railway company to take advantage of this process was the Underground Electric Railways of London, and at the present time it is stated that the woodwork of all the cars of the company has been subjected to the treatment. It is also stated that after exhaustive tests the British Admiralty has adopted the process, that the company is engaged in fireproofing large quantities of wood for 70 motor boats for the British warships *Indomitable* and *Monarch*, and that the two new super-dreadnoughts now building, the *Queen Elizabeth* and *Warspite*, are to have their woodwork fireproofed by this process.

The company using the process states that as a result of the recent disaster at Aisgill, the Midland Railway (on whose system the accident occurred) has requested the fireproofing company to submit a tender for erecting a fireproofing plant at the company's works in Derby, and that, pending the erection of such a plant, the company has sent 144,000 feet of timber to be treated by the fireproofing company.

The cost of rendering wood fireproof by this process is a uniform one of 73 cents per cubic foot, for all woods excepting oak and teak, for which the charge is 85 cents per cubic foot.

There is another fireproofing process, known as the "Snowdon process," the chief feature of which is a chemical mixture, but the formula is not disclosed. By the use of this mixture it is claimed that woodwork and all manner of fabrics may be rendered non-inflammable and insect proof. In the case of wood already in position, it may be painted or washed with three or more coats according to density, when the solution penetrates to a depth of about one-eighth of an inch. When treated prior to construction, the wood is usually soaked in the solution in tanks, but if it is desired to render the wood fireproof throughout, pressure cylinders are used to force the liquid into every fiber.

GERMAN UTILIZATION OF IRON-FURNACE SLAG

Consul-General A. M. Thackara reports, from Berlin, that the utilization of iron-furnace slag is well developed in Germany, and the problem of its further utilization is receiving the attention of the Prussian Government and the Association of German Iron Founders. In solid form it serves for highway and railway construction and as a body material for concrete; granulated, it is used for making building blocks, bricks, tiles, etc., and for the manufacture of cement. Slag is also employed to a lesser extent as a raw material in glass-making and in the production of artificial marble and artificial pumice stone.

Experiments have been made in the past with the use of slag paving blocks, but little or nothing seems to have come of them. The usual practice is to use slag in rubble form for road-making, the road being constructed after the system of macadam, the slag simply replacing the usual crushed stone. Its use ceases to be economical as soon as any considerable transportation charges are involved.

According to the Association of German Iron Founders, opinion varies as to the value of slag as ballast for railroad tracks. A number of German railroad administrations, particularly that of Alsace-Lorraine, use large quantities of slag as ballast, while others still regard its use with skepticism. One technical officer states that no opinion as to the relative durability of slag and hard-stone ballast is possible as yet, owing to the comparatively short time the former has been in use.

At the behest of the Iron Founders' Association, the Prussian Minister of Public Works has ordered exhaustive tests of slag concrete to be made at the Royal Prussian Material-Testing Station near Berlin. Investigation will be made as to reliable methods for determining the availability of particular slag for use in concrete. The test will extend to (1) observation of slag pieces left in the open air to determine changes in exterior appearance, volume, specific gravity, etc.; (2) chemical analyses; (3) tests of the compressive strength of rich and poor concrete mixtures, made of Portland cement and broken slag, the blocks to be tested having been exposed to air and water for varying intervals and under varying conditions; and (4) observation of the behavior of pieces of steel embedded in slag concrete blocks with special reference to rusting. The tests will continue for a number of years, but it is possible that a report may be published at the end of the first year.

Slag sand obtained from the granulation of basic slag has hydraulic properties and serves for the production of building blocks, bricks, etc., and of cement. One system of granulation is by cold water; another by air. Another is covered by a patent, according to which the hot, fluid slag is granulated by sprinkling with a salt solution; it does not appear, however, to have been put to any considerable practical use.

It is said of bricks made from slag that, as compared with glazed earthen bricks, they have a greater porosity and accompanying permeability. This is said to suit them especially for the construction of dwelling houses, as their strength increases with age.

IMPORTANT PROCESS FOR PURIFYING GAS FROM SULFUR COMPOUNDS

Charles Carpenter, chairman of the South Metropolitan Gas Co., London, describes in a paper prepared by him for the "Société Technique de l'Industrie du Gaz en France" a process of purifying gas from sulfur compounds which appears to have yielded truly remarkable results.

Mr. Carpenter, whose position is supported by Mr. Evans, the company's chief chemist, declares that it is possible to effect a reduction of the sulfur which is ordinarily left in so-called purified gas by more than 70 per cent, and this without causing any appreciable deterioration of the illuminating or calorific power of the gas, and at a cost of less than half a cent per 1,000 cu. ft. This is accomplished by passing the gas over heated nickel, deposited by the reduction of its chloride or other salt, on refractory material, the catalytic power of the metal causing the reaction to take place at a lower temperature than had hitherto been necessary. The finely divided condition of the metal also provides an extensive contact surface, so that practically the whole of the impurity in the gas is successfully acted upon. It furthermore is stated that when the process came to be applied in the works—on a small scale at first—it was found that to attain the best results with economy, it was necessary to give the gas a preliminary heating before submitting it to the contact material. By improvements and enlargement of plant, such perfection is claimed that since January last the whole of the gas produced at the company's works has been successfully treated, and a new plant now is being erected with a maximum production of 25,000,000 cu. ft. per day.

CARPENTER'S PROCESS

Mr. Carpenter found that the best conditions were obtained by using balls, one inch in diameter, impregnated with reduced nickel obtained by the reduction of the chloride in a stream of hydrogen. The gas was preheated to 212° F. below the temperature of the reaction before its contact with the catalyzer. This enabled the retort to be kept at 932° F. The installation worked for four months, the carbon deposited being burned out by a current of air once a week. During that period 3,500,000 cu. ft. of gas were treated and the sulfur was reduced from 38.675 to 12.031 grains per 100 cu. ft.

An installation was then put up comprising forty reaction tubes twelve feet long and six inches in diameter, through which the gas passed in ten streams. The preheating of the gas was effected by 230 tubes, 2 inches in diameter and 24 feet long. Regenerators enabled the gas to be heated in these to any required temperature. This installation, capable of treating 2,000,000 cu. ft. of gas per twenty-four hours, had been at work since November, 1911, and the catalyzer remained active. The quantity of sulfur at the inlet had been, on the average, 31.94 grains per 100 cu. ft.; at the outlet 8.45 grains; a mean reduction of 73.5 per cent. Since its erection, 29,000,000 cu. ft. from 23,673 tons of coal had been treated. The costs (not including the secondary purification from H_2S) had been for fuel 0.0728, for wages 0.0188, for interest, sinking fund and repairs, 0.0830 in cents per thousand cu. ft. of gas.

The Old Kent Road Works of the South Metropolitan Gas Co. has an installation capable of dealing with 10,800,000 cu. ft. per day. This installation has been divided into five units, fed with heat by a producer, so that the temperatures may be easily regulated. The arrangement provides for putting one unit out of action for the regeneration of the catalyzing material during the period of the greatest output. The combustion chambers are placed between the reaction retorts or tubes and the preheating tubes, and the flow of combustion products can be regulated in one or the other direction. In practice it is found necessary to regulate it only in the direction of the preheater. It may be considered that the function of the heating arrangement is to raise the temperature of the gas up to the point necessary for the reaction and to prevent, during the passage of the gas through the catalyzer, any fall of temperature due to radiation. The gas passes first through a couple of regenerators, counter-current fashion, then through the heating tubes and on to the catalyzer tubes; then it returns to the regenerators and gives up its heat to the gas newly arriving. Thanks to the progress made in the preheating, its temperature can be maintained at 770° F. before reaching the catalyzer; consequently the temperature of the latter has been reduced from 932° F. to 806° F.

The maximum content of sulfur was, before treatment, 62.86 grains per 100 cu. ft.; minimum, 16.01; average, 40.34 grains. After the treatment, maximum 8.71, minimum 5.82, average 7.79 grains. Since this installation was set in action, up to April 21, 1913, 650,000,000 cu. ft. of gas, from 50,800 tons of coal, had been treated. The quantity of CS_2 broken up corresponds to 13$^1/_2$ tons of sulfur, or 42 tons of sulfuric acid. Many tests have been made to find whether nickel-carbonyl was present in the gas; but no trace of deposit of nickel in a hot tube has been obtained. It is an established fact that nickel-carbonyl is completely decomposed at 392° F.; but care is taken never to let the gas touch the catalyzer unless the latter has a temperature above 572° F. The reaction has been conclusively determined by laboratory experiments to be

$$CS_2 + 2H_2 = 2H_2S + C.$$

When pure materials are used, the carbon is deposited on the catalyzer in the theoretical quantity.

This carbon diminishes the activity of the catalyzer by protecting it from contact with the gas; the loss of efficiency is shown by daily chemical tests. Each unit goes on for thirty days before it appears necessary to burn off the carbon deposited.

Burning off this carbon requires careful handling and a temporary lowering of the temperature. It lasts over a period of four or five days, in such fashion as to keep the temperatures below the limits at which the metal of the tubes might be injured. The burning-off is complete when the emergent gases contain no carbonic acid. Calculating from the amount of CO_2 obtained, the amount of carbon deposited would appear to be, in some cases, some 50 per cent above the calculated quantity. This excess may be due to the decomposition of hydrocarbons; but it is negligible in amount, as is shown by the following table of data:

	Before treatment	After treatment
Lighting power, English candles...	14.05	14.05
Heating power, B. t. u. per cu. ft.	590.0	594.0
Naphthalene, grains per 1,000 cu. ft.	45.5	47.2
HCN, grains per 1,000 cu. ft......	222.5	187.7
Carbonic acid, per cent..........	1.82	1.80
Hydrocarbons....................	3.61	3.79
Oxygen..........................	0.27	0.07
Carbonic oxide..................	8.85	8.62
Methane.........................	26.62	27.45
Hydrogen........................	52.45	52.19
Nitrogen (by difference).........	6.38	6.08

NOTES AND CORRESPONDENCE

SYNTHETIC RESINS

Editor of the Journal of Industrial and Engineering Chemistry:

In This Journal, 6, 167, there appears a criticism by Dr. Leo H. Baekeland of an original paper entitled "Synthetic Resins," which was published by the authors in This Journal, 6, 3. We are sorry that it is necessary for us to answer Dr. Baekeland's criticism but because of the erroneous impressions which may have been created in the minds of those who have not studied the subject matter of phenol condensation products at great length, we take the liberty of submitting the following statement:

Dr. Baekeland writes that the Industrial Fellowships are paid for "in the interests of purely commercial enterprises." Not only is this not true of a number of the Fellowships, but it may be stated that every Fellowship applies itself to a certain extent to purely scientific problems which have no ulterior remunerative consideration, and many of the results of these purely scientific researches are already known to our readers through the publications of This Journal. We presume that the Doctor does not believe an original paper would be of less value if it came from a purely commercial laboratory, such as his own, rather than from the laboratory of a State University.

The Doctor takes issue with the authors on the meaning of the Wetter patent as to whether it is the "wet process" or the "dry process." We can only state that the whole context of the Wetter-Lebach Patent is for the wet process and *that it is impossible for hexamethylenetetramine to yield formaldehyde in the presence of anhydrous phenol* and Wetter-Lebach states definitely that formaldehyde may be replaced "*by substances which yield formaldehyde,* such, for example, as hexamethylenetetramine:" the conclusion is very easy to draw. If the hexamethylenetetramine yielded formaldehyde, there must have been water present during the reaction.

It is unthinkable to the authors, who have worked for four years on this dry reaction that such a well-known chemist as Dr. H. Lebach did discover the anhydrous reaction between phenol and hexamethylenetetramine and that in the face of this discovery he did not take out basis and process patents on the reaction and the resulting resins. The position of the patent office, as Dr. Baekeland undoubtedly knows, is that the Wetter process is a wet process.

The Doctor intimates that "the authors show a fertile imagination" when they state "that the resins formed have very great commercial possibilities," and yet at the end of his criticism he assures us that these resins are identical with those formed by the wet process. While freely admitting that the wet process product of Dr. Baekeland and others has proven commercially valuable, the authors have no hesitation in stating that the dry process product which they have subjected to quite exhaustive tests is far superior for many reasons, some of which are mentioned herein.

With reference to raw materials, the process of producing hexamethylenetetramine from formaldehyde and ammonia with the removal of water from a *crystalline material,* such as hexamethylenetetramine, is surely not as difficult as the removal of the water and condensing agent from a *resinous material* such as phenol condensation products made in the wet way. The ammonia is not lost in our dry process but may be collected quantitatively and used over and over again indefinitely.

Dr. Baekeland states that "Bakelite" is a registered trade mark for phenolic condensation products. If so, the Doctor doubtless is entitled to its exclusive use as a trade mark on any such condensation product, whether involving any discovery of his or not. One should not confuse the trade mark, however, with the question of such discovery or inventive contribution to the art as may have been made by the user of the trade mark; and in this connection it is to be borne in mind. If our definition of the word Bakelite is "narrow and arbitrary," the Doctor's definition of his own products is too broad to be of any value when he says "Bakelite is a registered trade mark for phenolic condensation products." Such a definition would include saligeno-saligenin and saliretin resins which were made by Beilstein and Seelhein in 1816 and by Moitessier in 1866, and were well-known substances probably before the Doctor was born. If Bakelite is to be used simply as a generic term for all condensation products, the meaning of the word is reduced to a minimum, because it would then include the worthless, permanently soluble, fusible products as well as the infusible, insoluble porous products made without the use of counter pressure. And such a term would indeed include such phenolic condensation products as the resins patented by Smith in 1899, Luft 1902, Blumer 1902–3, Fayolle 1903–4, Story 1905–8, DeLaire 1905, Baeyer 1907, Helm 1907, Knoll 1907, Lebach (Knoll and Wetter)1907–8, Grognot 1908, all of which patents were taken out before Dr. Baekeland entered the field.

Our definition of the word Bakelite was from a purely scientific standpoint and had nothing whatsoever to do with its uses as a registered trade mark. We made a serious attempt, however, to use the word as defined by the Doctor in his earlier publications.

The experiments devised by us showed that dry hexamethylenetetramine and dry phenol heated together evolve no water and have "more than a theoretical significance." These experiments were designed especially to clear up the erroneous statements[1] which appear in recent literature to the effect that large quantities of water are produced during this reaction between phenol and anhydrous hexamethylenetetramine.

Dr. Baekeland objects when the authors describe a method for changing a porous mass of their material into a solid uniform body by welding together the ground-up material in a hot hydraulic press. This objection lies in the fact that we have not cited his U. S. patents, Nos. 939,966 and 942,700, wherein he described such a process accurately for molding his resin produced by the wet process. There is no claim made in the

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[1] Baekeland, This Journal, 4 (1912), 741.

article to this process as being new. The matter of molding powdered materials in a hot hydraulic press was known long before the discovery of our own materials or Dr. Baekeland's discoveries. The method is given simply to show that the porous material which Dr. Baekeland stated was of inferior value commercially can be made into homogeneous solid material which compares favorably with the best resins produced by the wet process, if we accept his own tables of the two materials.

We take decided issue with Dr. Baekeland when he makes the statement that the evolution of the ammonia is not a possible method for following the reaction between a phenolic body and active methylene groups and is "only true in case phenol is in large excess." The reaction may be followed easily by measuring the evolved ammonia when the phenol is not in excess at all, *e. g.*, when 6 mol. of phenol to one mol. of hexamethylenetetramine are present. We intend to discuss this in a later paper and we propose to show that the reaction is very easy to follow if carried on in the presence of ethyl alcohol, amyl alcohol or certain other solvents.

The Doctor intimates that we have dealt unfairly with Dr. C. P. Steinmetz, of Schenectady, in not mentioning in our paper the fact that Dr. Steinmetz had also prepared synthetic resins from anhydrous phenol and dry hexamethylenetetramine. However, Dr. Baekeland is in possession of the knowledge that we had made basic patent applications for these resins long before Dr. Steinmetz conceived of them, according to his sworn statement in the patent office. As prior discoveries in the art, it was not incumbent upon us to give Dr. Steinmetz credit for what was clearly our own invention. The Patent Office has ruled that Dr. Steinmetz is not the first inventor, and the office has also ruled that the interference in which Dr. Baekeland was involved should be dissolved, although this matter is now pending an appeal. Indeed, every claim made in the interferences was taken verbatim from our earlier applications.

The Doctor calls upon us to describe at greater length the qualities of the rods which we have in our laboratories which are two feet long and one and one-half inches in diameter. We are prepared to say that the tensile strength, crushing strength, dielectric properties and chemical inertness compare favorably with any of the products we have been able to produce from either the dry or wet process where a counter pressure was used.

At this time we do not deem it expedient to give the methods by which the rods were produced.

The table of analysis published[1] on page 11, column 1, is given with one specific idea in mind, *viz.*, to show that the chemical individual, phenyl-endeka-saligeno-saligenin is one of the principal intermediate products of all these reactions between phenolic bodies and active methylene bodies and also with other data went to show that phenyl-endeka-saligeno-saligenin was the particular intermediate product which transformed into the final insoluble resin. There was no attempt made to give an analysis of our most insoluble resins as the time required for analysis was too long, owing to the slow disintegration of the resin by the caustic and it was the object of the authors to produce a purely scientific treatise of the subject without discussing at unnecessary length its technical values.

The apparatus described[1] on page 11 for determining whether water is set free when hexamethylenetetramine reacts with an excess of phenol also finds objection from Dr. Baekeland. He believes the condensor marked "8" is the best means for *preventing* any water from entering the train of absorbing tubes. This we may concede without detracting from the value of the experiments. We are indeed very sorry the Doctor did not read the article more carefully. If the Doctor will again read the article he will see that we are trying primarily to absorb nitrogen compounds and not water and we were able to account for all the nitrogen in the hexamethylenetetramine present up to 99.5–100 per cent. The reaction does not come under the class of organic reactions of which Dr. Baekeland speaks which are considered quantitative when they lack 5 or even 7 per cent of the full 100 per cent.

Now, if the ammonia be evolved quantitatively there remains no reasonable chance for the remaining methylene groups and the dry phenol or the phenol less two of its hydrogens to yield water as a by-product during their reaction.

The condenser was the shortest type allowable which would guarantee a condensation of the phenol and a return of the same to the flask. Water, if it had been formed, would not have returned completely to the flask which was heated to 185° Centigrade, but it would have passed over in part at least into the train of absorbing tubes; or if it were formed in quantity and returned to the flask, it would have shown itself readily in either of two ways. Each drop as it fell from the condenser would have evaporated rapidly with a sizzling sound such as a lower boiling liquid makes when it falls upon the surface of a higher boiling liquid (which is actually boiling), or, which is more probable, it would have shown in a whitish ring around the top of the boiling liquid as the water in condensing ran down the sides of the flask and precipitated temporarily the resins out of the phenol. Such phenomena were not noticeable in any of the experiments.

Whatever may be Dr. Baekeland's objection, the fact remains indisputable that no water is formed during the reaction between anhydrous phenol and dry hexamethylenetetramine.

The experiments with anisol call forth some rather strange speculations on the Doctor's part. The non-reactivity of anisol and hexamethylenetetramine with each other when heated together and their activity when in the presence of phenol excites the Doctor. We feel like apologizing for having to point out that this is one of the commonest classes of reactions known where a substance A and a substance B do not react readily with each other but react readily in the presence of a third substance C. Indeed the very example the Doctor cites is among the most interesting in this respect. If we take pure meta-cresol and pure hexamethylenetetramine and let them react together they produce a resin which gives an inferior lacquer. The lacquer thus produced, heated for thirty minutes at 180° Centigrade, will darken and disintegrate in aqueous normal caustic solution in 150 minutes and darkens and dissolves in acetone in two hours while, if we accept Dr. Baekeland's statements, the meat-cresol in the presence of sufficient amounts of other cresols, will produce a resin which gives a lacquer film which is not attacked by caustic in 90 hours. We cannot understand why the Doctor accepts his own meta-cresol experiments and throws away our experiments with anisol. But we shall enter into a discussion of the relative merits of these lacquers in a later paper which we now have ready for publication.

The Doctor complains that his molecules do not obey him in the wet reaction so well as do ours in the dry reaction. We agree with the Doctor entirely on this point. We also found the wet reaction very hard to follow chemically while the dry reaction has considerable of the "Prussian Soldier" about it, especially in the precision with which it may be made to conform to orders. There are no deserters among the methylene groups in the hexamethylenetetramine—none of them are volatile—and none of them need to be *pressed* into service.

The tables with which the Doctor has concluded his criticism are misleading as he has arbitrarily selected examples from our tables and arranged them without regard to the original context. The tensile strengths for our anhydrous resins have no meaning, as no data is quoted of the conditions under which they are taken. The numbers quoted are neither the highest nor the lowest, nor the average of those we have published. But if the Doctor will read the paper again, carefully, he will

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[1] This Journal, 6 (1914), 11.

see that the numbers given in each table were given for special reason, *viz.*, to show the effect of time of heating, temperature, per cent rubber product present, etc., upon the final resins.

Indeed, we have tensile strength tests on our transparent almost water white materials which run higher than any of our published results (*i. e.*, from 5,000 to 6,200 lbs. per sq. in.), but since they have no bearing upon the scientific data given in our preliminary paper, we have not submitted them until now for publication.

There are many possible differences between our synthetic resins and the synthetic resins produced by the wet process which have not been mentioned in the Doctor's criticism; and it is to be carefully borne in mind that these very differences are the determining factors in many of the lines of industry in which our product is finding a market.

(1) The rate of discoloration in daylight or direct sunlight.

(2) The rate of disintegration in caustic or alkaline solutions.

(3) The solubility or discoloration in alcohol and acetone solutions.

(4) The effect of the lower fatty acids upon the resins, such as formic.

(5) The ability of the resins to withstand shock as in rapid valve work, under high pressure.

(6) The presence of free phenol in materials used for pharmaceutical apparatus.

(7) The presence of water as a by-product in the final transformation of the resins, especially in large impregnated armatures.

These are only a few of the possible and real differences between our anhydrous resins and the wet process resins.

We cannot close this reply without pointing out another of the Doctor's errors. He concludes that our resins are identical with his resins, but this conclusion is offset by his statement that he obtained by the wet process (1) "An infusible end-product resins which showed *incomparably* better dielectric properties than what we obtain in making a material by means of dry phenol and dry hexamethylenetetramine as described by Dr. Redman and his collaborators."

Just how a material can be at one and the same time equal to itself and incomparably better than itself would seem to call for explanation.

It has been no part of our purpose to engage in controversy with a gentleman who has shown untiring industry in studying the work of the earlier inventors and putting to industrial uses the results of their labors supplemented by his own discoveries. Our effort, in our earlier paper, was to set forth something of the history of the art of producing synthetic resins, and it did not occur to us that in so doing we should give offense to our highly esteemed contemporary or furnish the animus for Dr. Baekeland's criticism to which we have here made reply.

L. V. Redman
A. J. Weith
F. P. Brock

Amberiod Chemical Products Co.
636–678 West 22nd St., Chicago
February 16, 1914

VALUATION OF FLUORSPAR

Editor of the Journal of Industrial and Engineering Chemistry:

In This Journal, 4, 201 and 548, I published a quick method for the determination of the principal constituents of Fluorspar. This method is now used in our mine laboratory and has proved very satisfactory. In practical work, I have made some slight modifications, increasing thereby the accuracy of the results, so I believe the modifications may be of interest to some of my colleagues.

After dissolving the carbonates by diluted acetic acid, I evaporate to dryness, add 50 cc. water and heat to boiling to precipitate the iron, dissolved by acetic acid, as basic acetate. Thereby the small amount of iron soluble in acetic acid is not calculated in the amount of calcium carbonate, as it would be by filtering off the acetic acid solution. Furthermore, the amount of calcium fluoride brought in solution is smaller, since the solubility of calcium fluoride in acetic acid is higher than in water: 50 cc. hot water dissolve 0.8 mg. calcium fluoride, while 50 cc. acetic acid (1:10) dissolve 10 mg. of calcium fluoride.

After volatilizing the silica, I decompose the metal oxides, as formerly, by digesting and evaporating the residue with hydrofluoric acid and a few drops of nitric acid. By this operation under certain conditions, some calcium nitrate can be formed and left undecomposed, which would cause an error because of the solubility of calcium hydroxide in the alkaline extraction solution. Also in fluorspar high in iron, some iron nitrate can be left undecomposed, which will change to a basic salt by evaporating, which basic salt is insoluble in the extraction solution.

Therefore, I repeat the evaporation with hydrofluoric acid in all cases in order to be sure that all nitrates are transformed into fluorides. Investigating the action of nitric acid on calcium fluoride, I evaporated one gram of pure crystallized fluorspar, finely ground, with different amounts of nitric acid and calculated the amount of decomposed Calcium Fluoride from the increase of weight as follows:

G. CaF_2	Cc. HNO_3 Sp. gr. 1.42	G. CaF_2 decomposed
1	0.5	0.0034
1	1.0	0.0057
1	1.5	0.0089
1	2.0	0.0114
1	2.5	0.0131
1	3.0	0.0163

By digesting and evaporating these residues with 2 cc. hydrofluoric acid (50 per cent), I obtained the original weight of one gram fluorspar, showing that one evaporation with 2 cc. 50 per cent hydrofluoric acid is sufficient to decompose the calcium nitrate formed by evaporating one gram fluorspar with 3 cc. nitric acid (1.42).

Considering these results, I changed the method as follows: After volatilizing the silica and weighing the residue add 2 cc. hydrofluoric acid and 10 drops of nitric acid, cover the crucible with its lid and place on a moderately warm water bath thirty minutes; then remove the lid and evaporate to dryness, add 2 cc. hydrofluoric acid and evaporate again to dryness, etc., as described in my first paper.

Working in this manner, no calcium salt is dissolved by the extraction solution and only a small amount of calcium fluoride is washed out corresponding to the solubility of calcium fluoride in water.

The corrections I am using in this modified method, taking one gram of Fluorspar for analysis, are:

(1) For loss in weight by treating with acetic acid, evaporating to dryness and boiling after the addition of 50 cc. water.....	0.0010 g.
(2) For loss in weight by treating with HgO and HF..........	0.0002 g.
(3) For loss in weight by treating with ammonium acetate....	0.0010 g.
	0.0022 g.

E. Bidtel

Laboratory Fairview Fluorspar & Lead Co.
Golconda, Illinois
February 2, 1914

NOTE ON THE ELECTROLYTIC DETERMINATION OF COPPER

Editor of the Journal of Industrial and Engineering Chemistry:

In the electrolytic determination of copper from nitric acid solutions the deposit is very bright and adherent, if the correct acidity concentration conditions have been maintained. When the acid concentration is too low the film has a dull look and may not be adherent. If the acid concentration is too high a long time will be required to completely deposit the metal, although the deposit will be very bright.

In those cases where it is very convenient to limit the amount of free acid in bringing the copper into solution in preparing for the electrolysis, and where the results of the analysis are needed in the shortest possible time for control work, this excess acidity can be very easily controlled by the addition of a little powdered sodium acetate to the solution.

In preparing the solution for electrolysis all the nitric acid can be used that is necessary to quickly bring into solution the copper, copper salts, or compounds containing copper. Then after the electrodes have been mounted, the current switched on, and current density adjusted, if the copper does not promptly start to plate out, a little sodium acetate dusted into the solution will fix the excess of nitric acid which is dissolving the copper film as fast as formed.

The change in the character and speed of deposition will be almost instantaneous and the deposit will be bright, adherent, and formed in the minimum of time. The treatment of the solution with an excess of sodium acetate at the end of a deposition in order to change the free nitric acid to sodium nitrate and thus enable the electrodes to be removed without previous washing has been recommended often and the action is the same in both cases, differing only in degree.

H. Cloukey

Forest Products Laboratory
Madison, Wisconsin
December 27, 1913

REMARKS ON WHITE LEAD PAINT PUBLISHED IN 1810

Editor of the Journal of Industrial and Engineering Chemistry:

Mr. Frederick L. Hoffman, Statistician of the Prudential Insurance Company of America, has kindly sent me for perusal a rare volume of the *Memoirs of the Connecticut Academy of Arts and Sciences*, published in New Haven in 1810. On pages 135 and 136 occurs a letter from N. Webster, Jr., to Mr. Benjamin Silliman, Secretary of the Academy. I enclose a copy of this letter, thinking perhaps it might be interesting to the readers of the Journal. It is interesting no note that in those days they spoke of the "new chemistry" in pretty much the same way that we do to-day. The "new chemistry" of Webster, however, is not very new now.

G. W. Thompson

129 York St., Brooklyn
January 27, 1914

ON THE DECOMPOSITION OF WHITE LEAD PAINT

To Mr. Benjamin Silliman, *Secretary of the Connecticut Academy of Arts and Sciences.*

SIR,

It is well known, that a white paint, formed by mixing oil, and usually vegetable oil, with the white oxyd of lead, is very expensive, and not very durable. Within a few years after this paint is laid upon a building, it is observed that the oil has been separated from the lead, and the latter may be rubbed off with the hand, being reduced to a state in which it is easily pulverized. It is observable also, that the like paint on inside work, not exposed to water, is not liable to the same change. From these facts, it is probable that the oil, when exposed to water, undergoes a slow decomposition.

Oil is proved, by chemical analysis, to be composed of carbon, or pure charcoal, and hydrogene, or the base of inflammable air, in the proportion of nearly four parts of the former, with one of the latter. Now carbon has a very strong affinity for oxygene, one of the constituent elements of water. Is it not probable that the decomposition of the oil of paints is owing to that affinity—the carbon of the oil combining with the oxygene of water, and the hydrogene of the oil, being set free, escaping in the form of gas? If so, the art of rendering the paint durable will consist in fixing the oil, or preventing this decomposition. This is undoubtedly a great desideratum in the arts. In the course of my scanty reading on subjects of this kind, I have found nothing satisfactory. The experiments of M. de Morveau, as related in a paper communicated to the Academy of Dijon, of which an extract is found in the Encyclopedia, were evidently made before the date of the new Chemistry. It is believed that the causes of the changes which paints undergo, and which he ascribes to phlogistic vapors, are now better understood than when he wrote; and it is desirable that the attention of the chemist, as well as the artist, may be invited to the subject.

If the funds of the Academy would permit, it might be well to offer a premium for the discovery of a substance which should fix the oil in white paints, without changing their color.

I am, Sir, respectfully, your obedient servant,

N. Webster, Jun.

New-Haven, Oct. 30, 1804

FORTY-NINTH MEETING OF THE AMERICAN CHEMICAL SOCIETY, CINCINNATI, APRIL 7-10, 1914

A meeting of the American Chemical Society will be held in Cincinnati, Ohio, April 7th to 10th, inclusive, the beginning date having been changed from April 8th to April 7th since the announcement in the February Journal. A meeting of the Council will be held at the Hotel Sinton, at eight o'clock, P.M., on Monday evening, April 6th. The meetings of the Society will be held at the University of Cincinnati. The Hotel Sinton on the corner of Fourth and Vine Streets has been chosen as headquarters. Other hotels will be designated in the final program, which will be sent to all members who signify their intention of attending the meeting.

The following committees have been chosen to arrange the spring meeting:

F. W. Weissmann, *Chairman.*
Stephan J. Hauser, *Secretary.* Archibald Campbell, *Treasurer.*
CHAIRMAN OF SUB-COMMITTEES.
G. Farnham, *Transportation and Excursions.*
C. T. P. Fennel, *Publicity, Press and Printing.*
J. W. Ellms, *Reception.*
John Uri Lloyd, *Meeting Places.*
Mrs. J. W. Ellms, *Ladies' Reception.*
Richard Lord, *Entertainment.*
Lauder W. Jones, *Banquet.*
F. C. Broeman, *Smoker.*
Archibald Campbell, *Finance.*
F. O. Clements, *Reception at Dayton, O.*

All Divisions of the Society will meet, and the Water, Sewage, and Sanitation Section have announced that they are planning a special conference on Standard Methods of Water Analysis. As Cincinnati is near to some of our largest rubber manufacturing centers a large meeting of the Rubber Section is expected.

The Secretary of the Local Section announces the following detail:

"The Entertainment Committee is planning many interesting events, and special preparations are being made to provide entertainment for ladies, who may attend, at times when they cannot participate in the regular meetings. One particularly interesting feature will be the concert given by the Cincinnati Symphony Orchestra, under the direction of Ernst Kunwald, which has been arranged for Wednesday evening.

"The Transportation Committee has arranged a number of interesting visits to local industrial plants. It is a well known fact that Cincinnati has a very large variety of industries which are strictly chemical or very closely allied. This Committee has already arranged trips to the Filtration Plant, Proctor and Gamble's, the home of Crisco, Globe Soap Co., Diamalt Co., Andrew Steel Works, Boldt Glass Co., the New Cincinnati Hospital, the largest and most modern city hospital in the world, Machine Tool Plants, Rookwood Pottery, Lloyd Brothers, W. S. Merril Chemical Co. and many others.

"In addition to these inspection trips, the Committee is planning to devote Friday, April 10th, to visit adjacent industrial plants, an all day excursion. It is planned to go to Middletown during the morning and inspect the plant of the American Rolling Mills, the home of Ingot Iron. After visiting this plant, we shall go to Dayton, where members of the Cincinnati Section, residents of Dayton, have arranged an inspection trip through the plant of the National Cash Register Co. Negotiations are now in progress to have Mr. Wright give an exhibition of his latest Aeroplane, including the stabilizer.

"The following provisional program will give an idea of the plans for the Cincinnati meeting.

MONDAY,	Apr. 6,	*Evening*, Council Meeting
TUESDAY,	Apr. 7,	*Morning*, General Meeting *Afternoon*, Excursions *Evening*, Smoker at Zoo
WEDNESDAY,	Apr. 8,	*Morning*, Division Meetings *Afternoon*, Excursions *Evening*, Concert by the Cincinnati Symphony Orchestra at Emery Hall
THURSDAY,	Apr. 9,	*Morning*, Division Meetings *Afternoon*, Excursions *Evening*, Subscription Dinner
FRIDAY,	Apr. 10,	Excursion to American Rolling Mills, Middletown; to National Cash Register Co., Dayton."

All titles for papers should be in the Secretary's hands on or before March 23rd, or in the hands of the Secretaries of Divisions by March 21st, in order to be placed on the final program. By vote of the Council no papers can be presented at the meeting that are not printed on the final program.

ADDRESSES OF SECRETARIES

DIVISIONS

Agricultural and Food Chemistry, Glen F. Mason, H. J. Heinz Company, Pittsburgh, Pa.

Biological Chemistry, I. K. Phelps, Bureau of Chemistry, Washington, D. C.

Fertilizer Chemistry, F. B. Carpenter, Virginia-Carolina Chemical Co., Richmond, Va.

Industrial Chemists and Chemical Engineers, S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa.

Organic Chemistry, C. G. Derick, Morris Ave., Lincoln Place, Urbana, Ill.

Pharmaceutical Chemistry, A. P. Sy, University of Buffalo, 24 High St., Buffalo, New York.

Physical and Inorganic Chemistry, R. C. Wells, U. S. Geological Survey, Washington, D. C.

SECTIONS

India Rubber Chemistry, Dorris Whipple, The Safety Insulated Wire and Cable Co., Bayonne, N. J.

Water, Sewage and Sanitation, Harry P. Corson, State Water Survey, Urbana, Ill.

The final program will be sent to all members of the Cincinnati Section, to Secretaries of Local Sections, to members of the Council and to all members requesting same. The expense of printing and mailing this program is so great that it is sent only to those who especially desire it on account of their intention of attending the meeting. Other members will find it printed in the Society's Journals.

Cincinnati is centrally located, and is accordingly easily reached by all members of the Society. Every member of the Society should make an effort to be present, for it is hoped and expected that this will be the largest meeting of the American Chemical Society ever held in the spring.

CHARLES L. PARSONS, *Secretary*

BOX 505, WASHINGTON, D. C.
February 19, 1914

NOTE ON CERTAIN UNPUBLISHED WORK ON ELECTROLYSIS USING SUPPORTED MERCURY KATHODE—A CORRECTION

In THIS JOURNAL, 6, 166 my name was omitted as author of the article under the above title.

ERNEST A. LESUEUR

OTTAWA, ONTARIO

PERSONAL NOTES

The program of the first public meeting of the Radium Institute of America, held at Columbia University on Feb. 17th, was as follows: "Introductory Remarks," Pres. N. M. Butler; "The Experiment of Counting the Alpha Particles," Prof. Geo. B. Pegram; "Some Experiments with Radium Emanation," Prof. William Duane; "Therapeutic Use of Radium," Dr. Robert Abbe; "Some Biological Effects from Radium," Prof. Francis Carter Wood.

Dr. Wolfgang Ostwald, of the University of Leipsic, Germany, was the guest of honor at a dinner given by the Cincinnati section of the A. C. S. and the Cincinnati Research Society, at the Business Men's Club, on Feb. 11, 1914.

Dr. F. K. Cameron, of the Bureau of Soils, spoke before the Washington Section of the A. C. S. on Feb. 12, 1914. Dr. Cameron gave an illustrated lecture on "Potash from Kelp."

Prof. Harry C. Jones, of Johns Hopkins University, gave an illustrated lecture on "The New Era in Chemistry," before the Philadelphia Section of the A. C. S. on Feb. 21, 1914.

The Michigan Section of the A. C. S. met Jan. 22, 1914 and were addressed by Mr. W. L. Badger on "The Work of the Bureau of Standards."

Mr. Wm. H. Blauvelt, Consulting Engineer of the Semet-Solvay Co., Syracuse, N. Y., gave an illustrated lecture on "By-Product Coke Ovens from the Chemical, Engineering and Economic Standpoints," before the Pittsburgh Section of the A. C. S., Feb. 19, 1914.

Prof. W. P. Mason, of the Rensselaer Polytechnic Institute at Troy, N. Y., lectured on Jan. 29th before the Franklin Institute of Philadelphia on "Advantages and Disadvantages of Water Storage."

Dr. Walter P. Bradley has resigned as Professor of Chemistry after twenty-five years of service at Wesleyan University to take charge of the investigations of the United States Rubber Company in whose employ he recently spent a year's leave of absence.

The University of Illinois offered a two weeks' course on "The Technology of the Clay Industries," from Jan. 12th–24th, under the direction of Mr. A. V. Bleininger, of the Bureau of Standards at Pittsburgh, and Mr. R. T. Stull, Acting Director, Ceramics Department, University of Illinois. This course was intended for men actively engaged in the industries and an attempt was made to apply the chemical and physical principles underlying the operations of preparation, shaping, drying, burning and decorating. Additional subjects, such as Construction of Furnaces and Kilns, Power Plants, Power Transmission, Dynamos and Motors, Care of Machinery, etc., were presented. The engineering topics were treated by Acting Dean Richards, of the Mechanical Engineering Department and his associates. For the complete course, 51 men registered and a smaller number attended for a shorter time. All of these men are connected with the ceramic industries in the capacity of managers, superintendents or in charge of plant departments.

Mr. C. H. Teesdale, of the Forest Products Laboratory, Madison, Wisconsin, will address the Chicago Section of the

A. C. S. at the March meeting on his special work on Wood Preservation.

Mr. J. Lanison Wills, F.C.S., of the Stifel Laboratory of Fermentology, addressed the Feb. 9th meeting of the St. Louis Section of the A. C. S. on "American Beer from the Chemical and Biological Viewpoint."

Mr. W. D. Richardson, Chief Chemist of Swift & Co., Chicago, addressed the Detroit Chemists on Jan. 30th, his subject being "The History and Present Status of Food Preservation."

Walter Wallace Weir has been placed in charge of coöperative drainage experiments being carried on at Kearney Park, near Fresno, on the 5,400-acre ranch belonging to the University of California. The University and the Office of Experiment Stations of the U. S. Dept. of Agric. are making these investigations in the reclamation of alkali lands by drainage ditches and a pumping system.

The Nashville Section of the A. C. S. was addressed on Feb. 20, 1914, by Mr. E. J. Pranke, who spoke on "Some Problems of the Cyanamid Industry and their Industrial Solution."

Mr. Paul Poetschke has resigned from the position of Assistant Director of the Department of Chemistry of the Lederle Laboratories, New York, after ten years of continuous service with that company; he was presented with a beautifully inscribed loving cup by the officers, employees and friends associated with the Lederle Laboratories and Lederle & Provost. Mr. Poetschke's present position is that of Director of the Department of Chemistry of the L. D. Caulk Co., Milford, Del., manufacturers of dental materials: his new work will be in connection with various lines of research leading to scientific development and application of the materials used in dentistry, as well as improvements in processes of manufacture and the standardization of materials.

Mr. Frank A. Lidbury, Works Manager of the Olbury Electro-Chemical Co., of Niagara Falls, gave an experimentally illustrated address before the Rochester Section of the A. C. S., Feb. 2, 1914, on "Some Aspects of the Electro-Chemical Industry."

Mr. Lewis J. Seidensticker, formerly with the Warner Sugar Refining Co., Edgewater, N. J., has accepted the position of Manager of the Atlantic Sugar Refineries, Ltd., St. John, N. B., Canada.

Prof. A. H. Blanchard, in charge of the graduate course in highway engineering at Columbia University, delivered illustrated lectures on Jan. 26th at the University of Illinois, his subjects being: "Bituminous Surfaces and Bituminous Pavements," and "Modern Developments in Highway Engineering in Europe."

The Food and Drug Inspection work of the Bureau of Chemistry has been reorganized, the country being divided into three districts, each under a District Chief, who will be in charge of the branch laboratories and the work of the inspectors in his territory. It is expected that the Pittsburgh, Kansas City, Nashville, Portland and Omaha Laboratories will be closed by April 1st. The Eastern District, in charge of Mr. W. G. Campbell (now Chief Inspector) with headquarters at the Bureau in Washington, includes the laboratories at New York, Boston, Philadelphia, Buffalo, Pittsburgh, Savannah and San Juan. The Central District under Mr. L. M. Tolman (now Chief of the Washington, D. C., Food Inspection Division) takes in the laboratories at Chicago, St. Paul, St. Louis, Cincinnati, New Orleans, Nashville, Kansas City and Omaha. The Western District, in charge of Mr. B. R. Hart (formerly of the Cincinnati Laboratory) with headquarters at San Francisco, includes the territory west of the Rocky Mountains and the branch laboratories at San Francisco, Denver, Portland, Seattle and Honolulu.

Dr. Robert Kennedy Duncan, Director of the Mellon Institute of Industrial Research of the University of Pittsburgh, died at his home in Pittsburgh on February 18, 1914, after an illness of several weeks.

BOOK REVIEWS

Treatise on General and Industrial Organic Chemistry. By Dr. Ettore Molinari. Translated from the second, enlarged and revised Italian edition by Thomas H. Pope. Philadelphia: P. Blakiston's Son & Co., 1913. Pp. xix + 770. 506 illustrations. $6.00 net.

There are plenty of excellent modern textbooks on general organic chemistry already on the market and new ones are constantly appearing. There are also many admirable standard works on industrial organic chemistry and this number also is being steadily increased. It would therefore seem a rather difficult matter to find any places in the field not already fully occupied, or any need not already satisfactorily met. Yet, in the opinion of the reviewer, Dr. Molinari has found one of these few remaining uncrowded parts of the field and his book therefore meets a need not heretofore properly provided for. Mr. Pope has done a service to all English-speaking chemists in translating it into our own tongue. The recording of weights in quintals throughout the book will look more familiar to the Englishman than to the American.

In textbooks on general organic chemistry there is usually only an occasional brief reference to the industrial importance of the compound or reaction discussed, practically all of the space being given up to a consideration of the theoretical side of the subject. Similarly, the textbooks on industrial organic chemistry as a rule give but scant attention to the theoretical questions involved or attempt to arrange their material with regard to its proper place in a scientific classification of the whole field, the arrangement being almost without exception from the standpoint of the industrialist and not from that of the teacher. There is thus a gap between the two, and it is just this gap which Dr. Molinari has endeavored to bridge.

His book is essentially a textbook of general organic chemistry, in which all groups of organic compounds are classified as usual according to their structural formulas, and with which has been incorporated and properly distributed under this classification a textbook of industrial organic chemistry. In other words, the problem was to take a book like Sadtler's "Industrial Organic Chemistry" and add this material, in the proper places, to that already given in such a book as Bernthsen's "Organic Chemistry." The result of such a fusion is, as just pointed out, a textbook of general organic chemistry with special emphasis on and detailed treatment of its industrial side. Such an arrangement is of advantage both to the student of general chemistry and to the industrialist. To the former, it points out at once which are the compounds and reactions of commercial importance, what their significance is to the community, and what are the actual manufacturing processes by which they are produced. On the other hand, it teaches the industrialist the place of his own special line of manufacturing in the whole wide field of organic chemistry, what other compounds and reactions are most closely related to those which occupy his chief attention, and gives him a clearer insight into the importance of the underlying theoretical principles.

It will be admitted at the outset that it is not an easy problem to condense two such textbooks into one volume of convenient size. It was necessary, naturally, to sacrifice something of each, to keep down the size of the volume, but on the whole the work has been well done, and its author is to be congratulated. Where the trimming can be done with least injury in such a consolidation is a matter of opinion and will, of course, be decided by the viewpoint of the author. On the industrial side, it may be determined solely on the basis of the commercial importance of the subject or, on the other hand, the determining factor may be the extent to which chemistry enters into the processes involved. Personally, in a book of this kind, the reviewer, being a teacher, would like to see the latter the chief factor in deciding the question; more space being given to such matters as synthetic drugs and synthetic perfumes and less to sugar, textiles and the like, where the engineering features are so much more in evidence than the chemical. Where various methods are given for the manufacture of the same products, an indication of the relative commercial importance of each should be given, so that the reader may be able to pick out at a glance the leading present-day practice.

It is scarcely to be expected that a book of this size and scope should be wholly free from minor defects, and the rigorous critic who goes over it with a fine-tooth comb will discover here and there statements which are inaccurate or misleading. These occasional lapses presumably will be corrected in subsequent editions.

An immense amount of labor has been expended in gathering and properly distributing the mass of material contained in the volume. Much statistical information is included and constitutes a very valuable feature. References and special bibliographies are, however, generally lacking; and it is to be hoped that the author can include them in future editions. In fact, the reviewer would be glad to see the scope of the work enlarged, even though it involved the publication of two volumes instead of one.

The book is a welcome addition to the literature of the subject, and is just what is wanted in courses in organic chemistry for engineering students, especially for those intending to become chemical engineers.

Part I. General. This part comprises the usual introduction to textbooks of organic chemistry and deals with such topics as the purification and analysis of organic compounds, determination of empiric, molecular, constitutional and stereochemical formulas, valency, isomerism, polymerism, homology and isology, the bearing of chemical composition and constitution upon physical properties, classification of carbon compounds, official nomenclature and the like. It would seem desirable to add here also some facts of special interest to the future chemical engineer concerning chemical manufacturing processes in general, the most important factors governing industrial operations, standard forms of apparatus, the difference between test tube reactions and those of the plant, and the like; material similar in character to that contained in the recent address of O. N. Witt, before the general meeting in Prague of the Austrian Union for the Advancement of Chemical Industry, on the methods of work of the chemical laboratory and of chemical industry and their inter-relations.

Part II. Derivatives of Methane. A discussion of the more important groups of straight-chain carbon compounds. The classification employed in this part does not appeal to the reviewer as logical or as the best adapted to the purposes of the author. It seems unfortunate, for example, to discuss acetic acid and its salts in one part of the book (p. 270), acetic anhydride in another part (p. 320), and the esters of acetic in still a third place (p. 371); and not to consider the industries of the oils, fats, waxes, candles and soaps, in closer connection with the corresponding fatty acids. In addition to the industries just mentioned, this part contains a discussion also of the following: gas, petroleum, alcohol and alcoholic beverages, explosives, tartaric acid, citric acid, sugar, starch and paper, as well as many others (wood distillation, vinegar, glycerol, glucose, etc.) treated more briefly.

Part III. Cyclic Compounds. A discussion of the more important groups of cyclic carbon compounds. This includes descriptions of the following industries: coal tar, tanning, coloring matters, textile fibres; also briefer articles on synthetic perfumes, synthetic drugs, synthetic rubber, etc., several of which merit fuller treatment.

M. T. Bogert

Preservative Coatings for Structural Materials. Reports of Committee D-1 of the American Society for Testing Materials, 1903-1913. Edited by the Secretary and published by the Society. Philadelphia. 431 pages. Quarto. Cloth. Price, $2.00.

The study of protective coatings for iron and steel, begun by the American Society for Testing Materials in 1903 and continued unbrokenly and with increasing effectiveness to the present time, is described in detail in these reports, now published in combined form in a single volume.

During the first few years the Committee planned its investigations and formulated its standards but as soon as definite lines became clear, the work was taken up and pushed as vigorously as possible, consistent with the exercise of conservative judgment.

The first constructive work the Committee undertook was in the application of nineteen different paints on the Havre de Grace Bridge in 1906. Since then a great deal has been accomplished in the study of white paints, the influence of pigments upon corrosion, linseed oil, soya bean oil, China wood oil, turpentine, definitions of terms used in paint specifications, etc. There is probably no book which contains within its covers so much original work on the subject of paints.

The Committee, made up, half of representatives of producing interests, and half of representatives of consuming interests, constitutes a body of investigators, unhampered as to any line of investigation, but conservative as to the conclusions it draws.

The volume is arranged chronologically, and the contents give full information as to where the reports of the various subcommittees appear. These reports contain numerous tables giving analyses and classifications of paint materials unobtainable elsewhere. The volume is well printed and paged both with respect to the annual reports and serially for this volume only. All persons interested in paint technology will find much valuable material in this book.

Die Gerbstoffe-Botanische-chemische Monographie der Tannide. By J. Dekker. Borntraeger, Berlin. Translated to the German from the Dutch, by Otto Klipp. 586 pp. Price, $5.25.

The first synthetic tanning agent was prepared in 1912 and the next few years will undoubtedly see tremendous progress in this field, not only in our at present limited chemical knowledge, but also in the better control and understanding of their technical application.

The author has carried out the work so well that a brief description of the arrangement of the subject matter is all that is required.

The book is divided into two parts: Part I treating the Bibliography and Botany, and Part II dealing with the Chemistry of the Tannins.

Part I is divided into three chapters: Chapter I, Bibliography, Journals and Books, 1754–1913; Chapter II, Distribution of the Tannins in the Various Plants; Chapter III, (1) Analytical Methods of Identification; (2) Distribution of the Tanning Agents in the Plant; (3) Significance of the Tanning Agents to the Life of the Plant.

Part II, dealing with the strictly chemical side of the tanning agent, is divided into four chapters: Chapter I, Tannin and Tannin-Like Substances; Chapter II, Chemistry of the Tanning Agent; Chapter III, Analytical Methods; Chapter IV, Technical Applications of the Tanning Agents.

The author has produced a splendid book which brings together the available botanical and chemical knowledge of the tannins, which will be appreciated by all interested in either the scientific or technical application of the training agents.

Otto Kress

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian The Chemists' Club, New York

Analysis, Gas, Exercises in. By Hartwig Franzen. 12mo. 120 pp. Price, $1.00. Blackie & Son, London. (Translation in English.)

Asphalts, Natural and Artificial, Chemistry and Technology of the. By H. Koehler and E. Graefe. 2nd Ed. 8vo. Price, $4.75. Friedrich Vieweg & Sohn, Brunswick. (German.)

Atoms, The. By Jean Perrin. 8vo. 190 pp. Price, $1.50. Theodor Steinkopff, Dresden. (Translation in German.)

Constitution, Chemical, and Physical Properties. By S. Smiles. 8vo. 688 pp. Price, $5.25. Theodor Steinkopff, Dresden. (Translation in German.)

Cyanogen Compounds, The Industry of the. By H. Koehler. 8vo. Price, $1.75. Friedrich Vieweg & Sohn, Brunswick. (German.)

Electric Furnace, The. By Alfred A. Stansfield. 2nd Ed. 8vo. 415 pp. Price, $4.00. McGraw-Hill Book Co., New York.

Explosives, Permissible, Tests of. By Clarence Hall and Spencer P. Howell. 8vo. 313 pp. U. S. Bureau of Mines, Bulletin 66.

Inorganic Chemistry, Newer Views in the Domain of. By A. Werner. 3rd ed. 8vo. 419 pp. Price, $3.00. Friedrich Vieweg & Sohn, Brunswick. (German.)

Iron and Steel Production, Electrothermal, Methods of. By J. B. C. Kershaw. 8vo. 264 pp. Price, $2.25. Constable & Co., London.

Mechanics, Technical. By Edward R. Maurer. 3rd Ed. 8vo. 343 pp. Price, $2.50. John Wiley & Sons, New York.

Metals, Precious, The Sampling and Assay of the. By E. A. Smith. 8vo. 476 pp. Price, $4.00. Chas. Griffin & Co., London.

Metallurgy, General. By H. O. Hofman. 8vo. 909 pp. Price, $6.00. McGraw-Hill Book Co., New York.

Nickel and Cobalt, Methods of Determination of, and Separation from Other Elements. By H. Grossmann. 8vo. Price, $1.25. Ferdinand Enke, Stuttgart. (German.)

Paint Making and Color Grinding. By Charles L. Uebele. 8vo. 483 pp. Price, $10.00. Painters Magazine, New York.

Petroleum: Oil Production Methods. By Paul M. Paine and B. K. Stroud. 8vo. 240 pp. Price, $3.00. Western Engineering Publishing Co., San Francisco.

Poisoning, Industrial, from Fumes, Gases, and Poisons of Manufacturing Processes. By J. Rambousek. 8vo. 360 pp. Price, $3.50. Longmans, Green & Co., New York. (Translation in English.)

Potash Industry, Trade Effluents from the, their Removal and their Effect in and on Water Mains. By J. H. Vogel. 8vo. Price, $7.00. Gebrueder Borntraeger, Berlin. (German.)

Pyrotechnics. By Vannoccio Biringuccio, A. Mieli and E. Troilo. 8vo. 198 pp. Società Tipografica, Bari (Italy). (Italian.)

Radium Report. By Mr. Foster. 63rd Congress. 2nd Session, House of Representatives, Report No. 217. 18 pp.

Rubber, The Chemistry of. By B. D. Porritt. Cr. 8vo. 96 pp. Price, $0.50. Gurney & Jackson, London.

Rubber, Plantation, The Preparation of. By Sidney Morgan. Roy. 8vo. 269 pp. Price, $2.75. Rubber Growers' Association, London.

Rubber and Rubber Planting. By R. H. Lock. Cr. 8vo. 245 pp. Price, $1.50. Cambridge University Press, Cambridge.

Tannins, The. By J. Dekker. 8vo. 586 pp. Price, $5.00. Gebrueder Borntraeger, Berlin. (German.)

Technical Processes and Manufacturing Methods, The Application of Physico-Chemical Theory to. By R. Kremann. 8vo. 212 pp. Price, $3.00. D. Van Nostrand Co., New York. (Translation in English.)

Thermodynamics, A Textbook of. By James Riddick Partington. 8vo. 544 pp. Price, $4.00. D. Van Nostrand Co., New York.

Water Purification, Modern Methods of. By J. Don and J. Chisholm. 2nd Ed. 8vo. 416 pp. Price, $4.00. Ed. Arnold, London.

Yearbook of Chemistry for 1912. By Richard Meyer. 22nd Ed. 8vo. 577 pp. Price, $5.00. Friedrich Vieweg & Sohn, Brunswick. (German.)

RECENT JOURNAL ARTICLES

Ammonia, Inorganic, Syntheses of. By O. Serpek. *Zeitschrift fuer angewandte Chemie*, Vol. 27/I, 1914, No. 8, pp. 41–48.

Benzol of Commerce, Determination of the Total Sulfur in. By Konrad Schenk. *Chemiker Zeitung*, Vol. 38, 1914, No. 8, pp. 83–84.

Bromin, An Apparatus for the Manufacture of. By Konrad Kubierschky. *Chemische Apparatur*, Vol. 1, 1914, No. 1, pp. 2–5.

Carbohydrates, The Picrate Colorimetric Method for the Estimation of. By William M. Dehn and Frank A. Hartman. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 2, pp. 403–409.

Chemical Industry, Modern (Hurter Memorial Lecture). By Fritz Haber. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 2, pp. 49–54.

Coal, Bituminous, Natural Gasification of. By Ernst Schmatolla. *Chemiker Zeitung*, Vol. 38, 1914, No. 6, pp. 61–63.

Drying Apparatus. By F. A. Buehler. *Chemische Apparatur*, Vol. 1, 1914, No. 1, pp. 5–8.

Dyeing, The Theory of. By Wilder D. Bancroft. *Journal of Physical Chemistry*, Vol. 18, 1914, No. 1, pp. 1–25.

Dyestuffs, Notes on the Physical Synthesis and Analysis. By Eugen Grandmougin. *Chemiker Zeitung*, Vol. 38, 1914, No. 4, pp. 41–42.

Emulsions, Experiments on. By F. R. Newman. *Journal of Physical Chemistry*, Vol. 18, 1914, No. 1, pp. 34–54.

Glass Standards: A Necessity. By Alexander Silverman. *Trans. of the American Ceramic Society*, Vol. 15, 1913, pp. 684–693.

Iron-Bearing Materials, Sintering Processes for. By B. G. Klugh. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 9, pp. 618–651.

Iron Ore Analysis, Report of the Committee of the Verein Deutscher Chemiker on. By E. Hintz. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 27, 1914, No. 4, pp. 9–11.

Iron Smelting, Electric, at Hardanger in Norway. By Joh. Härdén. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 2, pp. 82–86.

Kaolin, The Interesting History of, and its Uses. By Thomas J. Keenan. *American Druggist*, Vol. 62, 1914, No. 2, pp. 31–33.

Kieselguhr Industry. By Percy A. Boeck. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 2, pp. 109–113.

Nitric Acid and Ammonia, Industrial Synthesis of. By Camille Matignon. *Chemical Trade Journal*, Vol. 54, 1914, No. 1391, pp. 68–71.

Nitrogen, Utilization of Atmospheric. By G. Cecil Jones. *Chemical Trade Journal*, Vol. 54, 1914, No. 1391, pp. 60–62.

Ores, Dry Chloridization of. By John L. Malm. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 2, pp. 128–129.

Paper: Chemical Utilization of Southern Waste. By John S. Bates. *Pulp and Paper Magazine*, Vol. 12, 1914, No. 2, pp. 33–40.

Paraffin Industry, The Use of Refrigerating Machinery in the, in Austria. By Philipp Porges. *Seifenfabrikant*, Vol. 34, 1914, No. 2, pp. 31–34.

Patents, Compulsory Working of. By Ivan Levinstein. *Chemical Trade Journal*, Vol. 54, 1914, No. 1391, pp. 57–59.

Petroleum: Oil Cracking. By F. M. Perkin. *Chemical Trade Journal*, Vol. 54, 1914, No. 1391, pp. 63–64.

Potash, Caustic, Determination of the Free, in Soap. By E. Bosshard and W. Huggenberg. *Zeitschrift fuer angewandte Chemie*, Vol. 27, 1914, No. 4, pp. 11–20.

Potassium Chlorid Manufacture by the Continuous Method. By E. Krueger. *Chemiker Zeitung*, Vol. 38, 1914, No. 6, pp. 60–61.

Producer Gas. Anonymous. *Chemical Engineering and the Works Chemist*, Vol. 3, 1913, No. 32, pp. 361–364.

Sewage Sludge, The Utilization of the Phenomena of Putrefaction with Special Reference to the Treatment and Disposal of. By F. R. O'Schaughnessy. *Journal of the Society of Chemical Industry*, Vol. 33, 1914, No. 1, pp. 3–9.

Slag Composition, Graphic Solution of. By Donald M. Liddell. *Engineering and Mining Journal*, Vol. 97, 1914, No. 6, pp. 318–319.

Sugar Analysis: Double Polarization of Cane-Sugar Products. By H. C. Prinsen-Geerligs. *Louisiana Planter and Sugar Manufacturer*, Vol. 52, 1914, No. 4, pp. 55–56.

Sulfite Waste Lyes, Utilization of the Wood Substances in, as Fuel and Reclaiming of the Sulfurous Acid and Lime Used. By R. W. Strehlenert. *Pulp and Paper Magazine of Canada*, Vol. 12, 1914, No. 2, pp. 46–47.

Sulfuric Acid, Modern, Manufacture of. By Withoff. *Revue de Chimie Industrielle*, Vol. 25, 1914, No. 289, pp. 5–11.

Sulfuric Acid, Norwegian and Spanish Pyrite as Raw Material for the Manufacture of. By P. W. Uhlmann. *Chemiker Zeitung*, Vol. 38, 1914, No. 6, pp. 59–60.

Textile Mill Chemist and His Laboratory. By Louis J. Matos. *Cotton*, Vol. 78, 1914, No. 3, pp. 97–100.

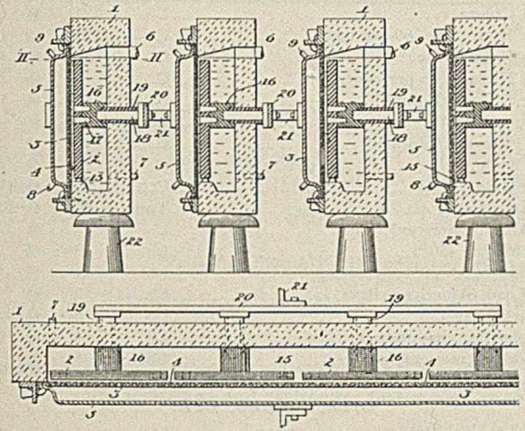
Textiles: Practical Testing of Fibres, Yarns and Cloths. By Ernest W. Tetley. *Textile Manufacturer*, Vol. 40, 1914, No. 469, pp. 9–11.

Water in Bottles, Slime Formation during the Storage of. Exact Determination of Silica, Iron and Aluminum in Natural Mineral Waters. By L. Dede. *Chemiker Zeitung*, Vol. 38, 1914, No. 5, pp. 53–55.

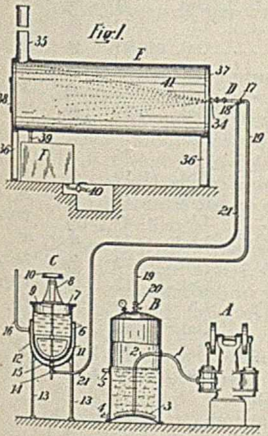
RECENT INVENTIONS

By C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Electrolytic Cell. C. W. Marsh, Oct. 14, 1913. U. S. Pat. 1,075,362. The cell is of the diaphragm type intended for the decomposition of sodium and potassium chlorids. The anode compartment is open at one side only. A substantially vertical pervious cathode and diaphragm is disposed across the opening and an anode connection extends horizontally through the wall of the cell opposite the electrode.

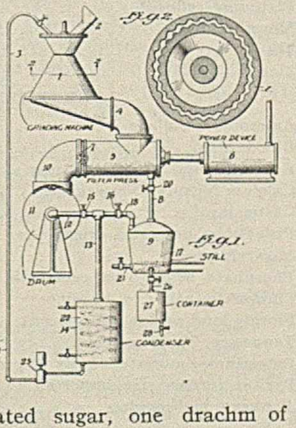


Restoring Coagulated Albumins to the Original State. A. H. Rasche, Oct. 21, 1913. U. S. Pat. 1,076,232. The liquid or emulsion containing the coagulated albumins is first heated, agitated and supersaturated with a compressed chemically indifferent gas. The treated material is then atomized by means of the chemically indifferent gas into an open vessel.



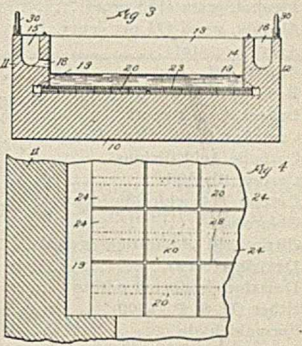
Art of Forming Chemical Compounds. T. A. Edison, Jan. 6, 1914. U. S. Pat. 1,083,355. Nickel hydroxid for use in storage batteries is produced by mixing intimately a dry pulverized salt of nickel containing water of crystallization and an excess of dry soluble hydroxid. The resulting mixture is dried, crushed, washed, and the residue, nickel hydroxid, dried.

Extracting Oils and Fats from Oil-Seeds, Etc. R. N. Riddle, Oct. 28, 1913. U. S. Pat. 1,076,997. The oil-containing materials are subjected to alternate crushing pressure and release of pressure while subjecting them to the action of the solvent. The alternate pressure and release of pressure are obtained by the action of the corrugated surfaces of the grinding mill 1.



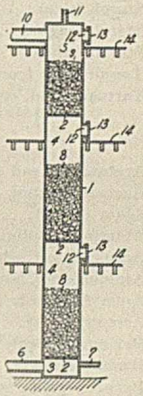
Gunpowder and Process of making the same. C. D. McDowell, Jan. 6, 1914. U. S. Pat. 1,083,371. The composition comprises eight ounces of potassium chlorate, seven ounces of granulated sugar, one drachm of glycerin and two drachms of water.

Chemical Filter. C. S. Bradley, Oct. 28, 1913. U. S. Pat. 1,077,037. Upon the foundation 10 are laid filter bricks forming a continuous flat outer surface. Within the bricks are formed passages 20 communicating from one brick to another, whereby pressure and suction are sustained upwardly and downwardly, thereby avoiding displacing tendencies.



Obtaining Aluminum. P. C. McIlhiney, Jan. 6, 1914. U. S. Pat. 1,083,691. Aluminum bearing silicious material is treated with hydrofluoric acid to produce aluminum fluorid. The aluminum fluorid is then electrolyzed to obtain metallic aluminum and hydrofluoric acid.

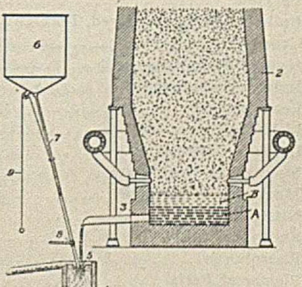
Recovering Escaping Acid-Gases from Sulfite-Towers. J. A. DeCew, Oct. 28, 1913. U. S. Pat. 1,077,243. The escaping gases are passed successively through chambers 4, containing moistened limestone and chamber 5 containing moistened magnesite in lump form. It is stated that the use of magnesite saves the 10% to 20% of the sulfur dioxid heretofore lost.



Manufacturing Phosphoric Acid. F. Brunschwig, Jan. 6, 1914. U. S. Pat. 1,083,429. Material containing calcium phosphate is treated with less sulfuric acid than is required to combine with the calcium of the phosphate and the reaction is stopped before the impurities go into solution.

Making Sugar from Cane. F. G. P. Leao, Jan. 6, 1914. U. S. Pat. 1,083,545. The sugar cane is finely divided and dried at a temperature below 158° F. The dried cane is then saturated with water to dissolve the saccharine matter and the solution separated from the cane by pressure. The resulting syrup is then evaporated and refined.

Utilizing Iron Blast Furnace Flue-Dust. R. Baggaley, Dec. 16, 1913. U. S. Pat. 1,081,921. The flue dust and fines are introduced into molten metal and the mixture subjected to a refining process. It is recommended that the dust and fines be introduced into the vortex 5 produced by the fall of the metal into the vessel 4 to insure the dust and fines being immediately enveloped by the molten metal.



Production of Fertilizers. A. Messerschmitt, Jan. 6, 1914. U. S. Pat. 1,083,553. Alkali metals containing silicates are decomposed with lime and the alkali metal compounds partially separated from the mixture by lixiviation. The residue is then treated with nitric oxid gas. Caustic lime is then added and the mixture lixiviated and evaporated to dryness.

Effecting Catalytic Reactions. Hagemann and Baskerville, Jan. 13, 1914. U. S. Pat. 1,083,930. Catalytic reactions are effected by the employment of catalytic metal in the form of very thin leaves.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF FEBRUARY, 1914

ORGANIC CHEMICALS

Acetanilid	Lb.	21	@	23
Acetic Acid (28 per cent)	C.	1.62½	@	1.77½
Acetone (drums)	Lb.	12	@	13
Alcohol, denatured (180 proof)	Gal.	35	@	37
Alcohol, grain (188 proof)	Gal.	2.52	@	2.54
Alcohol, wood (95 per cent)	Gal.	45	@	47
Amyl Acetate	Gal.	1.60	@	1.70
Aniline Oil	Lb.	10	@	10⅛
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	23	to	25
Camphor (refined in bulk)	Lb.	42½	@	45
Carbolic Acid (drums)	Lb.	8	@	10
Carbon Bisulfide	Lb.	6½	@	8
Carbon Tetrachloride (drums)	Lb.	7⅜	@	7⅞
Chloroform	Lb.	22	@	32
Citric Acid (domestic), crystals	Lb.	51	@	52
Dextrine (corn)	C.	2.62	@	2.83
Dextrine (imported potato)	Lb.	5	to	6
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	20	@	21½
Oxalic Acid	Lb.	7½	@	7¾
Pyrogallic Acid (bulk)	Lb.	1.20	@	1.40
Salicylic Acid	Lb.	25	@	30
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	1.94	@	2.60
Starch (potato)	Lb.	4⅛	—	4¾
Starch (rice)	Lb.	8	@	9
Starch (sago)	Lb.	2⅜	@	2¾
Starch (wheat)	Lb.	5¼	@	6½
Tannic Acid (commercial)	Lb.	35	—	36
Tartaric Acid, crystals	Lb.	31½	@	31¾

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¼	—	7¾
Acetate of Lime (gray)	C.	1.75	@	1.80
Alum (lump)	C.	1.75	@	2.00
Aluminum Sulfate (high-grade)	C.	1.25	@	1.75
Ammonium Carbonate, domestic	Lb.	8	@	8½
Ammonium Chloride, gray	Lb.	5⅞	@	6⅛
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3⅛	@	3⅜
Barium Chloride	C.	1.60	@	1.75
Barium Nitrate	Lb.	5	to	5¼
Barytes (prime white, foreign)	Ton	19.00	@	23.50
Bleaching Powder (35 per cent)	C.	1.20	@	1.30
Blue Vitriol	Lb.	4.80	@	5⅛
Borax, crystals (bags)	Lb.	3¾	@	4½
Boric Acid, crystals (powd.)	Lb.	7	@	7¾
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	60	@	90
Chalk (light precipitated)	Lb.	4	@	4½
China Clay (imported)	Ton	nominal		
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign	Ton	16.00	@	17.00
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.55	@	3.60
Lead Nitrate	Lb.	8⅛	@	8¼
Litharge (American)	Lb.	5½	@	5¾
Lithium Carbonate	Lb.	65	@	70
Magnesium Carbonate	Lb.	21	@	35
Magnesite "Calcined"	Ton	28.50	@	29.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	21½	@	25½
Phosphorus	Lb.	45	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°	Lb.	6¾	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%	C.	3.20	@	3.25
Potassium Chlorate, crystals	Lb.	7½	@	7¾
Potassium Cyanide (bulk), 98–99%	Lb.	16	@	18
Potassium Hydroxide	C.	4.00	@	4.25
Potassium Iodide (bulk)	Lb.	2.95	@	3.00
Potassium Nitrate (crude)	Lb.	4¾	@	5¼
Potassium Permanganate (bulk)	Lb.	9¾	@	10
Quicksilver, Flask (75 lbs.)		38.00	@	—
Red Lead (American)	Lb.	6	@	6¼
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	36½	@	38½
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	67½	@	72½
Sodium Acetate	Lb.	3¾	@	4⅛
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	4⅝	@	4⅞
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	7¼	@	7½
Sodium Hydroxide, 60 per cent	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	—	@	2.22½
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6¾	@	7
Sulfur, Flowers (sublimed)	C.	2.20	@	2.60
Sulfur, Roll	C.	1.85	@	2.15
Sulfuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	12½	@	13½
Tin Oxide	Lb.	41	@	43
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	Lb.	2½	@	3

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	45	@	47
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8¼	@	8½
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6.45	@	6.50
Cottonseed Oil (crude), f. o. b. mill	Gal.	44	@	44½
Cottonseed Oil (p. s. y.)	Lb.	7	@	7½
Cylinder Oil (light, filtered)	Gal.	21½	@	32
Japan Wax	Lb.	12	@	12½
Lard Oil (prime winter)	Gal.	93	@	95
Linseed Oil (raw)	Gal.	50	@	52
Menhaden Oil (crude)	Gal.	32½	@	36½
Neatsfoot Oil (20°)	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.)	Lb.	3½	@	3¾
Paraffine Oil (high viscosity)	Gal.	26	@	27
Rosin ("F" grade) (280 lbs.)	Bbl.	4.50	@	4.55
Rosin Oil (first run)	Gal.	27	@	28
Shellac, T. N.	Lb.	19	@	19½
Spermaceti (cake)	Lb.	30	@	35
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Spindle Oil, No. 200	Gal.	17	@	17½
Stearic Acid (double-pressed)	Lb.	9	@	12
Tallow (acidless)	Gal.	65	@	66
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	47½	@	48

METALS

Aluminum (No. 1 ingots)	Lb.	18½	@	19
Antimony (Hallet's)	Lb.	7⅛	@	7¼
Bismuth (New York)	Lb.	2.05	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	Lb.	14½	@	14¾
Copper (lake)	Lb.	14¾	@	14⅞
Lead, N. Y.	Lb.	4	@	—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43.50	@	44.50
Silver	Oz.	57½	@	58
Tin	C.	39.87½	@	—
Zinc	C.	5.35	@	5.40

FERTILIZER MATERIALS

Ammonium Sulfate	C.	2.85	@	2.90
Blood, dried	Unit	3.45	@	—
Bone, 4½ and 50, ground, raw	Ton	29.00	@	30.00
Calcium Nitrate (Norwegian)	C.	2.05	@	2.10
Castor meal	Unit	nominal		
Fish Scrap, domestic, dried	Unit	nominal		
Mowrah meal	Ton	nominal		
Phosphate, acid, 16 per cent bulk	Ton	7.00	@	—
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.75	@	3.00
Tennessee, 70–80 per cent	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	39.07	@	—
Pyrites, furnace size, imported	Unit	0.13¼		
Tankage, high-grade	Unit	3.40	&	10