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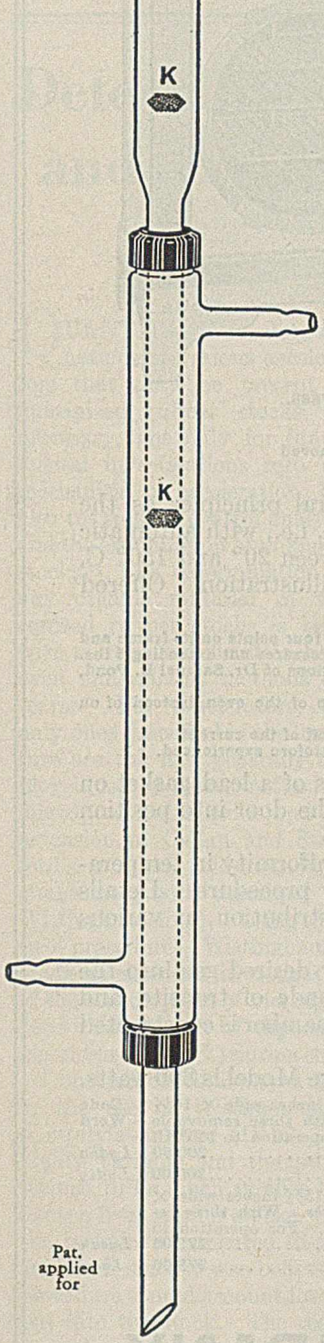

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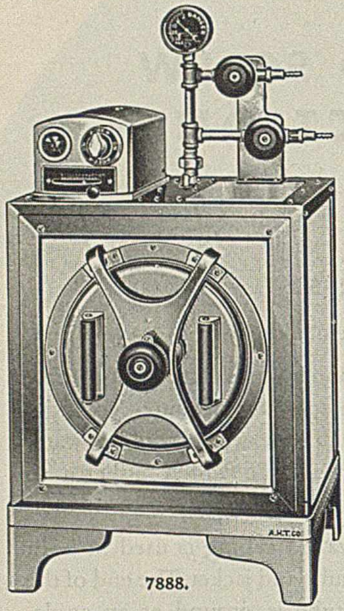
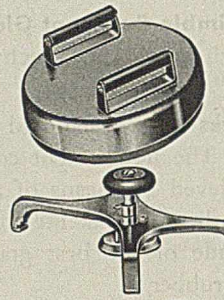
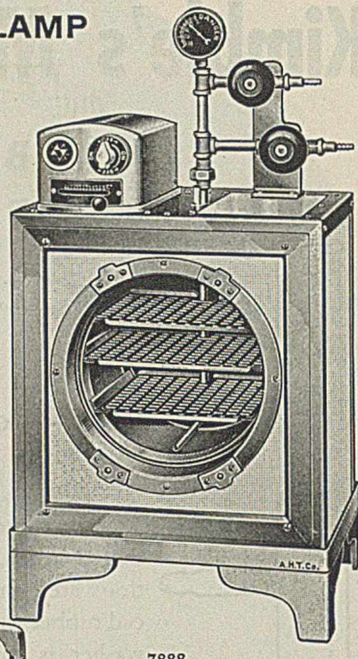


7888.

With door in position





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Harrison E. Howe, Editor

Determination of Guanidines in Rubber Stocks and Consumption of Guanidines during Cure

BINGHAM J. HUMPHREY

The Firestone Tire & Rubber Company, Akron, Ohio

When a guanidine accelerator is milled into acetone-extracted rubber, the guanidine cannot be completely recovered from the rubber by acetone extraction. If the mixture of rubber and guanidine is treated with a hydrolyzing agent, the bound guanidine is freed and 100 per cent recovery can be made. Bound guanidine is also present in cured stocks, for when these stocks are treated with benzene and dilute aqueous hydrochloric acid, or with wet acetone, higher guanidine recoveries are obtained than by extraction with dry acetone.

Based on the above findings, a new hydrolytic procedure for determining guanidines in cured stocks has been developed. Data on several stocks analyzed by this method and by the Wistinghausen (acetone extraction) method, and the resulting consumption–curing time curves are presented for comparison.

QUANTITATIVE determinations of various accelerators that may be present in vulcanized rubber stocks are necessary, not only for fundamental investigations into the mechanism of acceleration, but also for routine control analyses and the examination of unknown stocks. The determination of any organic material in vulcanized rubber stocks is beset with numerous difficulties, however, and reliable methods are scarce. For accelerators, the only ones described in the literature are the now generally employed copper oleate method for mercaptobenzothiazole and an extension of Callan and Strafford's (*1*) picric acid method for guanidines, both described by Wistinghausen (*2*). Using these two procedures, Wistinghausen made an extended investigation of the consumption of mercaptobenzothiazole and of diphenylguanidine (D. P. G.) during cure.

Considerable difficulty was encountered in this laboratory in the use of Wistinghausen's method. Especially with di-*o*-tolylguanidine (D. O. T. G.) stocks, the results were highly variable and the proportion of guanidine recovered seemed to be much smaller than that recovered by Wistinghausen from similar stocks. As a test of both the method and the technic, an uncured di-*o*-tolylguanidine tread stock was analyzed, since it was believed that, in this case, an effective procedure should account for substantially all of the guanidine put into the stock. The result was that little or no more guanidine was recovered from the uncured stock than from the same stock at an optimum cure. Guanidine recoveries from either one ranged from 30 to 50 per cent.

To find the reason why the guanidine could not be completely extracted from the uncured mixture, the procedure was applied to a series of stocks in which the ingredients of the original tread stock were omitted, one by one. Finally, it was found that when a simple mixture of acetone-extracted rubber and di-*o*-tolylguanidine was extracted with acetone, a part of the di-*o*-tolylguanidine, amounting to 0.2 to 0.4 per cent of the guanidine on the rubber, was unextractable. Apparently the di-*o*-tolylguanidine was bound by, or formed a compound with, the rubber and/or the nonextractable protein of crude rubber. It was already known, however, that if a mixture of rubber and guanidine is swollen in a rubber solvent and shaken with dilute acid, all the guanidine is transferred to the aqueous phase wherein it can be determined as the picrate or by backtitration with alkali. Accelerator master batches have been analyzed by such a procedure for some time.

Thus, it seemed probable that, if all the guanidine could be recovered from an uncured mix by such a method, whereas it could not be completely recovered by acetone extraction, a higher recovery of guanidine might be obtained from cured stocks by treatment with an aqueous acid and a swelling agent than by acetone extraction. This proved to be the case. The cured di-*o*-tolylguanidine tread, from which only 30 to 50 per cent of the guanidine could be recovered by acetone extraction, yielded 75 per cent or more of the original amount of guanidine when a method involving treatment with benzene and dilute acid was used. The increased amount of guanidine was obtained by the latter method because of the hydrolyzing action of the aqueous acid rather than the swelling action of benzene. This was shown by extracting the cured tread with benzene and then shaking the benzene extract solution with dilute acid. The amount of guanidine recovered in this way was essentially equal to that obtained by extraction with dry acetone. Furthermore, extraction with wet acetone removed much more guanidine from the stock than extraction with dry acetone, although a 20-hour extraction with acetone containing 2 per cent of water did not effect as high a recovery of guanidine as could be obtained with benzene and aqueous acid. It was also found that the guanidine recovery was highly variable if, when the Wistinghausen procedure was followed, the acetone extractions were run without particular attention to keeping the acetone absolutely dry.

A brief study of the apparent consumption of guanidine during cure was made, using both Wistinghausen's method and the new method, which yields a higher guanidine recovery from a cured stock and complete recovery from an uncured stock. A comparison of the accelerator consumption curves obtained by the two different methods is presented.

Four different stocks were investigated, A, B, C, and D. Stocks A and B are duplications of two stocks used by Wistinghausen. Stocks C and D are present-day tread compounds, the former containing diphenylguanidine, the latter di-*o*-tolylguanidine.

TABLE I. STOCKS INVESTIGATED

	Stock A *Parts*	Stock B *Parts*
Rubber (crepe)	100	100
Sulfur	3.8	3.8
Thermatomic black	38.3	38.4
D. P. G.	1.44	1.38
Zinc oxide	....	3.8
	143.54	147.38
D. P. G. content, %	1.00	0.94
	Stock C	Stock D
Rubber (smoked sheet)	100	100
Sulfur	2.8	2.8
Zinc oxide	6.6	6.6
Rubber channel black	46.2	46
Stearic acid	3.3	3.3
Pine tar	3.9	3.9
Antioxidant[a]	1.0	1.0
Accelerator	1.04 (D. P. G.)	0.82 (D. O. T. G.)
	164.84	164.42
D. P. G. content, %	0.63	
D. O. T. G. content		0.50

[a] 92.5 per cent phenyl-α-naphthylamine, 7.5 per cent *m*-toluylene diamine.

Each stock was cured 10, 30, 60, and 90 minutes at 307° F. (152° C.). Stock C was also cured 30, 60, 90, and 120 minutes at 290° F. (143° C.). Much of the preliminary work was done on stock D, cured 90 minutes at 290° F. (143° C.). Most of the other cures were beyond the optimum, as far as desirable physical properties are concerned. For the stocks cured at 307° F. (152° C.) the optimum time is probably about 25 minutes, while for those cured at 290° F. (143° C.) the optimum time is about 90 minutes.

In preparation for analysis, the stock, where possible, was finely ground to "springs" on a cold mill. Uncured or undercured stocks that could not be crumbled were sheeted as thinly as possible and cut into small pieces.

The procedure used for the analysis of the stocks by the acetone-extraction method varied slightly but not essentially from that described by Wistinghausen. This slight modification of the Wistinghausen method and the new method involving hydrolysis are described below.

Method of Analysis

WISTINGHAUSEN METHOD. A 20-gram sample of the stock is extracted with acetone for 16 hours in a Soxhlet extraction apparatus. The acetone is completely removed from the extract by evaporation and the residue is dissolved in 20 cc. of ether. Thirty cubic centimeters of approximately 0.1 *N* hydrochloric acid are added to the solution and the mixture is heated on the steam plate for 5 or 10 minutes longer than is required to evaporate the ether. The hot aqueous solution is then poured through a filter. This treatment with ether and hot dilute acid is repeated twice to transfer all the guanidine to the aqueous acid solution which is allowed to stand at least 12 hours and then again filtered cold. The volume is adjusted to approximately 100 cc. and an equal volume of saturated aqueous picric acid solution is added. This mixture is heated on the steam plate for 1 hour. Heating causes the precipitate that first forms to redissolve.

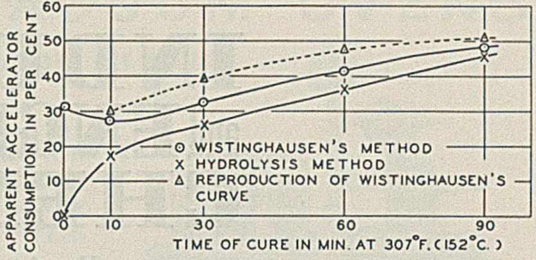

FIGURE 1. ACCELERATOR CONSUMPTION IN A

Wistinghausen's base stock

The heating period was found to be particularly necessary for di-*o*-tolylguanidine determinations, as di-*o*-tolylguanidine picrate forms slowly and incompletely in the cold. On cooling and standing, the diphenylguanidine picrate usually reprecipitates in crystalline form, but the di-*o*-tolylguanidine picrate only infrequently reprecipitates in this way. The precipitate should be allowed to stand for at least 12 hours before filtering. For di-*o*-tolylguanidine, especially, a longer period (48 hours) seems to help the character and quality of the precipitate. The filtration is carried out on a Gooch crucible lined with filter paper, the precipitate being completely transferred to the crucible with the aid of a "policeman" and a small amount of water. The precipitate is finally dried to constant weight in a 100° to 110° C. oven. An addition of 5 mg. is made to the weight of the picrate in the case of the di-*o*-tolylguanidine picrate and 8 mg. in the case of the diphenylguanidine picrate to correct for the slight solubility of these picrates in the 200-cc. mixture of saturated picric acid solution and 0.1 *N* acid. These solubility corrections were obtained from direct determinations of the solubility of the pure picrates in such a mixture at room temperature. For diphenylguanidine, the amount of guanidine is 48 per cent of the corrected weight of the picrate and for di-*o*-tolylguanidine, 51 per cent of the corrected weight of its picrate.

HYDROLYSIS METHOD. A 20.0-gram sample of the finely divided stock, 400 cc. of benzene, and 50 cc. of approximately 0.1 *N* hydrochloric acid are placed in a 1-liter flask so arranged that constant agitation of the mixture and refluxing of the benzene can be carried out together and the aqueous layer can be conveniently removed from the rest of the mixture, preferably without removing the whole mixture from the flask. A convenient apparatus for this purpose is a 1-liter Erlenmeyer flask to which has been sealed, near the base and projecting to the side, a stopcock outlet. By means of an ordinary addition tube placed in the neck with a cork stopper, the flask can be equipped with a stirrer and a reflux condenser. No mercury seal is necessary. The flask is heated, conveniently, by means of an electric hot plate.

Refluxing and brisk stirring of the mixture are continued for 1 hour. The condenser and stirrer are then removed, the flask is set on its side in a tripod, and the aqueous layer drawn off.

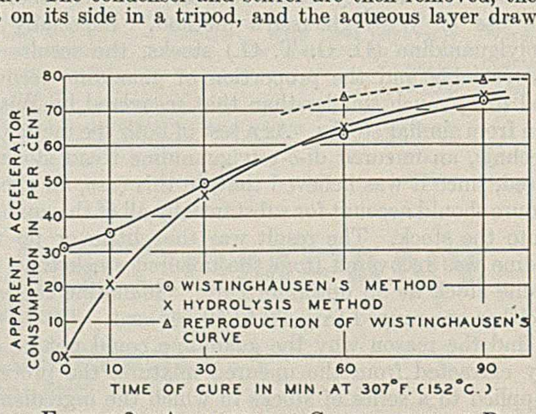

FIGURE 2. ACCELERATOR CONSUMPTION IN B

Wistinghausen's 3.8 per cent zinc oxide stock

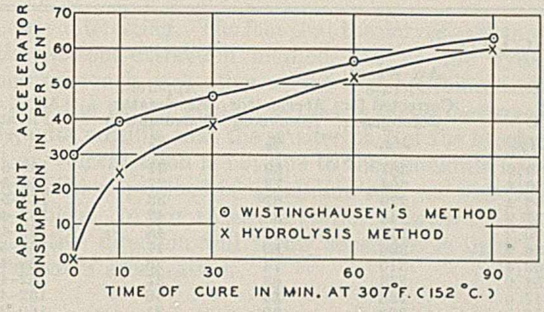

Figure 3. Accelerator Consumption in C

Diphenylguanidine tread stock, cured at 307° F. (152° C.)

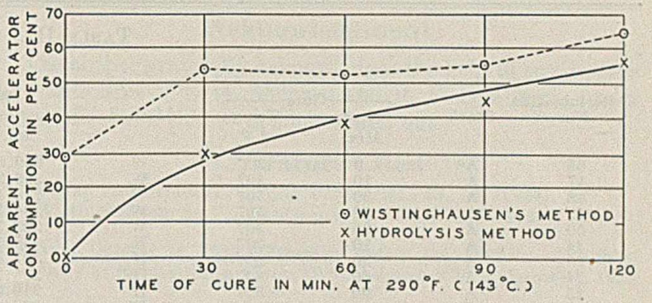

Figure 4. Accelerator Consumption in C

Diphenylguanidine tread stock, cured at 290° F. (143° C.)

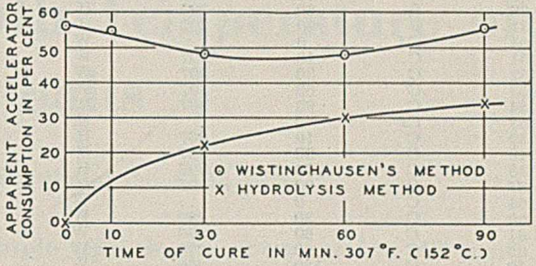

Figure 5. Accelerator Consumption in D

Di-*o*-tolylguanidine tread stock

At the temperature of refluxing benzene, little or no emulsification takes place. Another 50-cc. portion of dilute acid is added and the procedure is repeated. After a third similar treatment with acid, all the recoverable guanidine in the stock has been removed by the acid. The combined acid solution is allowed to cool completely and is then filtered. The filtered solution is clear and usually slightly yellow. The volume is adjusted by evaporation to about 100 cc. and an equal volume of saturated aqueous picric acid solution is added. The rest of the procedure is identical with that described above for the Wistinghausen method.

Besides the fact that it yields higher recoveries of guanidine through hydrolytic splitting of the bound guanidine complex, the hydrolysis method possesses several advantages as an analytical method over the Wistinghausen method. The quality of the picrates is much better, especially in di-*o*-tolylguanidine determinations. In the Wistinghausen method, picrates are frequently obtained which are noncrystalline, dark brown, and melt 20° C. lower than that of the pure picrate, whereas in the present method they are always crystalline, bright yellow, and seldom melt more than 6° C. lower than the pure picrate. Because the picrates obtained are purer and because the variability introduced by different moisture contents in the acetone extractions in the Wistinghausen procedure is not present, the results obtained by the hydrolysis method usually check much better than those obtained by the Wistinghausen method as used in this laboratory. For qualitative purposes only, the hydrolysis method is very rapid, a half hour's stirring and refluxing being sufficient to remove the greater portion of the guanidine. A qualitative determination requires only 2 or 3 hours' time from the beginning of the determination to obtaining the characterizing melting point of the picrate.

The modification of the above method to determine the guanidine in an uncured stock by precipitation as the picrate is as follows:

A 10.0-gram sample is dissolved in 400 cc. of benzene by means of stirring and heating. If small bits of incompletely dispersed stock persist in the cement, no harm is done. Fifty cubic centimeters of approximately 0.1 *N* hydrochloric acid and 50 cc. of water are added and the mixture is stirred and heated for 20 to 30 minutes. The benzene is then evaporated while stirring is continued. When evaporation is complete, the rubber remains in a porous, spongy mass in the aqueous solution. The latter, containing most of the guanidine, is poured off. The remaining traces of guanidine can be removed from the stock by digesting for a few minutes with each of two more successive 50-cc. portions of 0.1 *N* acid. The procedure is then continued as described above.

Analytical Data

The analytical results given in Tables II and III are largely self-explanatory. Table II covers the preliminary work.

In the first three tabulated determinations (Nos. 29, 1, and 2), the uncompounded guanidines, dissolved in 100 cc. of 0.1 *N* hydrochloric acid, were precipitated with an equal volume of

Table II. Preliminary Results

Determination No.	Stock	Method	Wt. of Picrate A Mg.	Wt. of Picrate B Mg.	Av. Wt. of Picrate Corrected for Solubility Mg.	Accelerator Recovered %	Apparent Accelerator Consumption %	M. P. of Picrate ° C.	Remarks
29	D. P. G. (50 mg., commercial)	...	94.1	95.1	102.6	98.7	..	163–5[a]	Theoretical wt. of picrate, 104.0 mg.
1	D. O. T. G. (50 mg., pure)	...	93.2	93.0	98.1	100.0	..	158–60	Theoretical wt. of picrate 98.0 mg.
2	D. O. T. G. (50 mg., commercial)	...	91.1	91.3	96.2	98.2	..	158–60	....
3	D.[b,c]	H[d]	144.3	145.4	150.0	76	24	..	Three 1-hr. periods
5	D.	H	142.2	138.3	...	...	..	..	Three 2-hr. periods
7	D.	H	132.5	138.5	...	...	..	..	Three 8-hr. periods
10	D.	W[e]	125.1	124.7	130	66	34	..	Commercial acetone
11	D.	W	86.3	86.0	91	46	54	..	Dry c. p. acetone
12	D.	W	113.5	117.4	...	...	..	..	Commercial acetone + 10% water
14	D.	W	127.9	127.3	...	...	..	..	Commercial acetone + 2% water
9	D.	...	80.0	78.8	84	43	57	..	Benzene extraction

[a] The m. p. of diphenylguanidine picrate is 170° C.; of di-*o*-tolylguanidine picrate, 162–3° C.

[b] Cured 90 minutes at 290° F. (143° C.).

[c] Theoretical amount of guanidine picrate for D, 196 mg.

[d] Hydrolysis method.

[e] Wistinghausen method.

Table III. Analytical Data

Determination No.	Stock	Cure Time	Cure Temp.	Method	Wt. of Picrate A	Wt. of Picrate B	Av. Wt. of Picrate Corrected for Solubility	Accelerator Recovered	Apparent Accelerator Consumption	M. P. of Picrate
		Min.	*° F.*		*Mg.*	*Mg.*	*Mg.*	%	%	*° C.*
65	A[a]	0	307	W	269.6	289.9	287	69	31	158–61[b]
47	A	10	307	W	296.3	296.4	304	73	27	163–5
48	A	30	307	W	273.1	268.4	279	67	33	163–5
49	A	60	307	W	234.3	237.9	244	58	42	162–4
50	A	90	307	W	208.7	209.2	217	52	48	162–4
34	A	10	307	H	338.1	336.9	306	83	17	163–5
23	A	30	307	H	301.4	302.4	310	74	26	162–4
24	A	60	307	H	255.7	254.9	263	63	37	162–4
25	A	90	307	H	219.3	217.6	226	54	46	162–4
66	B[c]	0	...	W	265.0	256.9	269	69	31	160–2
43	B	10	307	W	255.5	239.2	255	65	35	161–4
45	B	30	307	W	193.0	188.8	199	51	49	157–60
44	B	60	307	W	135.4	136.9	144	37	63	151–5
46	B	90	307	W	94.7	96.2	103	27	73	154–7
26	B	10	307	H	299.1	296.0	306	79	21	162–5
27	B	30	307	H	204.9	203.3	212	54	46	162–5
28	B	60	307	H	131.1	128.3	138	35	65	162–4
31	B	90	307	H	90.0	93.7	100	26	74	160–3
64	C[d]	0	...	W	182.7	174.6	186	71	29	158–61
51	C	10	307	W	152.7	...	161	61	39	160–3
52	C	30	307	W	132.5	134.2	141	54	46	161–4
53	C	60	307	W	112.8	101.7	115	44	56	155–9
54	C	90	307	W	86.6	88.9	96	37	63	160–2
63	C[f]	0		H	123.0	119.0	129	99	1	164–6
39	C	10	307	H	185.7	188.6	195	75	25	162–4
40	C	30	307	H	157.9	152.4	163	62	38	161–3
38	C	60	307	H	117.7	119.9	127	48	52	161–3
37	C	90	307	H	96.2	96.3	104	40	60	160–3
64	C	0	...	W	182.7	174.6	186	71	29	158–61
60	C	30	290	W	111.4	113.3	120	46	54	158–62
61	C	60	290	W	112.1	122.7	125	48	52	157–61
62	C	90	290	W	118.0	103.2	118	45	55	157–61
59	C	120	290	W	94.4	86.3	98	37	63	157–61
63	C[f]	0	...	H	123.3	119.0	129	99	1	164–6
19	C	30	290	H	174.6	173.1	182	70	30	162–4
17	C	60	290	H	156.7	153.3	163	62	38	162–4
20	C	90	290	H	136.3	135.6	144	55	45	162–4
21	C	120	290	H	108.3	108.5	116	44	56	162–4
67	D[e]	0	...	W	76.8	82.5	85	43	57	141–6
57	D	10	307	W	81.5	83.9	88	45	55	141–6
58	D	30	307	W	96.8	...	102	52	48	141–6
55	D	60	307	W	103.6	90.0	102	52	48	141–5
56	D	90	307	W	76.9	90.5	89	45	55	141–5
36	D	30	307	H	146.9	...	152	78	22	158–60
41	D	60	307	H	131.6	134.1	138	70	30	158–60
42	D	90	307	H	122.1	125.5	129	66	34	158–60

[a] Theoretical amount of guanidine picrate, 417 mg.

[b] The m. p. of diphenylguanidine picrate is 170° C.; of di-*o*-tolylguanidine picrate, 162–3° C.

[c] Theoretical amount of guanidine picrate, 390 mg.

[d] Theoretical amount of guanidine picrate, 262 mg.

[e] Theoretical amount of guanidine picrate, 196 mg.

[f] 10.0 gram sample.

picric acid solution to check the completeness of the precipitation. When the 5- and 8-mg. corrections for solubility were added to the weights of the picrates obtained, the results were satisfactory. The next three determinations (Nos. 3, 5, and 7) were run to gain some idea as to the proper length of time for the extraction period in the hydrolysis method. It was concluded that there was no reason for continuing these extraction periods for longer than an hour. The next four determinations (Nos. 10, 11, 12, and 14) were made, employing various acetone extraction procedures as indicated under "Remarks," and show the variation in results caused by the introduction of water. The last determination (No. 9) was run by extracting the stock with dry benzene and then determining the guanidine in the filtered extract by hydrochloric acid extraction and precipitation in the usual manner.

Since the results obtained were substantially the same as those obtained with dry acetone, it is evident that the acetone-insoluble guanidine in the stock is liberated by the hydrolytic effect of the acid rather than by the swelling effect of the benzene.

Table III is a tabulation of the results obtained on the various cures of stocks A, B, C, and D. The curves shown in Figures 1 to 5, inclusive, were obtained by plotting the apparent accelerator consumption—i. e., the difference between the theoretical and the determined value—against the time of cure. Figures 1 and 2 also contain a reproduction of Wistinghausen's curves for stocks A and B, which are inserted for the sake of comparison. In Figure 4, no reasonable curve representing accelerator consumption as determined by the Wistinghausen method can be drawn through the plotted points.

It will be necessary to obtain further data, especially for short curing periods, in order to determine the true course of the curve.

Discussion of Results

Reference to Figures 1, 2, and 3 shows that, for diphenylguanidine stocks, the curves obtained by the hydrolysis and Wistinghausen methods are approximately identical over the greater part of their range. From this it might be inferred that, for practical purposes, the guanidine could be determined by either method. This would be true if we were interested in overcured stocks, but it should be recalled that, for commercial stocks, only the first quarter of the curves (Figures 1, 2, or 3) would be involved. Figure 4 (diphenylguanidine stock cured at 290° F., 143° C.) shows the situation in the range of the optimum cure somewhat better, as far as distance between the curves is concerned, although the true course of the Wistinghausen curve is not known. In the case of di-*o*-tolylguanidine stocks (see Figure 5), the difference between the two curves is much more pronounced. There is apparently more extensive compound formation with di-*o*-tolylguanidine than with diphenylguanidine and this addition compound of di-*o*-tolylguanidine is less readily destroyed. This behavior may be the cause of the greater accelerating activity of di-*o*-tolylguanidine as compared to diphenylguanidine.

The present investigation has raised a number of questions which can be answered only by further research. Among other things, the probability that there is compound formation between the guanidine and the protein, or the rubber, is extremely interesting. The fact that the curves as determined by the acetone-extraction method and by the hydrolysis method approach each other as the cure continues indicates that it is the bound guanidine that is being destroyed. It seems quite possible that the greater part of the accelerating effect on vulcanization is not due to the guanidine itself but to an addition product of guanidine and an ingredient of crude rubber. In any case, the author believes that further work in this direction will throw considerable light on the mechanism of acceleration.

Acknowledgment

The author gratefully acknowledges the helpful suggestions and criticisms of N. A. Shepard and R. F. Dunbrook, under whose direction this work was carried out.

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Change of Penetration with Temperature of Various Asphalts

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In this investigation a simple equation, $p = A + B \times C^t$, was found to express the variation of the penetration of thirteen asphalts with the temperature.

Several sources and methods of processing are represented in the asphalts which were studied. The equation can be solved when three penetrations obtained with the same weight and for the same period of time at different temperatures are known. By means of this equation a simple index, $p_2 - p_1$, was found to represent adequately the order and the relative magnitude of the temperature susceptibility of the thirteen asphalts.

THE susceptibility of asphalts to temperature changes is probably the most important characteristic of these substances. To be able to evaluate this coefficient with precision is most essential both for purposes of identification and for revealing intrinsically the suitability of a given asphalt for a desired purpose. Though many attempts have been made to arrive at some method of determining this factor of susceptibility, no satisfactory procedure has as yet been worked out (*5*).

Abraham (*1*) observed that the difference in consistometer hardness at 46.1° and 0.0° C. (115° and 32° F.) divided by the Kramer-Sarnow fusing point (*2*) is a constant for all asphalts derived from the same source. This series of constants he terms "susceptibility factors." Whatever the technical objections to this method may be, these factors do not evaluate the susceptibility to temperature change of those asphalts which come from the same source but which are processed differently, nor does this method yield a definite relation between the true susceptibility and the group factors obtained.

The procedure generally adopted by asphalt technologists consists of obtaining a ratio of the difference between two penetrations at 46.1° and 0.0° C. (115° and 32° F.) divided by that at 25° C. (77° F.). The three penetration readings are obtained with three different loads and two different time periods (*3*). That this method is not satisfactory is conceded; although it is found useful for identification purposes, it is at times misleading.

Many other methods are in vogue (*6*). None of these, however, determines any intrinsic property of asphalts. Frequently the order of these various indexes is not the same as the order of the true susceptibilities, while the numerical relation between their magnitude is hardly ever the same as the relative susceptibilities for a series of asphalts. Perhaps the susceptibility of some other property of asphalts to temperature changes may be of greater utility (*5*), but the penetration still remains to be the best known and most generally used test for asphalts (*4*).

The aim of this investigation was not merely to find a factor or an index which would give the relative order of the susceptibilities of different asphalts, but also to obtain a concise expression by means of which the entire curve could be visualized or determined—i. e., the susceptibility of the penetration, dp/dt, at any desired point within a given range of temperature.

The equation suggested below represents experimental data well within the experimental error and gives a concise method of representation. By means of this equation, when three penetrations at three temperatures are known, it is possible to calculate with precision the entire susceptibility curve. Furthermore, an "index" of this susceptibility, yielding relative values over a desired temperature range with adequate precision for all practical purposes, is derived from this equation.

Experimental Procedure

The standard procedure (*3*) for measuring penetrations was employed. Great care was observed with regard to such important and well-known details as overheating, aging, etc.

A large bath, the temperature of which was varied and controlled, supplied a stream of water within which the cup, filled with the asphalt under investigation, was immersed. A thermometer was imbedded in the asphalt in the center of the cup. Preliminary studies showed that the temperature in the center of the cup and that 1.25 cm. (0.5 inch) away were identical, and that the presence of the thermometer did not affect the penetrometer readings taken half-way between the center and the side of the cup. The cups were allowed to remain at a constant temperature for 30 minutes before a reading was taken, and the thermometer was read before and after each set of readings. No variation larger than 0.2° C. was allowed. In determining the final value of the penetration at least five readings were taken, the average deviation of which, from the average, did not exceed 0.3 mm.

Thirteen asphalts, the characteristics of which are given in Table I, have been studied, including asphalts from Venezuelan and Midcontinent asphaltic base petroleums as well as native Trinidad Lake. Various processes of manufacture are represented: air-blown, steam-refined, and vacuum-refined.

Table I. Characteristics of Asphalts Studied

Asphalt No.[a]	Source	Process	Penetration[b]	Softening Point B & R[c]
1	Mexican and Texas	Air and steam	7	298
2	Mexican and Texas	Air and steam	11	245
3	Mexican and Texas	Air and steam	11	232
4	Trinidad Lake	Native	2	200
5	Venezuelan	Vacuum-distilled	8	170
6	Midcontinent	Air-blown	25	176
7	Mexican and Texas	Air and steam	26	193
8	Mexican and Texas	Air-blown	30	168
9	Venezuelan	Air-blown	26	169
10	Venezuelan	Vacuum-distilled	26	133
11	Fluxed refined Trinidad Lake	Batch steam	50	131
12	Venezuelan	Vacuum-distilled	42	119
13	Mexican	Steam-refined	220	96

[a] These numbers refer to the curves in Figures 1, 2, and 3.
[b] At 77° F., 100-gram weight, 5 seconds.
[c] Ball-and-ring method.

Change of Penetration with Temperature

The experimental data plotted against the temperature gave a group of smooth curves (Figure 1). The general similarity and nature of the curves suggested that some exponential equation should express the penetration of all asphalts. Equation 1 was found to represent the experimental results with a high degree of accuracy.

$$p = A + B \times C^t \tag{1}$$

where p is the penetration in decimillimeters
t is the temperature in degrees Centigrade
A, B, and C are constants characteristic of each asphalt

The validity of the equation is proved by plotting log $(p - A)$ against t. Straight lines are obtained (Figure 2). The equation is further tested by comparing the calculated values with those obtained experimentally. These compared values are given in columns 2 and 3, and 6 and 7 of Table II. The deviations in columns 4 and 8 are in only a few cases greater than 0.4 mm., and in terms of percentage the average deviation is less than 5 per cent.

Three penetrations at any three temperatures are sufficient for the solution of Equation 1. However, a simplification of the solution is gained if the three temperatures are so chosen that

$$t_3 - 2t_2 + t_1 = 0 \tag{2}$$

If 0° C. is taken for t_1, Equation 1 reduces to the simple form

$$\frac{p_3 - p_2}{p_2 - p_1} = C^{t_2} \tag{3}$$

The values of the three constants calculated for thirteen asphalts are given in Table III. In calculating these con-

Table II. Comparing Experimental and Calculated Values as a Proof of Validity of Equation 1

	Penetration[a]				Penetration[a]		
Temp. ° C.	Expt.	Calcd.	Deviation	Temp. ° C.	Expt.	Calcd.	Deviation
				Asphalt 1			
0.0	4	4.0	0.0	38.5	10.5	10.2	−0.3
22.5	6	6.2	+0.2	42.5	12.5	12.1	−0.4
26.2	7.5	6.9	−0.6	46.0	14	13.9	−0.1
32.5	8.5	8.4	−0.1	53.2	19	19.0	0.0
					Average deviation 2.6%		
				Asphalt 2			
0.0	5	5.0	0.0	35.0	16	16.2	+0.2
19.0	9.5	9.2	−0.3	41.0	19.5	20.1	+0.6
25.0	11.5	11.3	−0.2	44.0	22.5	22.5	0.0
30.0	14	13.5	−0.5	50.0	28	28.2	+0.2
					Average deviation 1.7%		
				Asphalt 3			
0.0	4.5	4.5	0.0	35.2	17	16.1	−0.9
16.5	8	7.8	−2.0	39.6	20	19.3	−0.7
20.0	9	8.9	−0.1	50.0	29.5	30.0	+0.5
26.4	11	11.3	+0.3	51.5	32	32.1	+0.1
					Average deviation 2.2%		
				Asphalt 4			
0.0	1	1.0	0.0	47.6	13	13.1	+0.1
33.0	3	3.3	+0.3	50.0	17	16.9	−0.1
38.0	5	5.0	0.0	51.7	21	20.3	−0.7
43.7	8.5	8.8	+0.3	55.0	31	29.1	−1.9
					Average deviation 3.0%		
				Asphalt 5			
0.0	3.5	3.5	0.0	39.8	21	21.5	+0.5
18.0	6.5	5.9	−0.6	43.5	29.5	28.3	−1.2
23.2	7.5	7.5	0.0	44.5	31	30.5	−0.5
30.0	10.5	11.1	+0.6	47.0	39	36.9	−2.1
34.0	13.5	14.3	+0.8	52.0	55	54.5	−0.5
39.5	20.5	21.1	+0.6	53.5	57.5	61.4	+3.9
					Average deviation 3.7%		
				Asphalt 6			
0.0	9	9.0	0.0	34.6	40.5	38.3	−2.2
15.0	15.5	16.7	+1.2	37.5	46	43.4	−2.6
20.0	19	20.6	+1.6	44.0	60	57.5	−2.5
22.0	22	22.4	+0.4	45.6	64	61.6	−2.4
25.2	25.5	25.6	+0.1	48.0	69	68.4	−0.6
29.5	32	30.8	−1.2	50.0	73.5	74.5	+1.0
33.0	36.5	35.8	−0.7	52.5	82	83.5	+1.5
					Average deviation 3.4%		
				Asphalt 7			
0.0	11	11.0	0.0	41.3	53.5	53.8	+0.3
19.0	20	20.0	0.0	44.0	61	61.5	+0.5
24.5	25	25.0	0.0	46.2	68.5	68.7	+0.2
27.0	28	27.8	−0.2	49.0	79	79.2	+0.2
30.0	32	31.7	−0.3	51.5	90.5	90.0	−0.5
34.0	37.5	38.0	+0.5	54.0	102.5	102.5	0.0
36.7	43	43.1	+0.1	55.3	112	109.6	−2.4
					Average deviation 0.6%		
				Asphalt 8			
0.0	11.5	11.5	0.0	34.5	45	45.0	0.0
5.8	14.5	14.2	−0.3	37.0	48	50.1	+2.1
11.0	18	17.3	−0.7	41.2	61	60.1	−0.9
20.0	25	24.6	−0.4	43.0	65	64.9	−0.1
24.5	29.5	29.6	+0.1	44.5	68	69.3	+1.3
28.0	34	34.2	+0.2	50.5	89	90.2	+1.2
29.0	34	35.7	+1.7	53.5	104	103.0	−1.0
					Average deviation 1.7%		
				Asphalt 9			
0.0	10	10.0	0.0	33.5	39	38.7	−0.3
16.5	18.5	18.1	−0.4	36.8	45.5	45.4	−0.1
21.0	21.5	21.9	+0.4	40.7	54	55.0	+1.0
26.0	28	27.3	−0.7	44.0	63.5	64.9	+1.4
29.0	31	31.3	+0.3	48.2	78.5	80.4	+1.9
30.5	34	33.6	−0.4	51.0	95	92.8	−2.2
					Average deviation 1.5%		
				Asphalt 10			
0.0	4.5	4.5	0.0	34.5	56.5	57.3	+0.8
17.8	15	14.8	−0.2	37.0	69.5	70.8	+1.3
24.1	24.5	24.3	−0.2	41.0	101	99.6	−1.4
27.2	30	31.2	+1.2	43.6	129	124.4	−4.6
31.2	42	43.5	+1.5	46.4	161	158.2	−2.8
					Average deviation 1.9%		
				Asphalt 11			
0.0	8	8.0	0.0	32.0	81	85.9	+4.9
10.0	12.5	15.2	+2.7	32.6	85	90.3	+4.7
12.5	16	18.1	+2.1	33.6	96	98.2	+2.2
15.9	21.5	23.4	+1.9	35.0	113	110.5	−2.5
20.7	35	34.0	−1.0	38.0	138	142.5	+4.5
24.0	46	44.4	−1.4	40.0	169	168.9	−0.1
28.8	65	65.8	+0.8	42.0	202	200.3	−1.7
					Average deviation 4.7%		
				Asphalt 12			
0.0	5	5.0	0.0	26.3	49	45.6	−3.4
14.0	12.5	12.7	+0.2	30.5	74.5	74.0	−0.5
20.0	22	22.9	+0.9	34.8	125.5	123.0	−2.5
23.2	34	32.3	−1.7	41.0	250	259.0	+9.1
					Average deviation 3.0%		
				Asphalt 13			
0.0	33	33.0	0.0	14.8	100.5	104.8	+4.3
5.7	50	50.8	+0.8	17.4	130	129.7	−0.3
9.2	66	66.8	+0.8	19.2	151	150.4	−0.6
13.0	86	90.6	+4.6	21.5	177	181.9	+4.9
					Average deviation 1.9%		

[a] 100-gram weight on needle 5-second time period.

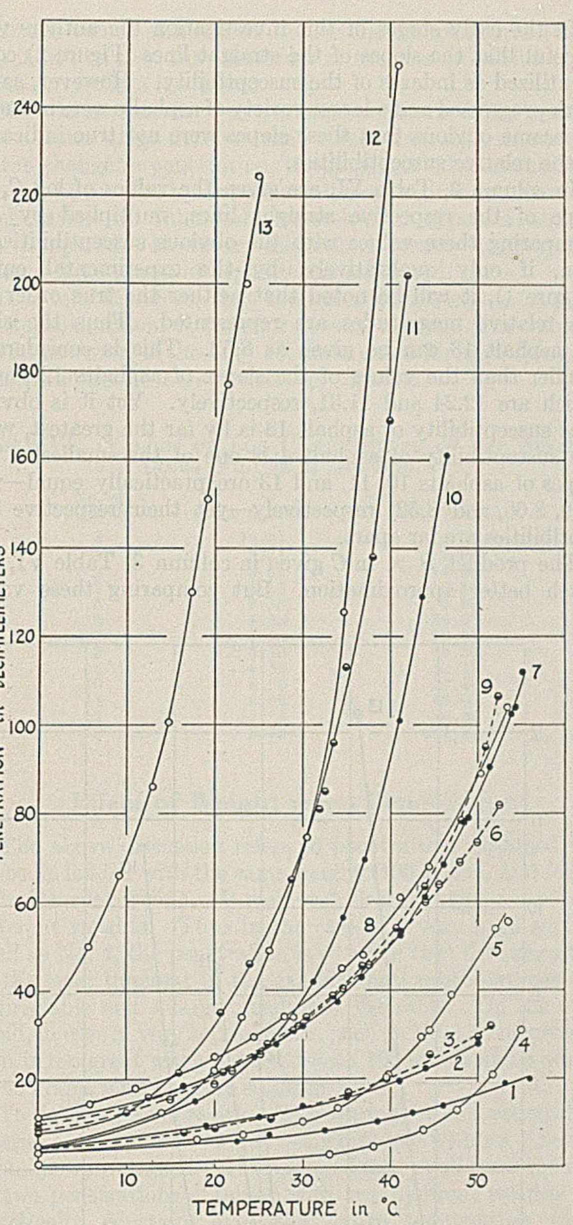

Figure 1. Experimental Data Plotted against Temperature

stants, penetrations were read off the experimental curve at 0.0°, 25°, and 50° C. (32°, 77°, and 122° F.) for all asphalts but Nos. 10, 11, 12, and 13. For asphalts 10, 11, and 12 the temperatures 0.0°, 20°, and 40° C. were used, and for asphalt 13 the temperatures 0.0°, 10°, and 20° C.

Constants B and C can be calculated or read off the curve of log $(p - A)$ vs. t (Figure 2). The slope of the straight line is log C, and the intercept with the ordinate is log B.

In plotting the straight lines of Figure 2, penetrations at round temperatures were read off experimental curves (Figure 1).

It may be of interest to point out that B is a dimensional constant, so that any temperature scale can be employed by modifying B correspondingly. Relation 2, however, will be changed.

Susceptibility to Temperature Changes

Differentiating Equation 1 we obtain $dp/dt = B \times \ln C \times C^t$. It follows that neither the first nor any other derivative is a constant. A further proof, however, that this conclusion is an inherent property of the penetration and not merely a consequence of the authors' particular empirical equation, can be obtained from the nature of the experimental curves given in Figure 1. These are not straight lines, nor do they exhibit uniform curvature. Any attempt, therefore, to express the susceptibility of the penetration to temperature changes by a constant factor cannot possibly yield an accurate representation of the true property. The rate of change is different at different temperatures and this difference is not the same for any two asphalts.

Table III. Constants of Equation 1 for Various Asphalts

No. of Asphalt	A	B	C
1	3.06	0.94	1.0545
2	1.18	3.82	1.0399
3	1.56	2.94	1.0465
4	0.944	0.056	1.1197
5	2.82	0.68	1.0869
6	0.77	8.23	1.0448
7	6.14	4.86	1.0569
8	2.63	8.87	1.0464
9	4.37	5.63	1.0555
10	1.73	2.77	1.0908
11	2.80	5.20	1.0905
12	3.31	1.69	1.1302
13	4.57	28.43	1.0889

Thus, observing the experimental curves in Figure 1, we note that in the case of Trinidad Lake asphalt (No. 4) the penetration hardly changes with the temperature up to 30° C., while above that temperature the penetration begins to rise very rapidly. The other extreme is shown in the case of asphalt 13, the penetration of which begins to rise rapidly even at the lowest temperature. Asphalt 7 and several others, on the other hand, give an even rise throughout the entire range.

These facts are not revealed by any one constant factor, whereas an accurate representation of fact can be gained by the derivative dp/dt. Or, to conform to the usage of expressing similar variations of other important characteristics of matter, such as the coefficient of compressibility, etc., we may define the susceptibility of asphalts by the coefficient

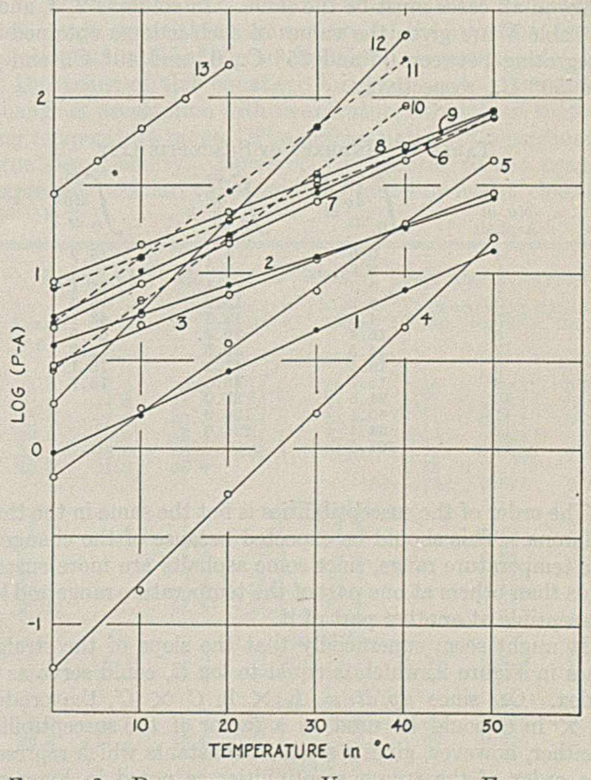

Figure 2. Demonstrating Validity of Equation $p = A + B \times C^t$

$1/p \times dp/dt$. Values of dp/dt for the thirteen asphalts at four different temperatures are given in Table IV.

TABLE IV. SUSCEPTIBILITIES AT FOUR DIFFERENT TEMPERATURES

No. of Asphalt	dp/dt, 0° C.	dp/dt, 25° C.	dp/dt, 46.1° C.	dp/dt, 50° C.
1	0.05	0.19	0.58	0.72
2	0.15	0.40	0.91	1.05
3	0.13	0.42	1.08	1.30
4	0.006	0.43	1.15	1.80
5	0.06	0.46	2.63	4.30
6	0.36	1.07	2.72	3.23
7	0.27	1.07	3.43	4.23
8	0.40	1.24	3.23	3.87
9	0.30	1.17	3.65	4.50
10	0.24	2.56	13.3	..
11	0.45	3.98	..	..
12	0.21	4.35	..	..
13	2.42	..	..	..

Index of Susceptibility

If a practical simplification is desired for the sake of conciseness, it is possible to obtain a constant which will express approximately the relative susceptibilities of different asphalts. This can be obtained by evaluating the area under the curve of dp/dt vs. t (Figure 3). This area is given by integrating the differential with respect to temperature between the limits of the desired temperatures.

Index of susceptibility = area under curve dp/dt vs. t

$$= \int_{t_1}^{t_2} \frac{dp}{dt}\, dt = p_2 - p_1 \qquad (4)$$

Thus we obtain not only a constant to express the relative susceptibilities of various asphalts, but the entire problem is a good deal simplified. Only two penetrations at specified temperatures are necessary. It must be borne in mind that in comparing the indexes of different asphalts the temperature range in all cases must be the same. In columns 2, 3, and 4 of Table V are given the values of such indexes obtained by integrating between 0° and 25° C., 0° and 40° C., and 0° and 50° C., respectively.

TABLE V. INDEXES OF SUSCEPTIBILITY

No. of Asphalt	$\int_0^{25} \frac{dp}{dt}\, dt$	$\int_0^{40} \frac{dp}{dt}\, dt$	$\int_0^{50} \frac{dp}{dt}\, dt$
4	0.9	5.1	15.9
1	2.6	7.0	12.4
2	6.3	14.4	23.1
3	6.2	15.2	25.9
5	4.8	18.3	43.1
6	16.4	39.4	65.5
7	14.5	39.5	72.3
9	16.1	43.2	78.1
8	18.7	45.5	76.7
10	21.6	87.0	..
11	40.1	160.9	..
12	34.4	224.6	..
13	191.5	..	..

The order of the susceptibilities is not the same in the three columns. This should be expected because of the change in the temperature range, since some asphalts are more susceptible than others at one part of the temperature range and less susceptible at another part of it.

It might seem superficially that the slope of the straight lines in Figure 2, which is equal to log C, could serve as an index. Or, since $dp/dt = B \times \ln C \times C^t$, the product $B \times \ln C$ could be used as a factor of the susceptibility. Neither, however, gives a series of constants which represent the order of the true susceptibilities as noted in Figures 1 and 3.

In the early stages of this investigation the authors were hopeful that the slopes of the straight lines (Figure 2) could be utilized as indexes of the susceptibility. However, as the work progressed and a larger variety of asphalts were included, it became obvious that these slopes were not true indicators of the relative susceptibilities.

In column 2, Table VI, are given the values of log C, the slope of the respective straight lines, multiplied by 100. Comparing these values with the obvious susceptibilities as seen, if only qualitatively, by the experimental curves (Figure 1), it will be noted that neither the true order nor the relative magnitudes are represented. Thus the slope for asphalt 13 can be given as 8.52. This is considerably smaller than the values of the slopes of asphalts 12 and 4, which are 12.24 and 11.31, respectively. Yet it is obvious that susceptibility of asphalt 13 is by far the greatest, while the susceptibility of asphalt 4 is one of the smallest. The slopes of asphalts 10, 11, and 13 are practically equal—viz., 8.69, 8.66, and 8.52, respectively—yet their respective susceptibilities are far apart.

The product $B \times \ln C$ given in column 3, Table VI, is a much better approximation. But comparing these values

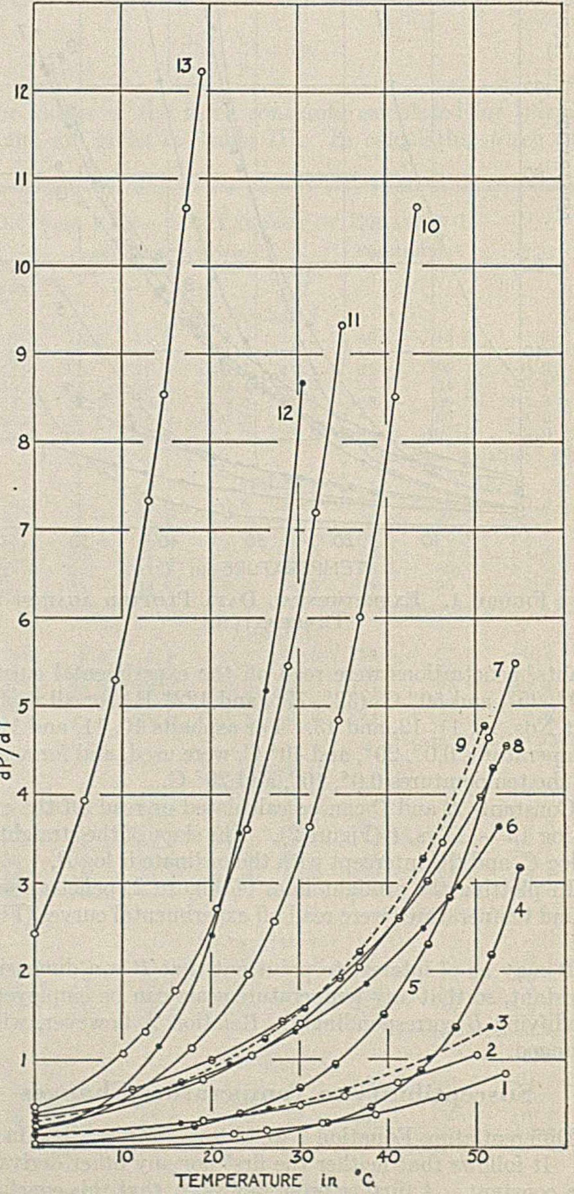

FIGURE 3. INDEX OF SUSCEPTIBILITY

with the values of dp/dt at the several temperatures (Table IV) it will be seen that the order of the susceptibilities is not quite correct in a few cases.

Since it is customary to express the susceptibility as some sort of ratio which involves the actual penetration in addition to the change in penetration, it was suggested that the index $p_2 - p_1$ be divided by the penetration at a given temperature. Such ratios are valid only when similar types of asphalts are compared. However, discordant results are obtained when a large group of asphalts are compared.

It is felt, therefore, that the index suggested, $p_2 - p_1$, as an approximation, is superior to any others. The value of dp/dt, however, is the only accurate guide for classifying the susceptibilities of large varieties of asphalts.

TABLE VI. VALUES OF LOG C, THE SLOPE OF THE STRAIGHT LINES (FIGURE 2) AND $B \ln C$

No. of Asphalt	Log $C \times 10^2$	$B \ln C \times 10^2$
4	11.31	5.32
1	5.31	4.98
2	3.91	14.93
3	4.55	13.34
5	8.33	5.66
6	4.38	36.04
7	5.53	26.86
9	5.40	30.36
8	4.53	40.19
10	8.69	23.46
11	8.66	45.00
12	12.24	20.66
13	8.52	241.87

Effect of Weight upon Penetration

The above discussion refers to penetrations obtained with a needle loaded with the same weight (100 grams) and for the same interval of time. It may be desirable at times to employ different weights. Thus in the case of a very hard asphalt, such as No. 4, the penetration is so small that the magnitude of the error inherent in the experimental procedure becomes appreciable and a larger reading is desirable. On the other hand, in case of very soft asphalts, such as No. 13, the penetration is too great when obtained with 100 grams and a weight of 50 grams may be more suitable.

To determine the relation between weight and penetration, a series of readings was made using different weights. Several asphalts were studied. It was found that in all cases the ratio of two penetrations obtained with two different weights was practically constant over the entire temperature range. The experimental results are given in columns 2, 3, 4, and 5 of Table VII. In columns 6, 7, and 8 are given the ratios of penetration obtained with three different weights. This fact can be utilized whenever it is desirable to measure penetration with a weight smaller or larger than 100 grams.

The index then for a soft asphalt is

$$(p_{50\text{g.}}/5\text{ sec.}/40^\circ\text{ C.} - p_{50\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}) \times \frac{p_{100\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}}{p_{50\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}}$$

or in case of a hard asphalt

$$(p_{200\text{g.}}/5\text{ sec.}/40^\circ\text{ C. or }50^\circ\text{ C.} - p_{200\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}) \times \frac{p_{100\text{g.}}/5\text{ sec.}/40^\circ\text{ or }50^\circ\text{ C.}}{p_{200\text{g.}}/5\text{ sec.}/40^\circ\text{ or }50^\circ\text{ C.}}$$

The accuracy of this conversion will depend upon the constancy of the ratio of the two penetrations throughout the temperature range.

As practical illustrations of the possible deviation we can calculate the index for a hard asphalt, No. 4, and a soft asphalt, No. 10, using the data given in Table VII.

For No. 4,

$$\text{Index} = p_{100\text{g.}}/5\text{ sec.}/50^\circ\text{ C.} - p_{100\text{g.}}/5\text{ sec.}/0^\circ\text{ C.} = 17 - 1 = 16$$

or

$$\text{Index} = (p_{250\text{g.}}/5\text{ sec.}/50^\circ\text{ C.} - p_{250\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}) \times \frac{p_{100\text{g.}}/5\text{ sec.}/50^\circ\text{ C.}}{p_{250\text{g.}}/5\text{ sec.}/50^\circ\text{ C.}} = (33.4 - 2)\,\frac{17}{33.4} = 15.98$$

In the case of a soft asphalt, accepting for the sake of illustration 25.8° C. as the upper temperature limit, for asphalt No. 10,

$$\text{Index} = p_{100\text{g.}}/5\text{ sec.}/25.8^\circ\text{ C.} - p_{100\text{g.}}/5\text{ sec.}/0^\circ\text{ C.} = 29.5 - 4.5 = 25.0$$

or

$$\text{Index} = (p_{50\text{g.}}/5\text{ sec.}/25.8^\circ\text{ C.} - p_{50\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}) \times \frac{p_{100\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}}{p_{50\text{g.}}/5\text{ sec.}/0^\circ\text{ C.}} = (20 - 3)\,\frac{4.5}{3} = 25.5$$

The agreement in both cases is excellent.

Conclusion

An equation is found which expresses concisely the variation of the penetration of various asphalts with temperature. The equation represents the experimental data for thirteen asphalts of different sources and methods of processing, well within experimental error. The present technic followed by routine asphalt laboratories of reporting penetrations at three different temperatures is found sufficient for solving the equation

$$p = A + B \times C^t$$

providing the weight and time period for all three penetrations are the same and the temperatures expressed in Centigrade are so chosen that

$$t_3 - 2t_2 + t_1 = 0$$

i. e., 50°, 25°, and 0° C., or 40°, 20°, and 0° C. This limitation is not essential for the solution of the equation, but the solution is simplified a good deal if the suggestion is followed.

By means of this equation it is possible to represent the change of penetration with temperature throughout the working temperature range. The differential dp/dt represents the true susceptibility. However, to conform to the usage of expressing similar variations of other important character-

TABLE VII. EFFECT OF WEIGHT UPON PENETRATION

Temp. ° C.	Penetrations 50 g.	100 g.	200 g.	250 g.	Penetration Ratios 100/50	100/200	100/250
				Asphalt 8			
0.0	5.0	9.0	14.0	16.0	1.80	0.653	0.562
20.0	14.5	24.8	36.2	41.2	1.71	0.685	0.602
25.0	17.5	30.0	44.5	51.4	1.71	0.674	0.583
30.0	20.9	36.3	54.7	65.0	1.74	0.663	0.558
35.0	25.6	45.2	68.2	84.0	1.76	0.663	0.538
40.0	31.8	56.4	..	..	1.74	...	...
					Av. 1.74	0.677	0.568
				Asphalt 4			
0.0		1.0	..	2.0		..	0.5
30.0		2.5	4.6	5.8		0.54	0.43
35.0		3.6	7.0	8.0		0.51	0.45
40.0		6.0	11.6	13.3		0.517	0.451
45.0		10.1	18.1	21.6		0.559	0.467
27.0		17.0	27.3	33.4		0.623	0.509
						Av. 0.550	0.468
				Asphalt 6			
0.0	4.5	7.0	11.0	12.0	1.55	0.636	0.583
25.8	17.0	25.5	40.5	46.0	1.50	0.603	0.550
				Asphalt 9			
0.0	5.5	9.0	13.5	16.0	1.63	0.666	0.563
25.8	17.5	28.0	45.5	51.0	1.60	0.615	0.550
				Asphalt 10			
0.0	3.0	4.5	7.0	8.5	1.5	0.643	0.529
25.8	20.0	29.5	49.0	56.5	1.48	0.602	0.522

istics of matter, such as the coefficient of compressibility, etc., we may define the susceptibility of asphalts by the coefficient $1/p \times dp/dt$. This can be advantageously used for classification of all asphalts, regardless of their sources or methods of processing, providing the above empirical equation, or a similar equation, expresses the experimental variation of the penetration with temperature.

Unfortunately, this coefficient is not a constant. The established usage of asphalt laboratories is to employ some sort of a constant factor for the classification of asphalts. The numerous methods of deriving these factors are no doubt found useful by the laboratories using them, and some laboratories find one factor more useful than another. None of these factors, using penetration as a basis, represents the true susceptibility, though for limited groups of asphalts the representation is no doubt sufficient for practical purposes, especially since such factors are employed primarily for purposes of identification rather than classification.

The authors suggest, therefore, as an approximation, a constant factor to represent the susceptibility, the definite integral of dp/dt between the limits of the desired temperature. This integral is equal to $p_2 - p_1$. It is found that this factor represents the true order of the susceptibilities and, approximately, the relative magnitudes of all asphalts studied in this investigation. Several other possible expressions which suggested themselves were found to be of no intrinsic value.

It is further shown that the ratio of penetration obtained with different weights at different temperatures is practically constant. This makes it possible to use penetration of a hard asphalt obtained with 200 or 250 grams and that of a soft asphalt with 50 grams and the respective indexes are nevertheless rigorously comparable.

Acknowledgment

The authors wish to thank R. N. Traxler of The Barber Asphalt Company for many valuable suggestions and criticisms.

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Determination of Nitric Oxide in Coke-Oven Gas

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ABOUT six or seven years ago the problem of stoppages in small orifices of gas distribution systems began to become acute. Investigation soon showed that minute amounts of organic nitro compounds were responsible for a considerable portion of this trouble. The original general theory was that nitric oxide (NO) formed in the combustion gas of the oven flues and perhaps elsewhere found its way through the oven walls into the gas, slowly oxidized to nitrogen peroxide, and combined with unsaturated hydrocarbons present in the gas to form gummy deposits in the distribution system.

It was found that the amounts of gum involved were almost unbelievably small, and that therefore no simple method of determination, such as filtering and weighing, was likely to be successful. The fact that a distinctly ultrasensitive method was needed sharply limited procedure. It was perhaps fortunate, however, that derivatives of nitrous acid were involved, since delicate color tests for this substance were well known and are among the most sensitive chemical tests available to the analyst. Therefore, the analytical attack was made against the nitro group.

Tropsch and Kassler (*5*) suggested introducing the gas into a large flask together with a large fraction of oxygen, and adding caustic soda solution which was later added to an acetic acid solution of an amine, such as Griess-Ilosvay reagent. The whole was shaken for 20 minutes and the color produced in the solution compared with standards. This was cumbersome and had the distinct disadvantage that the largest feasible size of sample was so small that the method was of practical value in only a few cases where the concentrations of nitric oxide were relatively high.

Shortly after this Schuftan (*2*) published a dynamic method in which the gas was scrubbed with potassium hydroxide solution, dried with potassium hydroxide pellets, mixed with one-half its volume of oxygen, passed through a delay bottle for an interval of 15 minutes, and then scrubbed with a solution of *m*-phenylenediamine (diaminobenzene) in dilute acetic acid. The color formed was a measure of the nitric oxide present.

This was a distinct improvement over the other methods. The size of sample was substantially unlimited and the shaking entirely eliminated by this procedure. Since only a fraction of the nitric oxide present was recovered, for both of these methods a reference curve was employed, apparently based upon the calculations of Bodenstein or upon direct calibration of nitric oxide-nitrogen mixtures. So far as the writer is aware, not many data have been presented for nitric oxide recovery based upon small known additions of nitric oxide to nitric oxide-free coke-oven gas.

Fulweiler (*1*) has described a modification of the Schuftan dynamic method which involves mixing the gas with an equal volume of oxygen, allowing the mixture to react for approximately 1.5 minutes, and then absorbing the nitrogen tetroxide (NO_2) formed directly in Griess reagent. He claims that there is a catalyst present in manufactured gas that accelerates the conversion of nitric oxide into nitrogen tetroxide. Later Fulweiler extended the application of this method to a continuous recording instrument for the determination of nitric oxide in gas.

Tests by the writer upon nitric oxide in nitrogen showed a very fair agreement with the Schuftan curve. This reference curve shows a marked variation in the amount of recoverable nitric oxide, depending upon the concentration of the nitric oxide originally present in the gas. Where there is a nitric oxide concentration of several hundred parts per million the correction factor is substantially unity. For 10 p. p. m. it is about 10, for 1.0 p. p. m. it is about 200, etc.

When the author's work was started on coke-oven gas it was apparent that this nitrogen curve did not apply. As an actual matter of fact, the particular method subsequently standardized by the writer for use on coke-oven gas shows a factor of very approximately 2 for all concentrations of nitric oxide tested.

This difference made a fundamental study of analytical methods a matter of first importance. A survey of available lines of attack seemed to indicate that the most profitable procedure would be to continue along the lines of Schuftan's initial effort.

One of the most difficult problems connected with the search was the preparation of a synthetic sample of known nitric oxide concentration. This involved the production of a nitric oxide–free gas. Since the composition of the gas had a marked effect upon the nitric oxide recovery as shown by the author's experience with nitrogen, it seemed that the least possible treatment of the gas to remove nitric oxide was the best. Chemical treatment in particular was open to question, especially since so little was known at the start about the chemical properties of the substances involved.

The method finally adopted for producing nitric oxide–free gas consisted in compressing the gas containing about 0.5 per cent of oxygen to 2.1 kg. per sq. cm. (30 pounds per square inch) gage pressure and allowing it to stand several hours, usually overnight.

A cylindrical pressure-tank having about 0.5 cu. m. (17 cubic feet) displacement was set up outside the building, and was connected to the gas main on the pressure side of the plant gas booster. Oxygen was added in the form of air before the tank was opened to the line pressure. After collecting the sample, the inlet valve was closed and the pipe connecting it to the gas main was vented to the air (as shown in Figure 1) to prevent any possible contamination of the sample with untreated gas. A Schuftan test of 7 hours' duration run upon gas treated in this manner gave a zero blank. It was therefore considered that this part of the problem had probably been solved.

The next step involved the addition of small known amounts of nitric oxide to this gas. The concentrations in which the author was interested were seldom greater than 1 p. p. m. and sometimes one one-hundredth of this. Since the author's apparatus used about 0.03 cu. m. (1 cubic foot) of gas per hour, this meant a distribution into the gas during a period of 1 hour of not more than 0.03 ml. of pure nitric oxide gas. Owing to the necessity of especially preparing a nitric oxide–free gas, there were distinct limitations upon the amount of gas it was practical to waste. On the other hand the nitric oxide could not be diluted with nitrogen with impunity because of the traces of oxygen that this gas usually contains and which would react with some of the nitric oxide. Therefore, while in actual operation the figure of 0.03 ml. of nitric oxide per hour was increased somewhat by dilution, etc., the additions of nitric oxide–bearing gas to the main gas stream were seldom more than 0.1 to 0.2 ml. per hour and sometimes much less. A flow sheet of the apparatus used in making this synthetic sample appears in Figure 1.

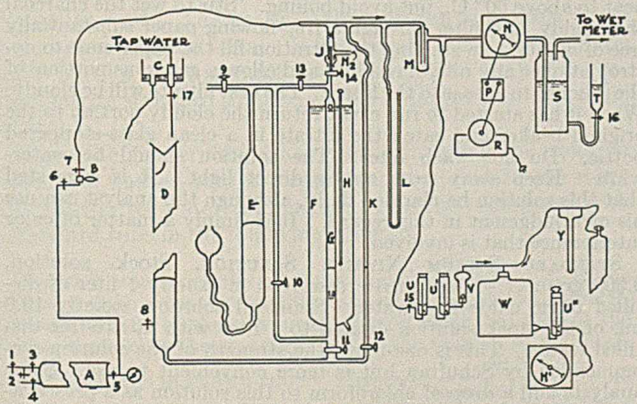

FIGURE 1. APPARATUS FOR MAKING AND ANALYZING SYNTHETIC SAMPLES OF NITRIC OXIDE IN COKE-OVEN GAS

The gas impounded in tank *A* at 2.1 kg. per sq. cm. (30 pounds per square inch) gage pressure, as previously described, passes through the service governor, *B*. This is a weight-type, "pounds-to-inches" governor. After passing the point of nitric oxide enrichment in the manifold, *J*, the gas is mixed as shown in an empty 19-mm. (0.75-inch) test tube, *M*. Immediately following this mixing, an aliquot is withdrawn for analysis. It was originally hoped that the gas could then be simply passed through a seal, measured, and wasted. However, this nitric oxide metering apparatus requires constancy of flow and constancy of pressure of a fairly high order throughout the period of the test, and the nearer the pressure is to that of the atmosphere the better the results obtained. A change of 2.5 mm. (0.1 inch) of water pressure at *L* has a marked effect on both gas rates. With the pressure at *A* varying from 30 pounds or more down to a few inches of water, the gas governor could not quite meet the requirements.

The combination *N*, *P*, *R* was, therefore, designed and installed. *N* is an ordinary 0.1-cu. foot wet test meter. The large indicating hand and meter shaft are soldered to the low-speed shaft of a worm-type reducing gear (200 to 1 ratio). The high-speed shaft of the reducer is directly connected to the shaft of a synchronous motor taken from a Saja pump, such as is used with aquariums. Since these meters have only about a 13-mm. (0.5-inch) water seal, the water in the meter was adjusted to a point slightly above its normal level to provide a somewhat greater margin of safety. After *N*, the gas passes through a water seal, *S*, and is wasted through a 0.1-cu. foot wet test meter not shown in Figure 1. The water level in *S* can be adjusted by means of tube *T* and cock 16. At the start the gas is turned into the line and the water level in *S* adjusted so that the amount of gas passing through *N* (with motor running) as shown by the waste gas meter reading is approximately equal to the amount that would normally pass through *N* if the meter were traveling at this speed under normal metering conditions. For this mechanical setup the speed was fixed at 1.7 liters (0.06 cu. foot) per minute. The net effect obtained then is that the meter *N* at the start is running approximately free or perhaps actually slightly impeding the gas flow; but as the pressure dies down during the run, the meter tends to pick up the load slightly. At intervals during the operation the waste meter is timed and factors calculated for *N* to arrive at a measure of the correct gas flow. These factors indicated that during a period of 4 hours the line pressure gradually dropped 5 to 8 mm. (0.2 to 0.3 inch) but giving a drop of only 2 or 3 per cent in gas flow.

The bottom of the system *D*, *G*, *K* is sealed with pure dry mercury. *D* is a glass tube 5 cm. (2 inches) in diameter and about 2.1 meters (7 feet) long. *G* is a 1-ml. pipet (Bureau of Standards certified) having a graduated scale about 18 cm. (7 inches) long and divided into 100 parts. It is therefore possible to read the scale to 0.001 ml. with fair accuracy from a mechanical standpoint. The capacity of the tube at a large number of points was determined gravimetrically and compared with the Bureau of Standards' delivery calibration. The accuracy of the scale was found to be well within the over-all accuracy of the work. The buret, *G*, is sealed into the system as shown. The capacity of the unknown gas volume at the top enclosed between the top of the scale and cocks 13 and 14 was determined for use in calculating the effect of temperature and pressure changes on the volume of nitric oxide delivered to *J*. *F* is a water jacket; *H* is a thermometer; *K* is a pressure-compensating device; *L* is a water-filled manometer. The top of *G* above cock 14 is 1-mm. capillary tubing, drawn down at the tip to a microscopic opening. In this instance the orifice was 0.01 mm. in diameter or less as determined by microscopic measurement. This provided a linear velocity for the nitric oxide at the tip sufficient to prevent diffusion of the coke-oven gas backward into *G*. The diffusion rate of this gas is of the order of magnitude of about 15 cm. per minute under these general conditions. The tip of *G* extends into a somewhat constricted arm of a T leading into the main gas line. Through a side arm a small amount of nitrogen is introduced to carry the nitric oxide definitely and regularly into the gas stream.

The storage tube, *E*, is filled with pure dry nitric oxide prepared in a manner described later, whence it is transferred to flush and to fill *G* as desired. During all tests, cocks 9, 10, 11, and 13 and the contiguous portions of the 2-ml. capillary tubes leading from them are filled with mercury, thus providing a positive gas seal. Care was always taken to keep a slight positive pressure differential on the nitric oxide at all times. During operation the nitric oxide is forced from *G* into *J* by allowing water from the overflow device, *C*, to run slowly down the sides of *D* onto the surface of the mercury. In this manner the apparatus could be run continuously for a period of 7 hours or more.

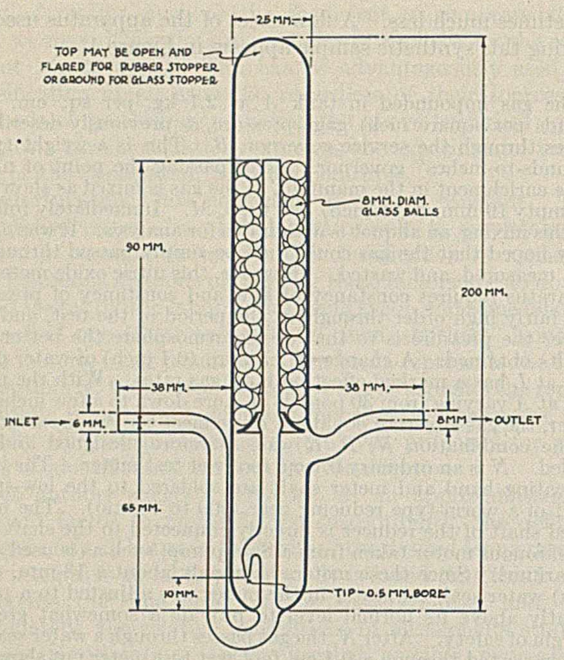

Figure 2. Absorber with Low Back Pressure

The measurement of nitric oxide added to the gas is accomplished by reading the mercury level in *G* at the beginning and at the end of any test together with the line pressure, barometric pressure, and temperature. The difference between the two corrected gas volumes represents the volume of gas (N. T. P.) forced from *G*. In connection with corrected meter readings and dilution factors, if any, the p. p. m. of nitric oxide in the gas can be calculated with considerable accuracy. The metering apparatus was run under conditions such that the temperature changes rarely amounted to more than 0.5° C. per day. The probable over-all accuracy of the metering apparatus is believed to be about 2 per cent.

For the preparation of the nitric oxide a nitrometer of the DuPont type was used. For the lower range of concentrations the nitric oxide was diluted with nitrogen. It was considered unsafe to use dilutions greater than 1 to 10, and in preparing even these dilutions a special technic was employed. A solution of a known amount of potassium nitrate was prepared and analyzed by means of the nitrometer. A measured amount of nitrogen was then introduced into the clean nitrometer, followed by a measured amount of the potassium nitrate solution and the required amount of sulfuric acid. The nitrometer was then shaken for 2 minutes and allowed to stand for 15 to 30 minutes with occasional shaking. The gas was then ready to transfer to tube *E* of the metering device through cock 9. *E* was always first flushed with nitrogen and then two or three times with the nitric oxide mixture to remove traces of oxygen before the final filling.

After passing through the mixing tube, *M*, the nitric oxide–enriched gas is ready for analysis or other study. Various analysts working separately found it desirable to make changes in the details of the Schuftan procedure as originally published. The bubbler tube scrubbers were not satisfactory from an efficiency standpoint and more efficient scrubbers were substituted. Also many analysts felt that the apparatus should be protected from any ammonia that might get into the line at times and which in any considerable quantity would certainly ruin the test. All these changes and additions increased the back pressure on the apparatus until the average Schuftan apparatus was operating under 0.10 to 0.15 kg. per sq. cm. (1.5 to 2.0 pounds per square inch) pressure. This usually required a pump which was disadvantageous from several viewpoints.

For these reasons the writer used a scrubbing apparatus which has previously been described by him (*3*). It is designed especially for removing a very small amount of substance from a large amount of gas with a small amount of reagent and with a very low operating back pressure [usually less than 13 mm. (0.5 inch) of water]. A sketch of this scrubbing apparatus is shown in Figure 2.

In the lower right-hand corner of Figure 1 is shown a flow sheet of the analytical apparatus as finally designed.

Materials Required

For the operation of this method the following materials will be required:

Apparatus

2 Shaw absorbers (*3*), rubber stopper type
1 Shaw absorber (*3*), glass stopper type
1 aspirator bottle, 2-liter capacity, with straight sides, approximately 11.5 cm. (4.5 inches) in diameter × 18 cm. (7.25 inches) to base of neck. Kimball's "Exax"
1 flowmeter, capable of indicating 0.00198 cu. meter (0.07 cu. foot) per hr.
1 wet test meter (0.1-cu. foot type)
1 set Nessler tubes, tall form, 50-ml. capacity
0.5 kg. (1 pound) solid glass balls, 5 mm. (Eimer and Amend catalog No. 17602)
1 calcium chloride drying tube 12.5 cm. × 1.5 cm. (5 × 0.61 inches) (Eimer and Amend Catalog No. 22532)
1 glass tee, 6 mm.
3 tool clamps, adjustable spring type (convenient for holding absorbers)
1 small gas governor (No. 28, Fisher Governor Company, Marshalltown, Iowa, optional)
Necessary supports and general laboratory apparatus
Suggested: 1 iron stand 12.5 × 20.0 × 50 cm. (5 × 8 × 20 inches) (Eimer and Amend catalog No. 31882); 4 clamps, 22.5 cm. (9 inches) (Eimer and Amend catalog No. 20206); 4 clamp holders (Eimer and Amend catalog No. 20240).

Chemicals

Sulfuric acid, c. p.
Potassium hydroxide, c. p., large pellets
Sodium nitrite (Baker and Adamson analyzed)
m-Phenylenediamine (Eastman technical) (1,3-benzenediamine)
Activated charcoal, Nuchar, powdered
Oxygen
Acetic acid, glacial
Acetone, c. p.

Solutions

Sulfuric acid, 10 per cent by volume of 95 per cent acid (approximately)

Potassium hydroxide 30 per cent solution (approximately)

m-Phenylenediamine Reagent Solution. Pour hot water on 5.0 grams of the crystals. Stir to dissolve, add 25 ml. of glacial acetic acid, and dilute to 1 liter. This solution will keep more or less indefinitely in a stoppered bottle. Portions must be clarified with charcoal before use, since light and air slowly cause a darkening of the solution. To clarify, place 300 to 500 ml. in a 1-liter beaker, add about one heaping teaspoonful of Nuchar, heat to above 60° C., but avoid boiling. Stir to wet the charcoal thoroughly, and filter through a free-flowing paper substantially free of nitrite. In starting the filtration fill the paper cone to destroy at once any nitrite residues and allow a generous portion of the Nuchar to pass into the filter. The first filtrate will be cloudy. When it has started to run clear, return the cloudy portion to the original beaker and catch the filtrate in a clean glass-stoppered bottle. Do not wash filter. The solution should be water-white. Keep away from strong direct light. It is suggested that this solution be clarified daily, although the analyst can use his own judgment in this regard. It is simply a matter of color interference that is involved.

Standard Sodium Nitrite Solution. Stock solution, 0.300 gram of sodium nitrite dissolved in exactly 1 liter of distilled nitric oxide–free water. Standard solution, exactly 10.0 ml. of the stock solution diluted to 1 liter with nitrite-free distilled water. This is one-tenth the strength of the solution recommended by Schuftan but is more convenient to use. Some analysts add a drop of chloroform to this solution as a preservative. The ultimate standard for this work is silver nitrite ($AgNO_2$) prepared according to Treadwell and Hall (*4*).

Mechanical Arrangement of Apparatus

The general idea of the procedure is to pass a known amount of gas through scrubbers containing acid and both liquid and solid alkali, to mix it with a known amount of oxygen (5 per cent in this case) and, after subjecting it to a time delay, to scrub it with an amine and read the color formed.

Accordingly, on a suitable support in series arrangement the two rubber-stoppered absorbers, *U* and *U'* (Figure 1), are set up followed by the calcium chloride tube, *V*, which delivers into a glass T, one end of which is fitted into the top of the 2-liter delay bottle, *W*, and the other end of which is connected to the oxygen supply. Following the delay bottle the glass-stoppered absorber *U''* is placed. This in turn is connected to deliver to the 0.1-cu. foot wet test meter, *N'*. Oxygen is introduced at the point above mentioned after having been measured by flowmeter *Y*. The calcium chloride tube, *V*, is in an inverted position. The large end at the bottom is closed by a rubber stopper carrying a glass lead tube which extends about 25 mm. (1 inch) into the calcium chloride tube beyond the edge of the rubber stopper. The end of the lead tube is shielded by a glass thimble. This makes a simple and effective potassium hydroxide drying tube.

During operation the first scrubber, *U*, contains 10 ml. of the dilute sulfuric acid plus 2 or 3 ml. of the *m*-phenylenediamine reagent. Scrubber *U'* contains 15 ml. of the potassium hydroxide solution. The calcium chloride tube contains 5 to 8 cm. (2 to 3 inches) of potassium hydroxide pellets. Bottle *W* is empty and dry. The glass-stoppered absorber, *U''*, contains 10 ml. of the *m*-phenylenediamine reagent solution.

This apparatus may be set up around an ordinary laboratory iron stand with iron clamps, in which case it is readily portable and easily cleaned, or it may be mounted on a board with the bottle in the rear. With the original Schuftan arrangement a large bottle filled with an explosive gas mixture was used and the board was more or less mandatory. The present bottle is much smaller, and the mixture containing only 5 per cent of oxygen is outside the explosive range for this mixture as determined by the United States Bureau of Mines.

Procedure

Gas is turned into the apparatus at such a rate that, when combined with 5 per cent oxygen, it will undergo in the bottle an average delay period of 3 minutes. This represents a flow of about 37.7 liters (1.33 cu. feet) of coke-oven gas per hour and 2 liters (0.07 cu. foot) of oxygen per hour.

Before connecting up the *m*-phenylenediamine absorber, the gas mixture is allowed to flow through the apparatus at least 20 minutes to establish equilibrium.

The absorber, *U''*, is then placed in the line, the meter read, and the gas rate adjusted if necessary. The test is allowed to run until a conveniently readable color has developed in the reagent solution in *U''*. This time may vary from a few minutes to several hours, depending upon the concentration of nitric oxide in the gas. The absorber is then removed and the meter read. The gas flow through the apparatus is not interrupted between tests. It is suggested that the optimum depth of color is the amount developed by 3 to 5 ml. of the sodium nitrite standard solution (0.003 gram per liter of sodium nitrite).

When the gas scrubbing has been completed, the absorber content is washed into a Nessler tube, diluted to the mark with nitrite-free water, and mixed. It is then compared with a standard tube in the following manner:

Choose a standard tube having a slightly paler color than the unknown tube. Into a roughly calibrated graduated cylinder, remove portions of the unknown solution until the color of the unknown matches the standard. Note the number of milliliters of solution in the unknown tube. Then $\frac{50}{\text{ml. in unknown tube}} \times$ ml. of sodium nitrite solution in standard tube = ml. of standard solution equivalent to the color developed in the test.

Both the amount of *m*-phenylenediamine and the concentration of acetic acid in these colored solutions are capable of affecting the depth of color. It is therefore recommended that for the final comparisons the tubes compared shall contain the same volume and depth of liquid and the same concentration of reagents.

The standard tube mentioned above is prepared by measuring into it with a Mohr pipet a chosen number of milliliters of the dilute sodium nitrite solution (0.003 gram per liter of sodium nitrite) and following with this 10 ml. of the *m*-phenylenediamine reagent solution. The tube is shaken to mix and let stand about 20 minutes. It is then diluted with nitrite-free distilled water to the mark, and upon mixing it is ready for use. The tubes containing 2, 3, 4, and 5 ml. of standard solution are usually most convenient.

From the above data the concentration of nitric oxide in the gas can be calculated. In most cases, the probable error of this comparison can be held under 3 per cent without great difficulty.

Calculations

Assume the following test data: Volume of mixed gas reduced to 60° F. and 30 inches of mercury = 0.444 cu. foot. Color developed during test = 4.2 ml. of standard solution.

Then $\frac{4.2 \times 0.0388}{0.444} = 0.37$ p. p. m. of nitric oxide in coke-oven gas (observed value).

Where gas volumes are corrected to 0° C. and 760 mm. of mercury, use factor 0.0362 instead of 0.0388.

Discussion of Method

Most analytical methods are empirical. This method is markedly so. Any change in apparatus or procedure is likely to produce a change in results, and even the shape of the bottle is important. The indicator is ultrasensitive. Ultrasensitive technic must, therefore, be employed.

This method is designed for use with coke-oven gas. It is believed that it cannot be used for water gas analysis without some change.

Griess reagent apparently cannot be used interchangeably with *m*-phenylenediamine. While the former is certainly more delicate, tests by various analysts in the author's organization indicate that it is less active at normal room temperatures.

The *m*-phenylenediamine reagent should be shielded from strong light which causes a darkening effect, giving falsely high results. It may be handled with impunity indoors or out of direct sunlight. Out-of-doors, it is recommended that the container be covered with a cloth or otherwise shielded. Any damage due to light is usually evident to the observant eye. This may have been the source of off-colors frequently reported in the early days of this work.

Because of a purging lag which is more or less inherent in this type of setup, the apparatus cannot be used on gas of high nitric oxide content and then after a short purge be safely used on gas of a low nitric oxide content. The apparatus must first be cleaned. This consists in rinsing out and replacing all chemicals and in rinsing out the delay bottle with water and with acetone, and in blowing with air or other nitric oxide–free gas to remove the acetone thoroughly. Small amounts of acetone seriously interfere with color formation in the *m*-phenylenediamine. This cleaning process requires about 10 minutes. It is recommended that this cleaning be done daily.

With this method of procedure, the observed value for nitric oxide was found to be almost exactly half the true value. Fairly authentic tests run at three different coke plants indicated that this factor is common to all of them.

Flowmeters have been used by some workers for measuring the gas as well as the oxygen. The writer has observed instances where the flowmeter orifice has caused a deposit of gum from the gas. A flowmeter is, therefore, not recommended for this purpose.

The small gas governor with spring-type adjustment affords a convenient, though not entirely necessary, means of keeping a constant pressure at the inlet of the apparatus, thus aiding gas flow adjustment. It would, of course, be open to the same objection as the flowmeter. It is possible that both might be placed after the apparatus.

The foregoing method applies only to gas carrying small amounts of ammonia and hydrogen sulfide, as will be realized upon considering the quantities of acid and alkali employed. If it is desired to use the method on unpurified gas, it is suggested that the gas be first passed through a single bubbling bottle each of the acid and alkali solutions. The bulk of the solutions should be no greater than necessary and the bottles should be as nearly full as convenient. The principal purpose of the potassium hydroxide appears to be the removal of active sulfur compounds and the control of humidity.

Apparatus of this type determines neither suspended gum particles nor nitrogen peroxide. It is obvious that either of these substances existing in the gas sample in a form that can be absorbed will be removed before the gas reaches the delay bottle. Ordinarily, though not always, these substances are present in negligible amounts only.

Some of the nitric oxide in the gas goes through the apparatus untouched, as shown by the fact that when two of these analytical setups are run in series, a small amount of color will be formed in the second. However, this seems to be a fairly constant percentage of the whole and is taken care of by the factor of 2 previously mentioned. This factor is an over-all correction figure derived from nitric oxide found divided by nitric oxide added.

It is customary to report observed values rather than actual values for nitric oxide, which in this case are half the actual. It is therefore important to indicate whether figures used are observed or actual.

The writer prefers to report the nitric oxide in parts per million (by volume). It is a universally understood unit, in plant work it is usually a simple decimal rather than a mixed number, and it has the advantage of being a scientifically correct and accepted nomenclature.

The 3-minute contact period was chosen as the result of a series of experiments which showed that the percentage of nitric oxide recovered increased very sharply up to a period of about 2 or 2.5 minutes' delay time and then gradually dropped off. A 3-minute period, therefore, gave a point of approximately maximum recovery, and at the same time allowed for small rate variations on either side of the theoretical without causing large errors in the results obtained. Figure 3 shows the result of this series of tests.

The oxygen required in the delay bottle is not a critical amount. The percentage recovery of nitric oxide was about the same with a concentration of 0.5 per cent and with one of 50 per cent.

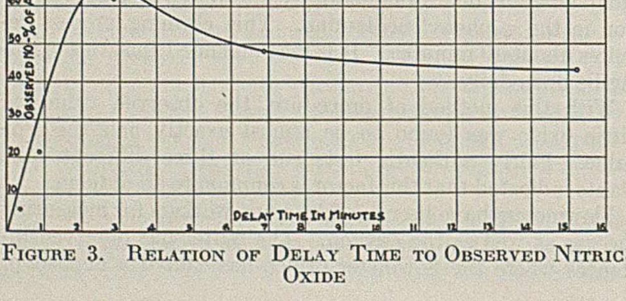

Figure 3. Relation of Delay Time to Observed Nitric Oxide

Table I. Effect of Temperature upon Nitric Oxide Analysis

Expt. No.	Observed NO, Per Cent of Actual	Actual NO in Gas	Temperature
		P. p. m.	° *C.*
69 T1	58	0.11	48
T2	55	0.11	48
70 T1	56	0.11	50
71 T1	52	0.12	25
T2	58	0.13	48
72 T1	53	0.16	23
76 T1	52	1.12	23
77 T1	60	1.07	44
T2	47	1.08	48
T3	53	1.06	50
T4	48	1.10	50
T5	52	1.07	49
T6	47	1.08	49

Table II. Accuracies Attained

Expt. No.	Added NO (Actual)	Observed NO, Per Cent of Actual	Remarks
	P. p. m.		
R-367-30	0.000	0.000	No color during 7-hr. run
E-63	0.057	60	
E-64	0.11	52	
E-64	0.12	51	
E-71	0.12	52	
E-72	0.16	53	
E-94	0.89	55	
E-94	0.91	54	
E-94	0.88	56	
E-95	0.90	57	Per cent of oxygen = 5.0
E-95	0.94	58	Per cent of oxygen = 9.2
E-93	0.93	52	
E-93	0.95	52	
E-98	1.02	57	
E-S125	1.51	51	Gas from plant II
E-S125	1.51	53	
E-96	1.91	53	
E-96	1.89	56	
E-96	1.84	53	

The delay bottle should be dry at all times. The gas in the bottle should be substantially below its saturation point. Very erratic results can be obtained by ignoring this point.

A sample line should never be heated during the time the nitric oxide apparatus is on the line. It is suggested that the sample lines be oversize and as short as possible and arranged so that they may be blown out with steam and cooled and purged before the nitric oxide apparatus is put on the line. Very high results can be obtained by heating a fouled sample line.

The apparatus should be used in a room having a reasonably even temperature. It was not observed by the writer that ordinary changes in temperature had any very drastic effect on the results. It is, however, possible to produce incorrectly high results by effecting a sharp and unusual rise in temperature, especially if the apparatus is unclean or has been operating for a long period. It is also true that at greatly reduced temperatures the *m*-phenylenediamine reagent appears to lose some of its activity. It is therefore recommended that when working below 18° C. (65° F.) low temperature be compensated for. It is believed that this condition will be encountered so seldom that it is unwise to burden the regular setup with a thermostatically controlled container.

A great deal of discussion has centered around the desirability of putting the setup under thermostatically controlled conditions. To do this properly would be expensive and would result in a cumbersome setup. The writer does not believe it is necessary. With a clean setup, good results can be obtained at advanced temperatures as Table I will indicate. During this test series, it appeared that the heated apparatus tended to give more erratic results than the unheated. In view of the conditions involved, this is not especially surprising.

Table II gives a general idea of the accuracies attained.

In E-95, the per cent of oxygen was nearly doubled without apparent effect upon the recovery of nitric oxide.

At a certain large coke plant, not included in the previous discussion, the gas was being experimentally treated for nitric oxide removal on a full plant scale. It was known that the method employed gave uniform and nearly complete removal of nitric oxide under optimum conditions. A series of routine efficiency tests, run daily upon this treater by this method for a period of about one week, showed removal efficiencies of 94, 93, 97, 93, 96, and 95 per cent.

Summary

An improved method for determination of the traces of nitric oxide usually found in coke-oven gas and the procedure used to check this analytical method, by adding extremely small measured amounts of nitric oxide to nitric oxide-free coke-oven gas, have been described.

By use of this analytical method approximately one-half of the nitric oxide actually in the gas is recovered and determined by a colorimetric method. Therefore, a factor of 2 is applied to the observed value to give the actual content of nitric oxide.

The effects of variables such as delay time, added oxygen, temperature, etc., have been described.

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Titration of Silver with Potassium Iodide

Ceric Ammonium Sulfate and Starch as Indicators

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According to Shapiro (*4*), in the determination of chlorides by the Volhard method, excess silver may be titrated in a nitric acid solution with potassium iodide. The end point is detected in the presence of starch when the nitric acid oxidizes the iodide to iodine. Schneider (*3*) suggests the use of palladium nitrate as an indicator, noting the end point by the formation of a red-brown precipitate of palladous iodide. Fleury and Courtois (*1*) and Josien (*2*) recommend the use of starch-iodine–potassium iodide solution, in which the silver solution must be added to the starch-iodine–potassium iodide solution.

Table I. Titration of Silver

Acidity *N*	0.1 *N* KI *Cc.*	0.1 *N* KI with Blank Correction *Cc.*
10 cc. of 0.1 *N* $AgNO_3$ solution in a volume of 110 cc.		
0.2	10.14	10.04
0.5	10.14	10.04
1.0	10.16	10.06
2.0	10.18	10.08
3.0	10.16	10.06
20 cc. of 0.1 *N* $AgNO_3$ solution in a volume of 110 cc.		
1.0	20.08	19.98
2.0	20.11	20.01
3.0	20.12	20.02

Table II. Titration of Silver Nitrate

(10 cc. of 0.1 *N* $AgNO_3$ solution in the presence of cupric and ferric ions. Volume approximately 110 cc., acidity approximately 0.5 *N*)

0.1 *N* $CuSO_4 \cdot 5H_2O$ and $FeNH_4(SO_4)_2 \cdot 12H_2O$ *Cc.*	0.1 *N* KI *Cc.*	0.1 *N* KI with Blank Correction *Cc.*
$CuSO_4 \cdot 5H_2O$		
10	10.10	10.00
30	10.13	10.03
50	10.14	10.04
$FeNH_4(SO_4)_2 \cdot 12H_2O$		
10	10.15	10.05
30	10.12	10.02
50	10.17	10.07
50 $FeNH_4(SO_4)_2 \cdot 12H_2O$ 50 $CuSO_4 \cdot 5H_2O$	10.12	10.02

The method described by the authors consists of the titration of silver with potassium iodide in the presence of ceric ions and starch. Oxidation of the iodide ion to iodine by the ceric ion is not permanent until the end point is reached. During the course of the titration a blue color appears, but is immediately discharged upon stirring. The method gave good results in the presence of ferric and cupric ions.

Analytical Procedure

Ten or 20 cc. of a 0.1 *N* silver nitrate solution were transferred to a 200-cc. beaker. To this were added water and a sufficient amount of sulfuric acid to give a volume of approximately 110 cc. (concentration of acid may vary from 0.2 *N* to 3 *N*), and then 3 cc. of 0.5 per cent starch solution and 0.1 cc. of an approximately 0.1 *N* ceric ammonium sulfate solution. It is important to add the sulfuric acid before the ceric ammonium sulfate. The silver was titrated with 0.1 *N* potassium iodide solution. The end point was sharp and easily detected when the last drop of potassium iodide gave a permanent blue-green color to the solution. Blank titrations were made under the same conditions omitting the silver nitrate. The blank consumed 0.1 cc. of the potassium iodide solution before a permanent color was obtained.

Summary

A method is described for the titration of silver with potassium iodide, using ceric ammonium sulfate and starch as internal indicators. The acid concentration may vary in the titration from 0.2 *N* to 3 *N* without appreciable error. The titration can be made in the presence of cupric and ferric ions.

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Turbidity in Sugar Products

IV. Preparation of Raw Sugar Solutions for Determination of Color and Turbidity

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IT HAS been shown previously (*5*) that the concentration of the turbidity present in a solution of a raw sugar may be measured, on the basis of transmittancy and Tyndall beam intensity, in terms of the specific absorptive index of an equivalent turbidity caused by particles of standard properties, and that the deviation in the properties of the particles actually present from those of the standard may be characterized by the "quality index" and by the dispersion quotient.

The question of determining the concentration of coloring matter or, in other words, of correcting the specific absorptive index of filtered solutions for the residual turbidity present was left open, but it was postulated that coloring matter shall be defined as that portion of the dispersed material which gives a Tyndall beam of zero intensity under the experimental conditions used. This correction for residual turbidity has been further investigated, and an attempt has been made to find a filtering material which would leave in the filtrate only the total coloring matter, as defined above. This opened up again the much discussed problem of the removal of turbidity and coloring matter by filtering agents, which was previously studied by Peters and Phelps (*3*), Brewster and Phelps (*2*), and by Balch (*1*).

Peters and Phelps did not give the detailed results of their investigation, but promised a later publication which has not yet appeared. In the original article they reported only comparisons between the specific absorptive index of solutions of about 52 to 53 Brix, filtered through specially prepared asbestos, and that of solutions of about 1 to 7 Brix, mixed with kieselguhr and filtered through paper. They found that the latter were always very turbid when examined in the dark room, whereas the highly concentrated asbestos filtrates showed only a faint Tyndall cone. The $-\log t$'s of the kieselguhr filtrates, at various wave lengths throughout the visible spectrum, were irregularly higher or lower than the corresponding values for the asbestos filtrates, and these discrepancies were ascribed to selective adsorption by the kieselguhr, to the presence of finely divided kieselguhr in the dilute filtrates, and to differences in the colloid equilibrium of dilute and concentrated solutions. Peters and Phelps concluded that a correct measure of the coloring matter could be obtained only by their method of filtering concentrated solutions through asbestos.

Brewster and Phelps rejected purified standard Filter-Cel even for the filtration of concentrated solutions, on the ground that it removes actual coloring matter, because decolorization is more extensive when more Filter-Cel is used.

Balch, on the other hand, concluded from his experiments that Filter-Cel does not adsorb coloring matter, or at most very little, and that it is permissible to use this agent for colorimetric analysis, or for preparing solutions to be used as standards of comparison for turbidity measurements.

In view of these divergent opinions, the entire subject of preparing sugar solutions for colorimetric analysis has been reinvestigated. The factors studied were concentration of the sugar solution, cell thickness, colloid equilibrium, and the effect of various filtering agents on the transmittancy and Tyndall beam intensity of the resulting solutions.

Concentration of Sugar Solution

The necessity of using, for colorimetric analysis, as high a concentration of dry substance as is compatible with reasonably rapid filtration has been well shown by Brewster and Phelps, who advocate solutions of at least 60 Brix, which is somewhat higher than the minimum figure given by Peters and Phelps. The proper choice of concentration is important not only for solutions to be filtered, but also in preparing raw sugar solutions for turbidity determinations. A 65 Brix solution of a raw sugar, when strained through a 250-mesh bronze screen to remove coarse suspended matter, gave consistently higher $-\log t$ values at three selected wave lengths in the blue, green, and red, than a 60 Brix solution, strained the same way; the dispersion quotients for red to green were lower, while those for blue to green changed irregularly. The Tyndall beam intensity and its dispersion quotients were also affected, changes in either direction being observed. This makes it necessary to standardize conditions for both color and turbidity measurements, and a concentration of 60 Brix has been chosen by the writers, because this permits a fairly rapid filtration even for poorly filtering sugars. It is also advisable to remove coarse suspended matter by centrifuging under standard conditions rather than by straining through a screen, because the coarse suspended matter forms a filter bed which is liable to retain varying quantities of the more highly dispersed particles whose quantity is to be measured.

Cell Thickness

If turbidity measurements are to be made according to Balch's or the writers' method, it is necessary to keep not only the concentration of dry substance but also the cell thickness constant. The constants in the formulas given in the preceding article of this series (*5*) apply only to the cell thickness used, 2.46 mm. No attempt has been made so far to derive formulas for varying thickness, but the fact has been well established that for turbid colored solutions there is no simple relationship between depth of layer and $-\log t$ or Tyndall beam intensity. When only filtered solutions are to be used for color determination, the depth of layer may of course be varied as desired.

Colloid Equilibrium

Possible changes in the colloid system in the solutions, between the time of preparation and the time of measurement, must be given proper consideration. The writers found irregular changes in the $-\log t$ as well as the Tyndall beam intensity, when 60 to 65 Brix solutions were allowed to stand in the refrigerator for 2 or more days. The changes were not very pronounced, but it has been found advisable to make the optical measurements as soon as colloid equilibrium is established, which is about 2 hours after the solutions have been prepared.

Some very interesting observations have been made regarding the effect which a change in water or sucrose concentration has on the colloid equilibrium. If an aqueous solution of caramel is carefully filtered through purified Filter-Cel, and then mixed with an equal volume of a 60 Brix raw sugar solution, which has likewise been filtered through Filter-Cel, the $-\log t$ of the mixture is higher than when the unfiltered solutions of caramel and raw sugar are first mixed and then filtered with Filter-Cel. The same is true to even a greater extent when pure sucrose or water is substituted for the raw sugar, as may be seen from Table I.

The dilution with water produces partial flocculation of the caramel particles, and the larger particles are removed by subsequent filtration. It is difficult to understand, however, why mixing the caramel solution with a 60 Brix sucrose solution, which amounts to addition of a protective colloid, should have the same effect, and of greater magnitude, as dilution with water. The probable explanation is that there is an interaction between the sucrose molecules and the caramel particles, with the formation of larger aggregates, which are then removed by filtration with Filter-Cel. If this explanation is correct, then it further follows that in a raw sugar solution similar aggregates between the sucrose and the coloring matter are already preformed, and less sucrose is available to combine with the caramel. This would explain why in the case of the raw sugar the difference in the $-\log t$'s was so much smaller than in that of sucrose or water. The same effects were noted when powdered glass (see below) was used as the filter medium, instead of Filter-Cel. After a mixture of caramel and sugar sirup had once been filtered through Filter-Cel, a second filtration through powdered glass had no further effect.

TABLE I. EFFECT OF CHANGE IN WATER OR SUCROSE CONCENTRATION

	Solutions Filtered Separately, Then Mixed, $-\log t$	Solutions Mixed and Mixture Filtered, $-\log t$
Caramel plus raw sugar solution	0.516	0.504
Caramel plus sucrose solution	0.371	0.258
Caramel plus water	0.374	0.275

In experiments similar to those described above, the aqueous caramel solution was replaced by a 60 Brix solution of a dark raw sugar. When this solution was treated with a 60 Brix solution of another, light colored sugar, the same $-\log t$ at 560 mμ was obtained, no matter whether the solutions were first filtered separately and then mixed, or first mixed and then filtered.

The results of the tests with caramel solution and with sugar sirups confirm the conclusion reached by Peters and Phelps that dark colored sugar products like molasses must not be diluted with water previous to color determination, but with a white sugar sirup.

As far as the $-\log t$ is concerned, the molasses could first be filtered separately, if that were physically possible, and then mixed with the filtered white sugar sirup, or else it could first be mixed with the white sugar sirup and the mixture then filtered, as is actually done in practice. There is, however, a slight difference in the colloid equilibrium of the mixtures prepared by the two methods, as is evidenced by Tyndall beam measurements in the following experiment:

A 60 Brix raw sugar solution was filtered through purified Filter-Cel, and then mixed with an equal volume of 60 Brix white sugar sirup which had also been carefully filtered (mixture *A*). Another, unfiltered portion of the raw sugar sirup was first mixed with an equal volume of filtered white sugar sirup, and the mixture filtered through Filter-Cel (mixture *B*). Tyndall beam readings were then taken with the Pulfrich photometer in cells of the same thickness, and the values given in Table II were obtained, in per cent of the intensity of the standard block, immediately after preparation, and again after equilibrium was established.

TABLE II. EFFECT OF METHODS OF PREPARATION

	Immediately after Preparation		At Equilibrium	
Wave Length	*A*	*B*	*A*	*B*
529 mμ	29.0	42.0	34.7	18.9
621 mμ	138.5	265.6	177.9	87.0

After equilibrium had been established, method *B*, which is the one usually followed, gave a solution better fitted for colorimetric analysis.

Filtering Materials

In the new investigation on filtering materials adapted for colorimetric and turbidimetric analysis the following substances were used: asbestos, Filter-Cel, filter paper, Jena fritted-glass funnels, the Seitz filter, ground glass, and silica gel.

The asbestos, XXX grade, was purified and used for the preparation of the samples as described by Peters and Phelps (*3*).

The Filter-Cel was the analytical filter aid marketed by the Johns-Manville Corporation. To purify it further, 75 grams were boiled with a mixture of 100 cc. of concentrated hydrochloric acid and 900 cc. of distilled water, then filtered hot and thoroughly washed with hot water. This treatment was repeated three times, and finally the material was dried and ignited in a muffle furnace.

Jena fritted-glass funnels of various porosities were employed, mostly as a backing for asbestos, instead of Gooch crucibles, but the No. 4 type was also used directly. The filter paper was S. & S. No. 575.

The Seitz filter was the small laboratory model pressure outfit. The disks furnished by the manufacturers were used, and the filtrations were carried out with the aid of compressed nitrogen, at pressures up to 5.62 kg. per sq. cm. (80 pounds per sq. inch), depending on the filterability of the solution.

The Jena ground glass was the grade G 20, No. 4, having an average particle diameter of 5 to 10 mμ. (The writers thank Murray Yawitz of the Fish-Schurman Corporation for his generous coöperation in supplying the ground glass and in investigating the Jena fritted-glass funnels adaptable for their work.)

The silica gel, kindly furnished by the Silica Gel Corporation, was the air-floated, medicinal type. It was found to be slightly acid, and was therefore boiled out twice with distilled water, filtered after each boiling, washed, dried, and ignited.

The Seitz apparatus was found to be an efficient ultrafilter. It easily reduces the turbidity in raw sugar solutions to that found in distilled water, but visibly decolorizes them. As an example, the figures in Table III are given for $-\log t$ and Tyndall beam intensity, *R*, of a 60 Brix raw sugar solution, treated as specified.

TABLE III. EFFICIENCY OF SEITZ FILTER

	log *t*		*R*	
	529 mμ	621mμ	529 mμ	621 mμ
Centrifuged	2.814	2.649	1157	4098
6 times through asbestos	2.424	1.257	354	1376
Same, then through Seitz filter	2.010	0.908	98	297
7 times through Seitz filter	1.463	0.656	35	90

Since the Seitz filter evidently removes a large proportion of the coloring matter, and since it requires pressure filtration, its use was not further investigated.

An example of the effect of some of the other filtering materials, as compared to asbestos, is shown in Table IV.

TABLE IV. EFFECT OF FILTERING MATERIALS

	$-\log t$, 560 mμ	$-\log t$, 620 mμ
Asbestos	1.187	0.672
Filter-Cel	1.062	0.599
Jena funnel No. 4	1.322	0.781
Ground glass, on Jena funnel No. 4	1.122	0.616
Filter paper	1.378	0.818

Ground glass gave a lighter filtrate than asbestos filtration, but was not as efficient as Filter-Cel. The Jena funnel No. 4 produced a much darker filtrate, and the filter paper a still darker one. In other experiments it was found that ground glass and Filter-Cel combined give practically the same result as Filter-Cel alone. When ground glass was used in connection with the Seitz filter, it reduced the Tyndall beam intensity to about one-half that obtained with the Seitz filter alone, but the $-\log t$ was not measurably affected. None of these materials, except asbestos and Filter-Cel, offered sufficient advantages to warrant further study.

Comparative Tests of Asbestos, Filter-Cel, and Silica Gel

Silica gel, however, gave such encouraging results in preliminary trials that its effects were more thoroughly investigated, in comparison with asbestos and Filter-Cel, the filtering agents already widely used.

MECHANISM OF REMOVAL OF TURBIDITY. The first problem taken up was the mechanism of the removal of turbidity from turbid solutions, in order to ascertain whether this removal is due to mechanical filtration or to adsorption, and whether there is a distinct demarcation between turbidity and coloring matter.

Balch had previously found, contrary to Brewster and Phelps, that when a raw sugar solution was clarified with Filter-Cel, the same $-\log t$ was obtained, no matter whether 1, 2, or 3 grams of the filtering agent were added.

In repeating and extending the experiments of these previous investigators, a 60 Brix solution of a raw sugar was prepared, and 50-ml. portions were filtered with from 1 to 5 grams of asbestos, Filter-Cel, and silica gel. The asbestos was used in the form of a pad on a No. 2 Jena fritted-glass funnel, and was allowed to pack itself under the pressure of a water-jet filter pump. The Filter-Cel and the silica gel were mixed with the solution to be filtered, and the mixture was filtered through a double layer of S. & S. filter paper, No. 589, blue ribbon, on a 7-cm. Büchner funnel. The results, in terms of $-\log t$, at wave length 560, of the filtrates, are shown in Table V.

TABLE V. EFFECT OF QUANTITY OF FILTER MEDIUM

Filter medium, grams	1	2	3	4	5
Asbestos	2.032	1.616	1.711	1.784	1.711
Filter-Cel	1.592	1.470	1.476	1.457	1.461
Silica gel	1.456	1.435	1.429	1.436	1.422

One gram of asbestos allowed a large portion of the turbid material to pass through. The figures obtained with the larger amounts of asbestos are very irregular, and this is probably due more to differences in the packing of the asbestos in the pads than to any other cause, as will be shown below. The average of the results with 2 and 4 grams agrees closely with the figures obtained by using 3 or 5 grams.

In earlier unpublished work carried out by Peters and one of the writers, working side by side, portions of the same raw sugar solution, prefiltered after shaking with asbestos, were passed six times through the final pads. Each worker used his own asbestos, Powminco XX and XXX, respectively, pretreated as described by Peters and Phelps. It was at once noticed that the pad prepared by Peters gave a much more rapid filtration than the other, and the filtrate was visibly darker in transmitted light. The $-\log t$'s, found with the spectrophotometer from readings made by both observers, are given in Table VI.

TABLE VI. TESTS WITH ASBESTOS

Wave Length, mμ	Peters 1.5 Grams of XXX Asbestos $-\log t$	 Q-ratio	Zerban 2 Grams of XX Asbestos $-\log t$	 Q-ratio
480	2.530	1.99	1.903	2.15
560	1.272	1.00	0.885	1.00
660	0.594	0.47	0.340	0.38

The fact that XX grade asbestos was used as the raw material for the pad in one case, and XXX grade in the other, may have some bearing on the results, but it should be noted that Peters and Phelps and also Brewster and Phelps recommend either grade for colorimetric analysis. The principal reason for the discrepancies must be the packing of the asbestos, made manifest by the speed of filtration. The slow pad evidently had a sort of ultrafiltration effect, similar to that noticed with the Seitz filter. The *Q*-ratios show that the particular coloring matter taken out by this pad was different in character from that remaining behind in the filtrate. The important conclusion to be drawn from these experiments is that asbestos removes coloring matter selectively, and does not differ from Filter-Cel in this respect. Workers in the same or different laboratories will obtain different results on the same sugar if their asbestos pads are of different permeability, a property which is very difficult to standardize.

The values obtained with Filter-Cel, Table V, are more uniform than those with asbestos. Again, 1 gram removed less dispersed material than the larger quantities, but the maximum difference between the $-\log t$ figures for 2 to 5 grams is only 1.3 per cent, which is well within the limits of error. All the results are decidedly lower than the corresponding ones for asbestos filtration.

In the case of another raw sugar, 200 grams of 60 Brix solution were filtered with 6 grams (5 per cent of dry substance) of Filter-Cel, and the $-\log t$ was found to be 0.619. When the filtrate was again treated with 6 grams of Filter-Cel, the $-\log t$ was 0.628, the same within the limits of error. While these results confirm similar observations made by Balch, still other sugars (50 ml. of 60 Brix solution) were found to behave differently, as may be seen from Table VII.

TABLE VII. TESTS WITH FILTER-CEL

Sugar 3

Grams of Filter-Cel	0.000	0.125	0.375	0.750	1.375	2.500
$-\log t$ at 560 mμ	0.471	0.431	0.419	0.417	0.391	0.374

Sugar 4

Grams of Filter-Cel	1	2	3	4	5
$-\log t$ at 560 mμ	1.248	1.225	1.204	1.180	1.163

In both cases there is a gradual falling off in the $-\log t$ with increasing quantities of Filter-Cel. It is evident that for these two sugars more Filter-Cel than the maximum quantity tested would have to be used, in order to reach the limiting effect. This was also recognized by Balch, who states that the quantity of Filter-Cel to be used depends on the quantity and character of the suspended material present.

The same observation applies also to silica gel. Sugar 1, Table V, has the same $-\log t$, within a maximum error of 1 per cent, whether 2, 3, 4, or 5 grams of the filtering agent are used, and this effect was almost reached even with 1 gram. But other sugars (50 ml. of 60 Brix solution) gave the figures in Table VIII.

TABLE VIII. TESTS WITH SILICA GEL

Grams of silica gel	1	3	5	10
$-\log t$, 560 mμ, sugar 5	..	0.413	0.356	0.357
$-\log t$, 560 mμ, sugar 6	1.064	0.983	0.982	..

Sugar 5 required 5 grams for the maximum effect, sugar 6 only 3 grams. With sugar 1 (Table V) silica gel gave a lighter colored filtrate than the same quantity of Filter-Cel, and a much lighter one than asbestos.

The selective effect of the three filtering materials was investigated with four other raw sugars, by making transmittancy readings at three wave lengths with the Pulfrich photometer. The first two sugars were dark in color, but the solutions were not very turbid; the third was light in color, with medium turbidity; and the fourth was also light colored but highly turbid. The asbestos was used according to the Peters and Phelps technic, 50 ml. solution of 60 Brix being filtered six times through a pad of 3 grams of asbestos in a No. 2 Jena fritted-glass crucible. Filter-Cel and silica gel were used at the rate of 3 grams per 50 ml. of solution, and the mixtures filtered through filter paper, S. & S. No. 589, blue ribbon.

The $-\log t$'s at the three wave lengths, and the *R*-ratios (dispersion quotients) based on wave length 529 mμ are shown in Table IX.

Table IX. Selective Effect of Filtering Materials

Sugar No.	Wave Length, mμ	Asbestos		Filter-Cel		Silica Gel	
		$-\log t$	R-ratio	$-\log t$	R-ratio	$-\log t$	R-ratio
7	449	5.915	2.01	5.317	2.00	5.201	2.02
	529	2.949	1.00	2.655	1.00	2.574	1.00
	621	1.301	0.44	1.118	0.42	1.092	0.42
8	449	3.679	1.77	3.258	1.89	2.795	1.91
	529	2.079	1.00	1.722	1.00	1.467	1.00
	621	1.211	0.58	0.986	0.57	0.841	0.57
9	449	0.588	2.09	0.525	2.20	0.511	2.30
	529	0.281	1.00	0.239	1.00	0.222	1.00
	621	0.135	0.48	0.115	0.48	0.107	0.48
10	449	0.595	1.60	0.316	1.77	0.242	1.80
	529	0.372	1.00	0.179	1.00	0.135	1.00
	621	0.249	0.67	0.120	0.67	0.078	0.58

Asbestos filtration again gave the highest $-\log t$ values at all wave lengths, followed by Filter-Cel and then by silica gel. The differences between asbestos on the one hand and Filter-Cel or silica gel on the other are most pronounced in sugar 10, of low color and high turbidity. In sugar 7, the R-ratios are about the same for the three filtering agents, and there is practically no selective action, but in the other three the ratios increase at the blue end, from asbestos through Filter-Cel to silica gel. At the red end the ratios are not affected to any great extent, except in sugar 10, where the silica gel gave a much lower ratio than either asbestos or Filter-Cel.

The question arose whether the selective action of the three filtering materials is due to adsorption or to a purely mechanical filtration effect. It is well known that when sugar coloring matter is removed by means of activated carbons, the mechanism is that of true adsorption, in accordance with Freundlich's equation:

$$\frac{x}{m} = KC^{1/n}$$

where C = concentration of color left in solution
x = concentration of color removed by adsorbent
m = weight of adsorbent

When the figures in Tables V, VII, and VIII are analyzed from this standpoint it is seen that the removal of the dispersed material by any of the three filtering agents is entirely irregular. Although Tables VII and VIII indicate a progressive decrease in the $-\log t$'s, the quantity of dispersed material taken out per unit of filtering agent bears no constant relation to the quantity of dispersed material left in the solution.

While these observations point to a purely mechanical effect of the filtering agents, it was nevertheless desirable to substantiate this finding by a more direct proof. The writers have previously shown that this proof may be furnished by a technic originally employed by Balch. The material to be tested is added in one case to a white sugar sirup, and in the other to a colored sugar sirup. Then the turbid white sirup is read against the clear white sirup in a spectrophotometer, and the turbid colored sirup is read against the clear colored sirup. If no adsorption occurs, then the two transmittancy readings must be the same. Balch showed that the bentonite used by him follows this rule. In similar experiments the writers were able to show (*4*) that Filter-Cel does not adsorb coloring matter from caramel solution, but that a sample of bentonite different from that used by Balch did adsorb coloring matter. It was decided to repeat these experiments, and to extend them to asbestos and silica gel as filtering agents.

Five grams of asbestos, Filter-Cel, and silica gel were each ground in a mortar with 50 ml. of a 60 Brix white sugar sirup. The suspension was poured into a flask and allowed to settle in the refrigerator for 4 days. It was then decanted into a fresh portion of white sirup, and the mixture was shaken and again placed for 4 days in the refrigerator. The suspension thus obtained was decanted into a clean, dry flask, and was gently shaken immediately before being used in the experiments.

It was necessary to employ a raw sugar to furnish the colored sirup, because results with caramel or any other coloring matter could not be accepted as proof for the behavior of sugar coloring matter. The turbidity naturally present in the sugar had to be removed as far as possible by prefiltration. Both the raw sugar and the white sugar sirup, of 60 Brix concentration, were therefore prefiltered with one of the three filtering agents mentioned above, and the turbid sirups were prepared with either of the others, or each of the three.

In the first series of tests Filter-Cel was used for the preparation of both sirups, by the same procedure as previously described. Two equal portions of the filtered raw sugar sirup and two of the filtered white sirup were measured from a microburet. One portion each of colored and of white sirup was then made up to a definite volume with asbestos suspension, to produce the turbid sirups, while the remaining two were diluted to the same volume with filtered white sirup, to produce the clear sirups, one colored, the other white. The turbid colored sirup was read in the spectrophotometer, at wave lengths 529 and 621 mμ, against the clear colored sirup, and the turbid white sirup against the clear white sirup. Exactly the same experiments were made with silica gel suspension instead of asbestos suspension.

In the second series of tests the prefiltration was carried out with silica gel; asbestos, Filter-Cel, and silica gel were used to produce the turbidity in the filtered sirups. In the third series the sirups were prefiltered with asbestos, and suspensions of Filter-Cel or silica gel were added to the filtered sirups. The results of the transmittancy measurements are shown in Table X.

Table X. Transmittancies of Turbid *vs.* Clear Sirups

Wave Length, mμ	Asbestos		Filter-Cel		Silica Gel	
	Colored sirups	White sirups	Colored sirups	White sirups	Colored sirups	White sirups
	A. Filter-Cel used for prefiltration					
529	40.4	40.5	..	..	42.8	43.2
621	45.9	46.9	..	..	49.9	51.3
	B. Silica gel used for prefiltration					
529	64.2	64.3	47.4	47.1	56.1	57.2
621	69.9	70.9	55.7	55.8	65.2	65.5
	C. Asbestos used for prefiltration					
529	..	27.1	26.5	..	62.9	72.1
621	..	33.4	33.1	..	68.6	77.0
					(Other concn.)	
529	..	..	..	..	29.7	40.0
621	..	..	..	..	37.3	48.0
	Very thorough prefiltration with asbestos					
529	..	..	..	..	41.4	45.4
621	..	..	..	..	50.7	54.4

When either asbestos or Filter-Cel is used to produce turbidity, the transmittancies are the same within the limits of error, showing that neither of these filtering agents adsorbs coloring matter. The silica gel behaves differently, however. In the raw sugar sirup prefiltered with asbestos, the silica gel apparently produces adsorption, but in those prefiltered with Filter-Cel or silica gel it does not, or only to a very limited extent. The effect is also greatly reduced by thorough prefiltration with asbestos. These facts indicate that silica gel adsorbs only particles of a certain size, not removed by prefiltration, but has no effect beyond that limit. Filtration with silica gel is therefore not essentially different from filtration with asbestos or Filter-Cel, but is more effective than either.

Having established the mechanism of the removal of dispersed matter by the three filtering agents, all three were used on another series of twelve raw sugars of varying characteristics, transmittancy and Tyndall beam measurements being made on the unfiltered and the filtered solutions by the procedure described in the preceding paper (*5*).

All filtrations were made by suction with a water-jet pump. Large filtering tubes were used, in the top of which the Büchner funnel or Gooch crucible was inserted by means of a rubber stopper. The filtering tube (Figure 1) had a side arm near the top and a glass stopcock at the lower end. The side arm of the filter tube was connected by means of a Y-tube with the side arm of the filter flask and then with the suction pump. This arrangement made it possible to discard the first 25 ml. of filtrate and to collect the very clear portion of the filtrate without breaking the vacuum, which would disturb the filter bed already formed.

The method described by Peters and Phelps for the preparation of the asbestos pads, by suction only, had always given rather poor filtrates when examined in the dark room. For this reason the asbestos layer in the present series of experiments was first moistened with the sugar solution to be filtered, and then packed down tightly, while under suction, by means of a flattened glass rod. The filtrates thus obtained were visibly better than those prepared by the old method. In all other respects the standard procedure of preliminary shaking with asbestos and filtration, followed by six successive filtrations through the optical pad, was followed.

In the case of Filter-Cel, 3 grams of this material were added to 50 ml. of the 60 Brix sugar solution, and the mixture was thoroughly shaken and filtered by suction through a double layer of S. & S. filter paper No. 589, blue ribbon, in a 7-cm. Büchner funnel. About 25 to 30 cc. of the filtrate were allowed to pass through before a sample was collected

Table XI. Measurements on Raw Sugars

No.		$-\log T$	R	N	C	$\frac{-\log T_u}{-\log T_f}$	$\frac{-\log T_f}{C}$	$\frac{N_u}{-\log T_u - C}$
				A. Blue Filter				
11	U	1.199	228.5	0.750	0.449	...	...	...
	FA	0.377	10.6	0.025	0.352	0.822	1.071	0.885
	FC	0.372	6.9	0.016	0.356	0.827	1.045	0.890
	FS	0.324	5.4	0.011	0.313	0.875	1.035	0.847
12	U	0.566	123.7	0.252	0.314	...	...	...
	FA	0.316	13.6	0.026	0.290	0.250	1.090	0.913
	FC	0.322	8.6	0.017	0.305	0.244	1.056	0.966
	FS	0.261	9.9	0.016	0.245	0.305	1.065	0.785
13	U	1.303	188.6	0.775	0.528	...	...	...
	FA	0.453	9.9	0.029	0.424	0.850	1.068	0.882
	FC	0.429	7.5	0.022	0.407	0.874	1.054	0.865
	FS	0.364	5.4	0.013	0.351	0.939	1.037	0.814
14	U	1.007	67.8	0.388	0.619	...	...	...
	FA	0.597	9.2	0.042	0.555	0.410	1.076	0.860
	FC	0.577	7.7	0.035	0.542	0.430	1.065	0.834
	FS	0.517	6.7	0.024	0.493	0.490	1.049	0.755
15	U	0.983	89.8	0.423	0.560	...	...	...
	FA	0.668	9.4	0.052	0.616	0.315	1.084	1.156
	FC	0.617	9.2	0.045	0.572	0.366	1.079	1.032
	FS	0.551	4.5	0.019	0.532	0.432	1.036	0.938
16	U	1.118	409.4	0.811	0.307	...	...	...
	FA	0.216	9.9	0.014	0.202	0.902	1.069	0.885
	FC	0.229	13.5	0.020	0.209	0.889	1.096	0.892
	FS	0.182	12.8	0.014	0.168	0.936	1.083	0.854
17	U	0.851	94.2	0.356	0.495	...	...	...
	FA	0.565	7.8	0.033	0.532	0.286	1.062	1.116
	FC	0.525	4.9	0.019	0.506	0.326	1.038	1.035
	FS	0.489	4.3	0.016	0.473	0.362	1.034	0.942
18	U	1.067	136.6	0.510	0.557	...	...	...
	FA	0.512	15.0	0.051	0.461	0.555	1.111	0.842
	FC	0.459	6.1	0.019	0.440	0.608	1.043	0.813
	FS	0.394	6.5	0.016	0.378	0.673	1.042	0.740
19	U	1.606	105.3	0.871	0.735	...	...	...
	FA	0.682	5.3	0.034	0.648	0.924	1.052	0.909
	FC	0.683	8.2	0.049	0.634	0.923	1.077	0.896
	FS	0.590	8.2	0.038	0.552	1.016	1.069	0.826
20	U	0.674	118.6	0.300	0.374	...	...	...
	FA	0.360	21.0	0.044	0.316	0.314	1.139	0.838
	FC	0.353	8.3	0.019	0.334	0.321	1.057	0.882
	FS	0.318	7.4	0.015	0.303	0.356	1.049	0.809
21	U	0.726	142.7	0.359	0.367	...	...	...
	FA	0.345	13.5	0.028	0.317	0.381	1.088	0.878
	FC	0.318	6.9	0.014	0.304	0.408	1.046	0.853
	FS	0.301	7.2	0.014	0.287	0.425	1.049	0.818
22	U	0.512	180.0	0.282	0.230	...	...	...
	FA	0.225	19.6	0.028	0.197	0.287	1.142	0.898
	FC	0.218	8.0	0.012	0.206	0.294	1.058	0.922
	FS	0.184	9.2	0.012	0.172	0.328	1.070	0.829
				B. Green Filter				
11	U	0.767	1334.0	0.487	0.280	...	...	...
	FA	0.170	48.9	0.013	0.157	0.597	1.083	0.798
	FC	0.171	30.3	0.008	0.163	0.596	1.049	0.806
	FS	0.146	23.3	0.006	0.140	0.621	1.043	0.777
12	U	0.350	486.6	0.143	0.207	...	...	...
	FA	0.162	47.5	0.012	0.150	0.188	1.080	0.715
	FC	0.180	35.9	0.010	0.170	0.170	1.059	0.794
	FS	0.129	38.0	0.009	0.120	0.221	1.075	0.622
13	U	0.885	1061.0	0.505	0.380	...	...	...
	FA	0.224	53.1	0.016	0.208	0.661	1.077	0.746
	FC	0.211	39.1	0.012	0.199	0.674	1.060	0.736
	FS	0.181	24.6	0.007	0.174	0.704	1.040	0.710
14	U	0.611	459.0	0.225	0.386	...	...	...
	FA	0.269	45.1	0.016	0.253	0.342	1.063	0.630
	FC	0.274	45.3	0.016	0.258	0.337	1.062	0.637
	FS	0.239	35.8	0.011	0.228	0.372	1.048	0.587
15	U	0.590	569.9	0.250	0.340	...	...	...
	FA	0.326	50.7	0.020	0.306	0.264	1.065	0.880
	FC	0.302	47.0	0.017	0.285	0.288	1.060	0.817
	FS	0.251	28.1	0.009	0.242	0.339	1.037	0.718
16	U	0.765	1600.0	0.524	0.241	...	...	...
	FA	0.094	24.0	0.005	0.089	0.671	1.056	0.775
	FC	0.092	32.5	0.007	0.085	0.673	1.082	0.771
	FS	0.075	29.9	0.006	0.069	0.690	1.087	0.753
17	U	0.507	499.9	0.198	0.309	...	...	...
	FA	0.275	37.8	0.013	0.262	0.232	1.050	0.808
	FC	0.251	22.2	0.008	0.243	0.256	1.033	0.750
	FS	0.226	21.7	0.006	0.220	0.281	1.027	0.690
18	U	0.665	782.1	0.335	0.330	...	...	...
	FA	0.249	62.3	0.020	0.229	0.416	1.087	0.768
	FC	0.219	29.8	0.009	0.210	0.446	1.043	0.736
	FS	0.172	29.9	0.008	0.164	0.493	1.049	0.669
19	U	1.001	990.0	0.576	0.425	...	...	...
	FA	0.305	35.2	0.013	0.292	0.696	1.044	0.811
	FC	0.289	25.6	0.009	0.280	0.712	1.032	0.799
	FS	0.271	27.3	0.009	0.262	0.730	1.034	0.779
20	U	0.418	544.2	0.180	0.238	...	...	...
	FA	0.194	80.0	0.021	0.173	0.224	1.121	0.602
	FC	0.187	34.4	0.009	0.178	0.231	1.051	0.612
	FS	0.164	29.2	0.008	0.156	0.254	1.051	0.570
21	U	0.472	651.9	0.223	0.249	...	...	...
	FA	0.167	53.0	0.014	0.153	0.305	1.092	0.699
	FC	0.153	28.6	0.007	0.146	0.319	1.048	0.681
	FS	0.136	30.1	0.007	0.129	0.336	1.054	0.650
22	U	0.330	642.8	0.169	0.161	...	...	...
	FA	0.106	63.4	0.014	0.092	0.224	1.152	0.710
	FC	0.096	29.1	0.006	0.090	0.234	1.067	0.704
	FS	0.088	32.5	0.007	0.081	0.242	1.086	0.679
				C. Red Filter				
11	U	0.516	6443.0	0.372	0.144	...	...	...
	FA	0.070	148.6	0.007	0.063	0.446	1.111	0.821
	FC	0.074	96.0	0.005	0.069	0.442	1.072	0.832
	FS	0.063	85.2	0.004	0.059	0.453	1.068	0.814
12	U	0.222	2182.0	0.111	0.111	...	...	...
	FA	0.091	191.1	0.010	0.081	0.131	1.123	0.793
	FC	0.098	127.7	0.007	0.091	0.124	1.077	0.847
	FS	0.072	149.1	0.007	0.065	0.150	1.108	0.707
13	U	0.640	5776.0	0.412	0.228	...	...	...
	FA	0.115	205.3	0.015	0.100	0.525	1.150	0.763
	FC	0.109	153.6	0.008	0.101	0.531	1.079	0.764
	FS	0.096	95.2	0.005	0.091	0.544	1.055	0.752
14	U	0.368	2863.0	0.185	0.183	...	...	...
	FA	0.119	185.1	0.010	0.109	0.249	1.092	0.714
	FC	0.123	183.0	0.010	0.113	0.245	1.088	0.728
	FS	0.108	145.2	0.007	0.101	0.260	1.069	0.693
15	U	0.360	3154.0	0.194	0.166	...	...	...
	FA	0.159	216.3	0.012	0.147	0.201	1.082	0.911
	FC	0.139	195.2	0.011	0.128	0.221	1.086	0.863
	FS	0.107	105.0	0.006	0.101	0.253	1.059	0.745
16	U	0.542	6969.0	0.402	0.140	...	...	...
	FA	0.039	98.9	0.004	0.035	0.503	1.114	0.793
	FC	0.025	124.7	0.005	0.020	0.517	1.250	0.769
	FS	0.025	114.0	0.005	0.020	0.517	1.250	0.770
17	U	0.288	2782.0	0.152	0.136	...	...	...
	FA	0.120	166.3	0.009	0.111	0.168	1.081	0.859
	FC	0.101	92.2	0.005	0.096	0.187	1.052	0.796
	FS	0.101	88.1	0.005	0.096	0.187	1.052	0.796
18	U	0.433	4233.0	0.255	0.178	...	...	...
	FA	0.120	247.4	0.013	0.107	0.313	1.121	0.782
	FC	0.091	110.1	0.006	0.085	0.342	1.071	0.733
	FS	0.063	105.6	0.005	0.058	0.370	1.086	0.680
19	U	0.641	6067.0	0.421	0.220	...	...	...
	FA	0.123	125.0	0.007	0.116	0.518	1.060	0.802
	FC	0.127	90.1	0.005	0.122	0.514	1.041	0.811
	FS	0.118	91.5	0.005	0.113	0.523	1.044	0.799
20	U	0.279	2386.0	0.137	0.142	...	...	...
	FA	0.113	321.6	0.016	0.097	0.166	1.165	0.753
	FC	0.118	107.2	0.006	0.112	0.161	1.054	0.820
	FS	0.102	93.3	0.005	0,097	0.177	1.052	0.753
21	U	0.306	3061.0	0.171	0.135	...	...	...
	FA	0.082	165.4	0.008	0.074	0.224	1.108	0.737
	FC	0.077	90.7	0.004	0.073	0.229	1.055	0.734
	FS	0.058	97.6	0.004	0.054	0.248	1.074	0.679
22	U	0.232	2745.0	0.147	0.085	...	...	...
	FA	0.061	217.8	0.010	0.051	0.171	1.196	0.812
	FC	0.051	87.1	0.004	0.047	0.181	1.085	0.795
	FS	0.041	110.1	0.005	0.036	0.191	1.139	0.754

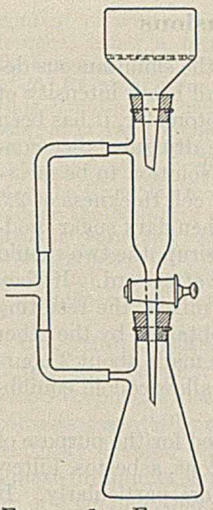

FIGURE 1. FILTERING TUBE

in a dry, clean flask. The same procedure was used with silica gel.

The results obtained with the twelve sugars are shown in Table XI (compare with Table III, *5*). *U* or *u* stands, as previously, for unfiltered, *F* or *f* for filtered; *A* denotes asbestos, *C* Filter-Cel, and *S* silica gel.

Table XII gives the *R*-ratios for $-\log T$ of the unfiltered and filtered solutions, and the dispersion quotients for N_u, the total turbidity in the unfiltered solutions, all based on those for the green filter.

A glance at Table XI shows that Filter-Cel filtration often gives lower but in many cases higher results for $-\log T$ and *C* than does asbestos, while the silica gel filtrates always result in considerably lower values. The turbidity (*N*) figures for the filtrates obtained with all three filtering agents are low, especially in the case of Filter-Cel and silica gel, where they are usually of the same order of magnitude as in a white sugar sirup which has been filtered first with activated carbon, and then through an ultrafilter.

TABLE XII. *R*-RATIOS, AND DISPERSION QUOTIENTS, BASED ON GREEN FILTER

	R-Ratio for $-\log T$								Dispersion Quotients for N_u Unfiltered	
	Unfiltered		Asbestos filtrate		Filter-Cel filtrate		Silica gel filtrate			
No.	Blue	Red	Blue	Red	Blue	Red	Blue	Red	Blue	Red
11	1.56	0.67	2.22	0.41	2.17	0.43	2.22	0.43	1.54	0.76
12	1.62	0.64	1.95	0.56	1.79	0.54	2.03	0.56	1.76	0.78
13	1.47	0.72	2.02	0.52	2.03	0.51	2.01	0.53	1.53	0.82
14	1.65	0.60	2.22	0.44	2.11	0.45	2.16	0.45	1.72	0.82
15	1.66	0.61	2.05	0.49	2.05	0.46	2.20	0.43	1.69	0.78
16	1.46	0.71	2.30	0.42	2.49	0.27	2.43	0.33	1.55	0.77
17	1.68	0.57	2.05	0.44	2.05	0.40	2.16	0.45	1.80	0.77
18	1.60	0.65	2.06	0.48	2.10	0.41	2.29	0.37	1.52	0.76
19	1.60	0.64	2.24	0.40	2.36	0.44	2.18	0.44	1.51	0.73
20	1.43	0.59	1.86	0.58	1.88	0.63	1.94	0.62	1.67	0.76
21	1.54	0.65	2.07	0.49	2.09	0.50	2.22	0.43	1.61	0.77
22	1.55	0.70	2.12	0.57	2.26	0.53	2.10	0.47	1.67	0.87

The differences between the Filter-Cel and silica gel filtrates, as compared to the asbestos filtrate, are summarized in Table XIII, for both $-\log T$ and *C*.

TABLE XIII. COMPARISON OF FILTER-CEL AND SILICA GEL FILTRATES

	$-\log T$		*C*	
	Range	Average deviation	Range	Average deviation
	%	%	%	%
Filter-Cel *vs.* asbestos				
Blue screen	+ 6.0 to −10.4	− 3.33	+ 5.7 to − 7.1	− 0.76
Green screen	+11.1 to −12.0	− 4.09	+13.3 to − 8.3	− 1.69
Red screen	+ 7.7 to −35.9	− 7.64	+15.5 to −42.9	− 4.33
Silica gel *vs.* asbestos				
Blue screen	−11.7 to −23.0	−15.87	− 4.1 to −18.0	−12.93
Green screen	−11.2 to −30.9	−18.27	− 9.8 to −28.4	−16.05
Red screen	− 4.1 to −47.5	−22.03	− 2.6 to −45.8	−19.57

The range in the differences is rather wide for both Filter-Cel and silica gel, owing to selective effects, but the average differences between Filter-Cel and asbestos are rather small, and in the case of *C* within the limits of error of spectrophotometric analysis, certainly at least in the blue and green. Since it has been shown that asbestos also acts selectively, Filter-Cel may as well be used instead, even by those who believe that asbestos filtration is the correct procedure. If the asbestos pad is packed still more tightly than in these experiments, the results may well fall below those for Filter-Cel. Silica gel gives in all cases lower values than asbestos, and the averages are from 13 to 22 per cent lower.

The selective effect of the three filtering agents is best shown by the *R*-ratios in Table XII. The ratios vary irregularly from one sugar to another and show no definite trend, proving that the effect of the filtration depends not only on the filtering agent but also on the turbidity and coloring matter present in the sugar itself.

Further examination of the results in Table XI leads to some very important conclusions regarding the mechanism of filtration with all the three agents compared. If we calculate the ratio between $-\log T_f$ (total dispersed material in the filtrate), and *C* (dispersed material corrected for that portion which causes a Tyndall effect), the figures shown in Table XIV are found.

TABLE XIV. RATIOS BETWEEN $-\text{LOG } T_f$ AND *C*

	Range	Average
Asbestos		
Blue	1.05 to 1.14	1.09
Green	1.04 to 1.15	1.08
Red	1.06 to 1.20	1.12
Filter-Cel		
Blue	1.04 to 1.10	1.06
Green	1.03 to 1.08	1.05
Red	1.04 to 1.25	1.08
Silica gel		
Blue	1.03 to 1.08	1.05
Green	1.03 to 1.09	1.05
Red	1.04 to 1.25	1.09

In spite of the fact that silica gel gives much lower values for $-\log T$ and *C* than either Filter-Cel or asbestos, the average ratios are very much alike for all three, and even the total range, showing the extent of selective action, is not very wide in each case. This shows that even though one filtering agent may remove much more total dispersed material than another, the ratio between turbidity and coloring matter remaining in the filtrates is on the average about the same. This phenomenon has been predicted by Balch: "It is very doubtful whether it is actually possible to remove all the material causing turbidity, if judged by the Tyndall beam, without changing the color of the solution." As the reason for this he gave the fact that the particles causing turbidity are themselves colored, and transmit as well as reflect light selectively.

The results obtained by the writers suggest another, more important reason. It is well known that the intensity of the Tyndall cone decreases with the difference between the refractive indices of the dispersed phase and the dispersion medium, and that the coloring matter in sugar products consists partly of condensation products of sugars—that is, substances of the caramel type, the refractive index of which is about the same as that of sucrose. These coloring matters, of the emulsoid or hydrophylic type, may therefore be expected to produce only a faint or no Tyndall cone, although consisting of particles of the same size as the suspensoids which give a distinct Tyndall cone under the same experimental conditions. But being of the same size, both are filtered out simultaneously. It may therefore be expected that, even though there be no adsorption, each filtering agent, whether it be asbestos, Filter-Cel, or silica gel, will reduce both turbidity and coloring matter to a definite maximum particle size. Silica gel appears to be much more effective in this respect than either asbestos or Filter-Cel, as used by the writers. There is still another possibility. The filtering agents may, because of electrical charges, or for other reasons, act as sensitizers and promote the flocculation of emulsoids in the presence of suspensoids. Silica gel was highly electrified when it was rubbed in a mortar.

Whatever the correct explanation may be, it is evident that filtration with asbestos, Filter-Cel, or silica gel does not remove turbidity, as judged by the Tyndall effect, without removing coloring matter at the same time. The separation of turbidity and coloring matter on the basis of a Tyndall beam of zero intensity, postulated by the writers, is thus found to be unattainable by filtration methods. In practice, the choice between the three filtering media, when used for the purpose of color determination, becomes therefore merely a matter of arbitrary agreement, which can best be reached by international action. From the practical standpoint, asbestos is the least desirable of the three filtering agents, because its effect depends so largely on its method of preparation and the permeability of the pad, which is very difficult to standardize. Filter-Cel and silica gel are much more promising in this respect because standardized grades of both are commercially available and can be purified very easily. When only color is to be determined, the residual turbidity in the filtrates may or may not be corrected for, as desired. If no correction is to be made, silica gel has the advantage of requiring such a small correction that it may in practice be neglected. In all cases the coloring matter should be expressed in terms of $-\log T$ for a specified dry substance concentration and depth of layer, or better directly as $-\log t$. The quality of the coloring matter may be further characterized by the *Q*- or *R*-ratios.

Since there is no actual dividing line between color and turbidity, both varying in particle size and both showing selective absorption and reflection or scattering, it is logical to express turbidity in the same way as the color, according to the practice followed by Balch and by the writers. The latter have shown, however, that the $-\log t$ arrived at by Balch's procedure is merely an optical measure having no direct relation to the turbidity concentration, and that it does not consider the turbidity remaining in the filtrate. In the writers' system, on the other hand, the total turbidity concentration is expressed as the $-\log t$ of an equivalent concentration of a standard turbidity, and the difference in the properties of the turbidity present and of the standard turbidity is characterized by the quality index and by the dispersion quotient of the turbidity. In the preceding paper the quality index was defined as the ratio between the filterable turbidity, $N_u - N_f$, and the turbidity according to Balch. Since this ratio applies only to the filterable turbidity, it is better to use instead that for the total turbidity—that is, the ratio of N_u to $-\log T_u - C$. Similarly, the dispersion quotients should be given for N_u itself rather than for $N_u - N_f$. Both of these changes have been made in the present paper in Tables XI and XII.

Summary and Conclusions

In a study of the factors which affect the simultaneous determination of transmittancy and Tyndall beam intensity of raw sugar solutions with the Pulfrich photometer, it has been found necessary to standardize both the dry substance concentration and the depth of layer of the solution to be measured. A concentration of 60 Brix and a cell thickness of 2.5 mm. have been tentatively adopted. When dark sugar products have to be diluted with white sugar sirup, the two should first be mixed, and the mixture filtered afterward. If they are filtered separately, and the filtrates mixed, the resulting solution is not as good optically as that obtained by the other method. The optical readings should be made about 2 hours after the preparation of the solutions, to allow colloid equilibrium to be established.

Among a number of filtering agents used for the purpose of removing turbidity from raw sugar solutions, asbestos, Filter-Cel, and silica gel have been studied more particularly. It has been shown that all three of these remove both turbidity and coloring matter selectively. Silica gel is most effective in removing total dispersed material. There is little difference in this respect between Filter-Cel and asbestos, provided that the latter is used in the form of a tightly packed pad, but the filtrates obtained with any of the three filtering agents contain turbidity, as judged by the Tyndall effect, and coloring matter in about the same proportions. It is thus not possible to remove turbidity by means of any of them, without removing coloring matter at the same time. The choice thus becomes a matter of agreement. Proposals are made to serve as a basis for such an agreement.

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A New Rubber Particle Count in Hevea Latex

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SO MUCH confusion has grown up in the literature concerning the number of rubber particles in Hevea latex that at the present time there exists a thousandfold error in the currently published reports (*1*, *3*, *8*) of the one original determination of this number. Harries (*4*), Hauser (*5*), and Noble (*8*), each reporting the original work of Henri (*6*), give a count of 50,000,000 particles per cubic centimeter of latex, Harries not specifying the concentration, while Hauser and Noble indicate it to have been 8.7 per cent solids. On the other hand, Dubosc and Luttringer (*2*), also reporting the work of Henri, record a count of 50,000,000 particles per cubic millimeter in latex of unspecified concentration. The original paper of Henri (*6*) reported that he had found an average of 50,000,000 particles per cubic millimeter of latex having a specific gravity of 0.973 and containing 8.7 grams of solids per 100 cc. Preliminary counts undertaken by the author with a view to developing a rapid microscopic method for the determination of the dry rubber content of latex indicated that the results of Henri were considerably low. Since the number of microscopically visible particles is a fundamental property of latex, it was felt that a redetermination of this number would be of value.

Experimental Method

Preparation of Solutions. From 1.0 to 2.0 grams of ammonia-preserved 38 to 40 per cent latex, the solids and dry rubber content of which had been determined, were weighed by difference, using a medicine dropper, into a 1-liter volumetric flask nearly filled with water to which had been added 15 ml. of 26° Bé. ammonium hydroxide solution to prevent any tendency to flocculation of the latex. The mixture was made up to volume and, after careful shaking, 20 ml. were pipetted out into a 500-ml. volumetric flask almost filled with a filtered 20 per cent sodium chloride solution. The sodium chloride solution was used to stop the Brownian movement of the rubber particles which would render the counting difficult. After being made up to volume with the same salt solution, the necessary amount of the solution, which represents a dilution of the original weight of latex to 25,000 ml., was transferred to the counting chamber using, for convenience, a Thoma blood-diluting pipet.

Counting Chamber. A Levy counting chamber with the improved Neubauer ruling (*9*), such as is used in counting blood corpuscles, was used in this work. The counting cell consists essentially of a plane surface of glass containing a centrally located square 1 mm. on a side. This central square millimeter is ruled into 400 equal squares. By means of double marginal rulings these 400 smallest squares are grouped into 25 squares, each containing 16 small squares representing an area of 0.04 sq. mm. Facilities are provided for supporting an optically plane cover glass 0.1 mm. above and parallel with this ruled surface, thus forming a chamber of 0.1 cu. mm. capacity. The volumetric accuracy of the counting chamber is of the order of 4 per cent. One group of 16 of the smallest squares is visible simultaneously with a 4-mm. objective and a 10× Huygenian ocular.

The Microscope. A Hartnack and Prasmowski microscope was used. A No. 7 objective, with corrective lens for cover glass thickness, and a No. 3 eyepiece were used in making the counts. This combination of lenses represents a magnification of about 400 diameters. Since no mechanically operated stage was available, it was necessary to provide otherwise for the orderly movement of the counting chamber. This was accomplished by daubing a small quantity of a mixture of 70 per cent rosin and 30 per cent rapeseed oil onto each end of the under surface of the counting chamber, which, by its viscous drag, prevented the capricious movement of the counting chamber when touched by the hand to bring a new group of squares into view. Because the counting chamber depth was great in comparison to the depth of focus of the objective used, it was necessary to focus slowly upwards from the ruled surface of the counting cell to the lower surface of the cover glass in counting each small square in order to assure the inclusion of all the particles. To prevent duplication, the particles were counted only when they came into sharp focus. It was noticed that because the Brownian movement had been stopped there was a pronounced tendency for the particles to settle upwards towards the cover glass and that after the counting chamber had been filled for about 10 minutes fully 75 per cent of all the particles were found in the focal plane nearest the cover glass. Since the boundary lines were least distinct in this focal plane, it was necessary to refill the cell frequently.

The Latex. The samples of latex used were obtained from drums of commercial 38 to 40 per cent ammonia-preserved latex. Two of these samples were of the brand known as "No. 4 Plantation Latex," marketed by the Vultex Chemical Company, Cambridge, Mass., and one sample of the brand "Lotol," marketed by the Naugatuck Chemical Company, Naugatuck, Conn.

Results of Counts

The results of the several counts on the different latex samples appear in Table I. The number of particles per gram of latex is the value reported, and for the purpose of comparison among the several samples of latex, which varied slightly in dry rubber content, all the counts are corrected to a common basis of 35 per cent dry rubber content.

Table I. Results of Counts

Brand of Latex	Sample No.	Dry Solids	Dry Rubber Content	Groups Counted[a]	Particles per Gram[b]
		%	%		
No. 4 Plantation	1	38.4	35.3	2	0.62×10^{12}
	1	38.4	35.3	3	0.65×10^{12}
	1	38.4	35.3	1	0.62×10^{12}
	2	38.5	34.6	4	0.63×10^{12}
	2	38.5	34.6	3	0.60×10^{12}
Lotol	3	39.0	35.9	1	0.64×10^{12}
	3	39.0	35.9	3	0.69×10^{12}

[a] Group of 16 small squares.
[b] Corrected to 35 per cent dry rubber content.

An average of all the counts recorded in Table I, weighted on the basis of the number of groups counted, gives a figure of 640,000,000,000 rubber particles per gram of latex of 35 per cent dry rubber content. The count of Henri, calculated to the same basis, using the factor 0.92 for conversion from per cent solids to dry rubber content, gives a figure of 218,000,000,000 particles.

Discussion of Results

It must be realized that because there is known to be numerically considerable material of ultramicroscopic proportions in latex which cannot be included in any such particle count as is reported here, but which does contribute slightly to the rubber content of the latex, such a count is inevitably low. If, however, we are willing to neglect the contribution of the ultramicroscopic material to the rubber content of the latex, it is possible to calculate an average particle diameter. In making such a calculation based on the count reported here spherical shape has been assumed for the particles, and a density of 0.914 for the material of the particles was used. On this basis the average rubber particle size in the latex samples used in this investigation is 1.04 microns. The average diameter of the rubber particles of Hevea latex has been determined by Wightman and Trivelli (*10*), using motion photomicrographs, to be between 0.7 and 0.8 micron. On the other hand, Madge (*7*) states that "the particles of commercial latex have on an average a diameter of approximately 1.5 microns as measured with a microscope."

Acknowledgment

The author's grateful thanks are due to the Union Paste Company of Medford, Mass., whose facilities and materials were graciously extended for the conduct of this investigation, and to Purcell G. Schube, Boston State Hospital, Boston, Mass., not only for the use of the blood-counting apparatus, but for much helpful advice and many suggestions.

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Determination of Sulfur in Rubber Compounds

I. Precipitation of Barium Sulfate in the Presence of Picric Acid

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THERE is probably no single operation in analytical chemistry that has received more attention from investigators than that of precipitation of barium sulfate by means of a soluble barium salt for the determination of sulfate or of barium. The literature on this subject is voluminous and the conclusions reached by different investigators as to the proper procedure to employ in order to obtain a precipitate which will be filterable and reasonably pure are highly contradictory. The procedure which seems to be in most general use at present for the determination of sulfate is that of adding the barium chloride solution to the hot sulfate solution very slowly, stirring vigorously meanwhile, then allowing the whole to digest at an elevated temperature for several hours before filtering.

The diversity of opinion as to the proper procedure arises, the author believes, from the fact that the barium sulfate precipitate is exceedingly sensitive to its environment and that a very slight change in the amount or kind of impurities present in the solutions during precipitation has a profound effect upon the crystal size and shape of the precipitated particles as well as upon their purity. Kolthoff and Vogelenzang (*2*) have stated that it is impossible to prescribe a general procedure for the accurate precipitation of sulfate in arbitrary mixtures. In other words, a precipitation procedure which gives satisfactory results in the determination of sulfur in copper ores, for instance, may not yield a satisfactory precipitate when applied to the determination of total sulfur in hard rubber dust, and a study of each type of determination, with due consideration for the amount and kind of impurities present, must be made in order to find the conditions necessary to obtain a precipitate which is pure and easily filterable.

For several years it has been known to a few analysts that the presence of picric acid in the sulfate solution at the time of precipitation would yield a precipitate which could be filtered immediately without the necessity of prolonged digestion before filtration. This bit of information has not appeared in the literature, although Dubrisay and Toquet (*1*) in 1919 suggested the use of phenol; and at present picric acid is being used in a number of laboratories throughout the country. Thus, the author does not claim in any sense that the use of picric acid is original with him, but presents this study in the hope that its use will become as widespread as it deserves.

The technic employed in the use of picric acid is simple. From 1 to 5 cc. of a saturated solution of picric acid in water are added to the acidified sulfate solution and stirred in before adding the barium chloride. The barium chloride may be added quickly, as nothing is gained by adding it slowly. After adding the barium chloride (which should be in excess as small as practicable) the solution should be gently boiled for from 5 to 10 minutes. It will then be ready to filter. In case the sulfate solution contains large quantities of sodium salts, as in sulfur determinations on Parr peroxide bomb residues, or strong oxidizing acids, as in the perchloric acid method for total sulfur in rubber compounds, the amount of picric acid necessary to produce the desired effect may be greater than that given above and in these cases from 10 to 25 cc. of the saturated solution should be used.

In the company's laboratories, picric acid has been in constant use for the past 8 years in the determination of free sulfur in rubber compounds by the bromine-oxidation method and of total sulfur by oxidation with perchloric acid. It has been known all this time that its use greatly improved the filterability of the precipitated barium sulfate without deleterious effect on the quantitative results, but no systematic study of the phenomenon was made until within the last few months.

When the use of picric acid was first under consideration, a long series of parallel determinations showed that the quantitative results obtained with and without picric acid were, if not identical, at least within the limits of accuracy of the methods of analysis themselves. These observations have been confirmed in the recent study, as shown in Table I, which gives the results obtained using pure solutions of sulfuric acid as the source of sulfate ions. In each case, the numerical result given is the average obtained from determinations run in triplicate.

TABLE I. PRECIPITATION OF BARIUM SULFATE

No.	Water	0.1 *N* H_2SO_4	Picric Acid	10% $BaCl_2$	Bromine	$BaSO_4$
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Gram*
1	100	20	0	15	0	0.2333
2	100	20	1	15	0	0.2359
3	100	20	0	15	3	0.2337
4	100	20	1	15	3	0.2364
5	400	20	0	15	0	0.2355
6	400	20	1	15	0	0.2358
7	250	4	0	10	3	0.0457
8	250	4	1	10	3	0.0464
9	400	1	0	1	0	0.0105
10	400	1	1	1	0	0.0105

In each case, the result obtained where picric acid is present is slightly higher than where it is absent. When the gravimetric factor for converting barium sulfate to sulfur (0.13136) is applied to this difference, it is divided by approximately 7.3 and becomes smaller than the usual difference between duplicate determinations, although it is always positive in sign. These results removed any fear that picric acid might increase the solubility of barium sulfate and cause incomplete precipitation.

Runs 3 and 4 differ from 1 and 2 in the fact that before the barium chloride was added 3 cc. of bromine were added, allowed to stand for 30 minutes, and then boiled off, after which the picric acid was added and the precipitation performed as usual. This was done to determine whether bro-

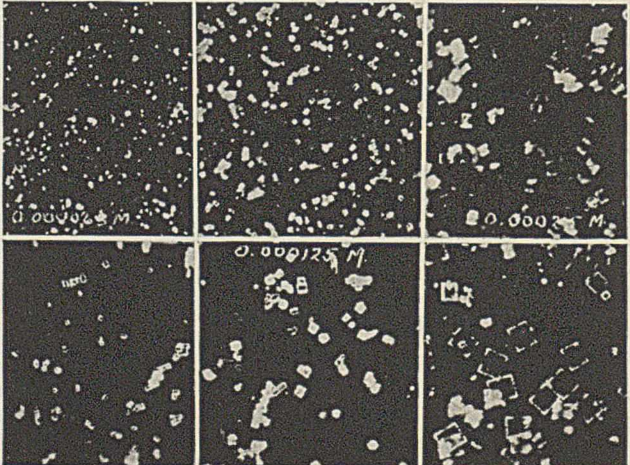

FIGURE 1

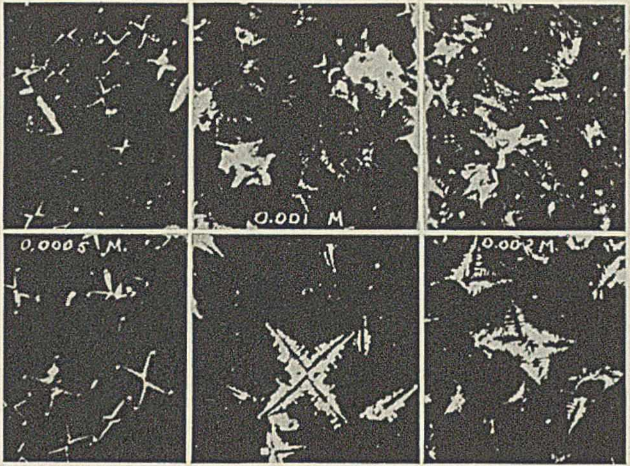

Figure 2

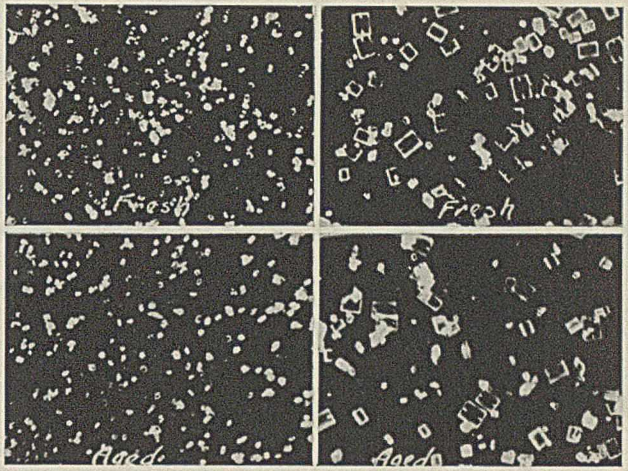

Figure 3

mine or hydrobromic acid would have any appreciable effect upon the result, which is apparently not the case. Runs 7 and 8 are in approximately the range of concentration which is encountered in free sulfur determinations on nonblooming tire stocks. Runs 9 and 10 are very dilute, and the excess of barium chloride is low in concentration. The exact agreement obtained in these last runs would make it appear that the differences in results obtained in the previous runs were due to increased occlusion or adsorption of barium chloride brought about in the presence of picric acid. The results given in Table II show that this probably is the case.

Table II. Precipitation of Barium Sulfate

No.	Water	0.1 *N* H_2SO_4	Picric Acid	0.5 *N* $BaCl_2$	$BaSO_4$
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Gram*
1	250	25	0	20	0.1163
2	250	25	1	20	0.1161
3	100	20	0	15	0.0870
4	100	20	1	15	0.0873

In these runs, the barium chloride present was insufficient to react with all the sulfuric acid present, so that there was no excess, but rather a deficiency of barium chloride. The results are well within the limits of accuracy of the ordinary volumetric buret and the differences are opposite in sign in the two pairs of runs, which differ considerably in concentration, runs 3 and 4 being twice as concentrated as runs 1 and 2.

Since we now have very good evidence that picric acid increases the adsorption of barium chloride by barium sulfate, to a very small extent, it was logical to believe that it might have a similar effect upon other ions which might be present as impurities in the solution. Since iron is commonly present in solutions from which barium sulfate is precipitated, a pair of runs was made in which ferric chloride was present. After filtering the precipitates obtained, they were analyzed and the iron was determined. The results are shown in Table III.

Table III. Determination of Iron

No.	Water	0.1 *N* H_2SO_4	1% Picric Acid	10% BaCl	15% $FeCl_3$	Fe in $BaSO_4$
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Gram*
1	250	25	0	10	2	0.057
2	250	25	5	10	2	0.0051
3	250	25	0	10	2	Faint trace
4	250	25	5	10	2	Faint trace

In runs 1 and 2 an appreciable amount of iron was picked up. It had been foreseen that iron might be adsorbed by the filter paper, so extraordinary precautions were taken in washing. The filters were washed at least 30 times with boiling water and the washings tested colorimetrically for iron. In the last 5 or 6 washings no iron was detectable, yet the appearance of the ignited barium sulfate led to the belief that the filter paper itself was responsible for a considerable portion of the total iron present. Accordingly, runs 3 and 4 were made, using fritted glass filters instead of paper for the final filtration. The precipitate was then removed from the filter and analyzed for iron as before. This time, the colorimetric test for iron was so faint as entirely to prevent its quantitative estimation.

Table IV shows the results obtained in actual free sulfur and total sulfur determinations. These figures are typical of those obtained from hundreds of comparison determinations made during the last 8 years.

Table IV. Results in Actual Sulfur Determinations

Sample	Sulfur without Picric Acid	Sulfur with Picric Acid
	%	%
156A (free sulfur)	0.35	0.37
	0.35	0.37
159	0.40	0.40
	0.40	0.40
160	0.32	0.33
	0.32	0.33
1 (total sulfur)	1.944	1.946
2	2.561	2.562

That the effectiveness of picric acid in increasing the ease of filtration is due to an actual increase in particle size of the barium sulfate crystals and not to any coagulating effect of the reagent is illustrated in the accompanying photomicrographs.

Figures 1 and 2 show the crystals obtained from sulfuric acid solutions of various concentrations. In Figure 1, upper row, the concentrations were 0.000063 *M*, 0.000125 *M*, and 0.00025 *M*, respectively, reading from left to right. The lower row shows the precipitates obtained from solutions of the same concentrations, containing in addition 0.0025 per cent of picric acid. The precipitates in the first two photographs, top row, were not entirely held up by a Carl Schleicher Schull 589 Blue Ribbon filter, while all the precipitates formed in the presence of picric acid were held up completely by this grade of paper. In Figure 2, the concentrations of the solutions were 0.00050 *M*, 0.001 *M*, and 0.002 *M*, respectively, the lower row containing the same amount of picric acid as in Figure 1. In all these experiments, the precipitates prepared without picric acid were digested at 80° C. for 16 hours before photographing, while those prepared with picric acid were photographed immediately after precipitation.

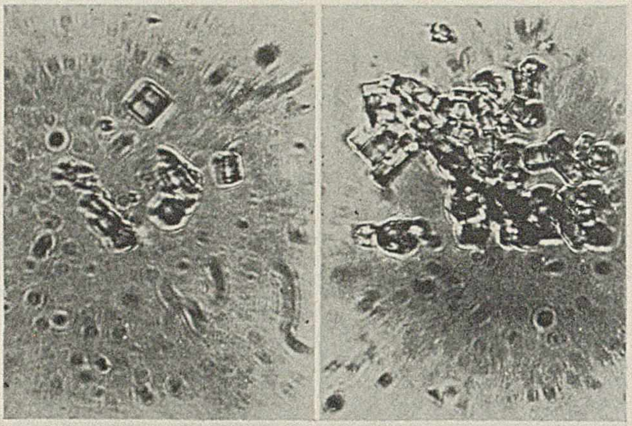

Figure 4

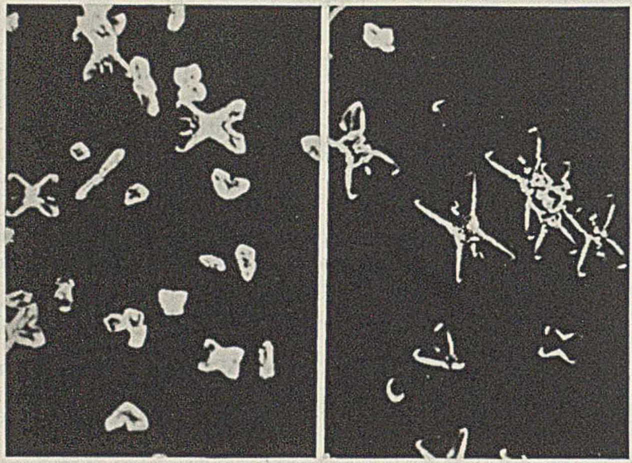

Figure 6

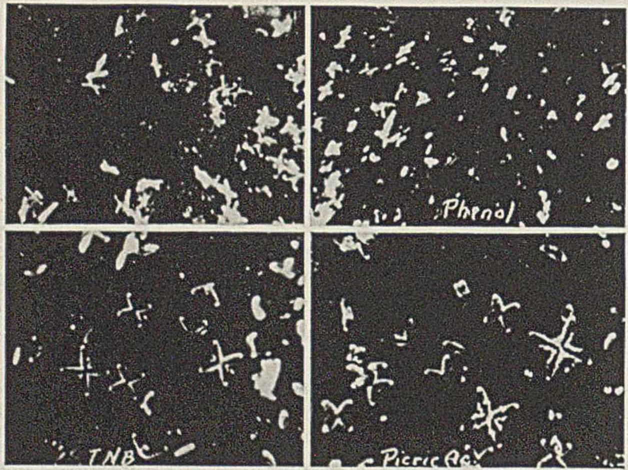

Figure 7

In this connection it was interesting to note that digestion of the barium sulfate for 16 hours at a temperature of 80° C. had no significant effect upon the particle size. In no case could any change in particle size be detected until the digestion had progressed for several days. There is a generally accepted belief that during digestion the smaller crystals tend to pass into solution, while the larger crystals grow still larger at the expense of the smaller ones. There is no doubt that this process will take place if sufficient time be given, but it is much too slow to have any appreciable effect during the usual overnight digestion.

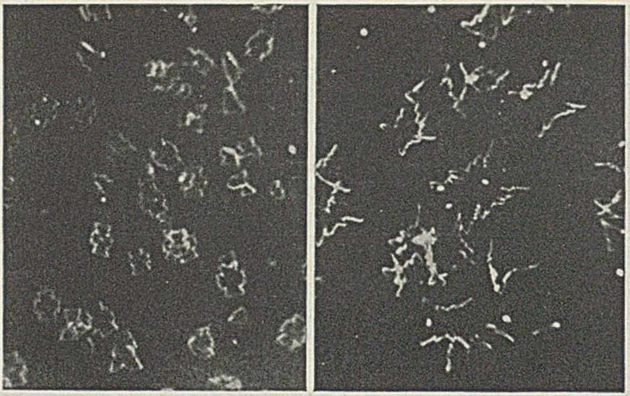

Figure 5

Figure 3 shows the appearance of fresh precipitates, without and with picric acid (top row), and the same precipitates after 16 hours' digestion (bottom row). There is no perceptible difference in the crystal size of the fresh and aged precipitates. Since there can be no doubt that overnight digestion does improve the filterability of barium sulfate, some other process must take place and a further investigation showed that there occurred a cementation of the individual particles into larger groups or aggregates as shown in Figure 4. On the left is shown the fresh precipitate and on the right the same precipitate after 16 hours' digestion, special precautions having been taken to prevent the breaking up of the rather loosely cemented aggregates in mounting them on the microscope slide. This process of aggregation has also been observed by other investigators, notably Trimble (*3*) of the University of Oklahoma.

Figure 5 shows the appearance of the precipitates obtained in a regular free sulfur determination by the bromine-oxidation method, without and with picric acid, respectively. In Figure 6 are shown the precipitates obtained in the determination of total sulfur by oxidation with perchloric acid. Figure 7 shows the effect of materials other than picric acid. The upper left photograph shows the crystals obtained from pure sulfuric acid and barium chloride solutions; those in the upper right were precipitated in the presence of approximately 0.5 per cent of phenol; those in the lower left were precipitated from a saturated solution of trinitrobenzene; while those in the lower right were precipitated in the presence of 0.0025 per cent of picric acid. In the presence of phenol, the crystals are actually decreased in size. Trinitrobenzene increases the particle size to some extent, but its low solubility in the aqueous solution probably prevents its being as effective as picric acid.

It has been the author's experience that, in every case, the particle size of the barium sulfate precipitates has been materially increased by the presence of picric acid. It is not recommended in any sense as a cure-all for filtration troubles with barium sulfate, but its use will save a great deal of time and trouble if properly applied to the particular type of sulfur determination in question.

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Received October 14, 1935. Presented before the Division of Rubber Chemistry, Akron, Ohio, October 1, 1935.

(*Part II follows*)

II. Sources of Error in the Determination of Free Sulfur in Rubber Compounds Containing Rapid Accelerators and Sulfur Bearing Accelerators

IT HAS been known for many years that the classic analytical methods for determining the degree of vulcanization of rubber stocks—namely, determination of the combined sulfur directly on an acetone-extracted sample, or indirectly by determining the free sulfur and subtracting it from the total sulfur—possessed certain inherent errors. In the older types of stocks, using relatively slow accelerators, those errors were either too small to be disturbing or could be compensated for by fairly simple calculations, taking into consideration the amounts of sulfur-bearing ingredients such as lithopone, barytes, rubber substitute, mineral rubber, etc., known to be in the stock. Furthermore, the physical properties of the stocks had been cataloged in the minds of the compounders by long experience, as fairly simple functions of the temperature and time of cure. Hence, little attention was paid to these errors in sulfur determinations, and the compounder could obtain a fairly good mental picture of the state of cure from the total sulfur and free sulfur results furnished him by the laboratory.

Of late, however, the picture has been changed by the introduction and widespread use of sulfur-bearing accelerators and of accelerators of the "ultra" and "semi-ultra" type. The compounder has found that he must accustom himself to physical properties which no longer vary as simple functions of the temperature and time of cure, and the analyst finds that the free sulfur which he still tries to determine by the bromine-oxidation method is no longer simply elemental sulfur which failed to react with rubber during the vulcanization process, but may be in the form of a number of other things enormously more complicated. Furthermore, he may find that extraction with acetone—the foundation upon which his free sulfur determination rests—is not the clean-cut solvent operation that it was in the days before the more rapid accelerators came into common use.

The American Society for Testing Materials defines "free sulfur" as "that which is removed during acetone extraction" (*1*). No explanation is given as to whether this definition shall be construed to mean all sulfur extracted by acetone or only the elemental sulfur.

Free sulfur determinations on stocks containing rapid accelerators or sulfur-bearing accelerators are subject to the following errors:

1. Elemental sulfur introduced into the compound as an impurity in the accelerator
2. Sulfur in the molecule of the accelerator
3. Sulfur in the acetone-soluble products of the vulcanization reaction
4. Sulfur in acetone-insoluble combinations other than with rubber
5. Curing of the stock during extraction with acetone

These sources of error are, of course, in addition to the sources of error found in the older types of compounds—namely, combination of a part of the elemental sulfur with resins and with various fillers to form sulfides, introduction of sulfur into the stock in fillers such as barytes, rubber substitute, etc.

The first source of error—elemental sulfur occurring in the accelerator as an impurity—is probably the smallest and least disturbing of all. The commercial sulfur-bearing accelerators may contain 6 per cent or even more of elemental sulfur, but its net effect is simply a change in the total elemental sulfur as shown in the recipe. Because of the small amounts of accelerator usually used, this change is small.

Items 2, 3, and 4—sulfur in the accelerator molecule, sulfur in the acetone-soluble, and in the non-acetone-soluble products of the vulcanization reaction—are closely related and may be considered together. For simplicity in explanation, let us see the effect of these three sources of error on the results of sulfur determinations on stocks containing a specific accelerator—mercaptobenzothiazole (MBT). This material contains two atoms of sulfur in the molecule: a mercapto sulfur or —SH group and a ring sulfur in the thiazo group.

Upon treatment with bromine, as in the bromine-oxidation method for free sulfur, the mercapto sulfur is readily oxidized and appears in the result. The ring sulfur is not appreciably oxidized and is lost unless a more drastic oxidizing agent such as perchloric acid is used. Thus, of whatever unchanged mercaptobenzothiazole in the cured stock goes into the acetone extract, approximately half of its sulfur (the mercapto sulfur) appears in the result. The amount of unchanged mercaptobenzothiazole present in a cured stock is a function of various factors, such as time of cure, composition of the stock, etc., and so long as any unchanged mercaptobenzothiazole is present which can go into the acetone extract (and it is probably always present, no matter how long the cure) there is a positive error in determining the extracted sulfur. This error is dependent, among other things, on (1) mercaptobenzothiazole-sulfur ratio in the recipe—that is, the lower the proportion of sulfur, the greater will be the error—and (2) the extent of the cure, which progressively removes a part of the mercaptobenzothiazole as a source of sulfur available for oxidation with bromine.

It is possible that the mercaptobenzothiazole-sulfur ratios at various stages of a cure can be such that the acetone-extractable sulfur due to the accelerator may be several times greater than the actual amount of elemental sulfur. Table I, illustrating such a condition, shows results obtained from a stock containing rubber 100, zinc oxide 5, stearic acid 1, MBT 3, and sulfur 0.5 parts.

TABLE I. DETERMINATION OF SULFUR

Cure, at 25 pounds (130.4° C.), min.	Raw	30	45	60	240
Free sulfur, bromine method, %	0.82	0.37	0.30	0.29	0.21
Elemental sulfur, %	0.50	0.128	0.046	0.059	0.045
Difference, %	0.32	0.242	0.254	0.231	0.165
MBT in acetone extract, %	2.91	2.28	1.95	1.80	1.64

The elemental sulfur was determined on the stock by the method of Guppy (*2*), which does not appreciably decompose mercaptobenzothiazole in the short time required for the determination, while the mercaptobenzothiazole determinations were made by precipitation of its copper salt from benzene solution by means of copper oleate.

From these results it is obvious that the error due to mercapto sulfur is by no means constant. The numerical error is progressively smaller but proportionally larger as the cure increases and the extractable mercaptobenzothiazole decreases. With such proportions of curing ingredients, it is of such magnitude as seriously to affect the result, especially in long overcures. In the cures above 30 minutes, the elemental sulfur has practically disappeared, yet the "free sulfur" is still appreciable.

Regarding the sulfur compounds present in the acetone-soluble products and in the acetone-insoluble products of the vulcanization, very little is known except that they exist. It is not unlikely that during the cure, the mercapto group splits off from some of the mercaptobenzothiazole, leaving the benzothiazole group either combined with other sub-

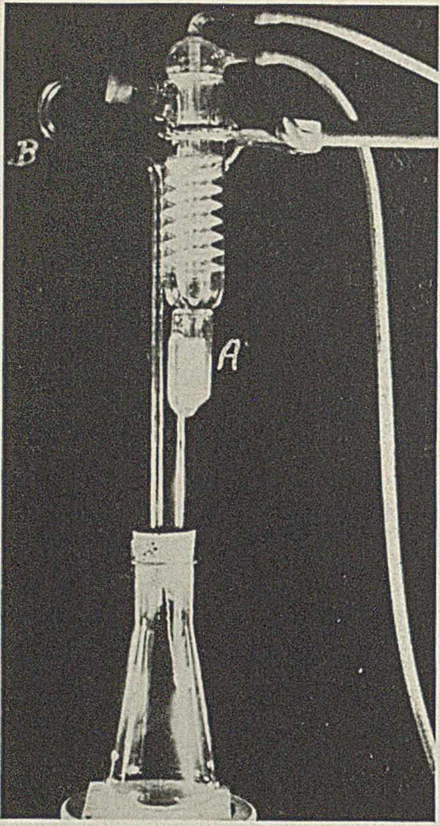

FIGURE 1

stances, split up in various ways or in the form of metallic complexes. Some of these reaction products may be readily soluble in acetone, others very difficultly soluble, and removed only by very prolonged extraction, while still others are not removed by acetone at all. These last, unless removed by some solvent other than acetone, remain in the extracted sample, later to appear as "combined" sulfur upon oxidation with perchloric acid.

The last item of error—cure during the extraction with acetone—is probably the largest of all, and is certainly the most disturbing, since it eliminates at one stroke all analytical methods which depend upon the accepted methods of acetone extraction. The extraction maintains the sample at a temperature of 57° C. (135° F.) and many accelerators cure noticeably at this temperature, while some may even be activated somewhat by the acetone. An indication of the significance of this phenomenon will be seen in Table II, which shows the results obtained by the regular extraction and bromine-oxidation method and by Guppy's method on a stock containing rubber 100, zinc oxide 5, stearic acid 1, MBT 0.5, and sulfur 3 parts.

TABLE II. COMPARATIVE RESULTS

Cure, at 25 pounds (130.4° C.), min.	Raw	30	45	60	240
Free sulfur by extraction and bromine oxidation, %	2.37	0.73	0.37	0.20	0.06
Elemental sulfur by Guppy's method, %	2.42	0.85	0.44	0.29	0.06

Here, it will be seen that the elemental sulfur result is higher than the "bromine free sulfur" result, even though the bromine oxidation gives the elemental sulfur plus the mercapto sulfur in the acetone extract. In other words, sufficient cure has taken place in the process of extraction to make the bromine free sulfur appear lower than the elemental sulfur, in spite of the positive error due to the mercapto sulfur.

Various methods have been tried to prevent, or at least reduce, the magnitude of this cure during extraction and the most effective method so far developed has been that of cold extraction—that is, by using an apparatus in which the acetone is cooled to or below room temperature before coming in contact with the sample. The apparatus used was one built up of glassware available in most laboratories and is shown in Figure 1.

The sample is placed in the siphon cup, *A*, which is an ordinary Pyrex cup having an extension sealed to the lower end of the siphon, so as to give it sufficient length to pass through a cork stopper which is placed in the regular A. S. T. M. extraction flask. The vapor tube, *B*, carries the acetone vapors from the flask to the top of a Friedrich condenser, through which the condensed vapors pass, cooling the acetone to approximately tap-water temperature before it comes in contact with the sample. The top of the siphon cup is in loose contact with the bottom of the condenser, thus keeping evaporation at a minimum and at the same time allowing sufficient venting for the apparatus. The sample is extracted on this apparatus for 16 hours and then is transferred to a regular A. S. T. M. siphon cup, and the flask with its contents is removed from the stopper and placed on the customary hot plate where the extraction is continued, hot, until complete. Thus the first stage removes a large portion of the curing ingredients without heating the sample to a curing temperature, and the process is finished at the higher temperature to insure complete extraction.

In Table III is shown the effect of such an extraction upon the combined sulfur.

TABLE III. EFFECT OF COLD EXTRACTION

Stock	Z-516	Z-517
Rubber	100	100
Zinc oxide	5	5
Stearic acid	1	1
MBT	0.5	3
Sulfur	3	0.5
Total sulfur, elemental and in MBT, calculated, %	2.914	1.505
Combined sulfur, left by hot extraction of raw stock, %	1.09	0.44
Combined sulfur, left by cold extraction of raw stock, %	0.05	0.19

Thus, with the present bromine method the "free sulfur" determined is actually the elemental sulfur plus a more or less indefinite fraction of the sulfur in the accelerator molecule and minus the sulfur lost in cure during extraction. Therefore, the definition given for free sulfur and the method given for its determination are incompatible, and until the definition is changed to remove its ambiguity and the method changed to fit the revised definition, the rubber analyst is left in a rather embarrassing position with regard to this very important determination.

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(1) A. S. T. M. Standards, p. 1135 (1933).
(2) Guppy, W. D., *Rubber Chem. Tech.*, 5, 360–2 (1932).

RECEIVED October 14, 1935. Presented before the Division of Rubber Chemistry, Akron, Ohio, October 1, 1935.

CORRECTION. In the article "A Thermionic Titrimeter without Batteries," by Willard and Hager, which was published in the ANALYTICAL EDITION for March 15, 1936, the sentence beginning at the bottom of page 144 and running over to the top of page 145 should read as follows: "Since the power requirements are low, any good radio power transformer designed for midget sets and capable of delivering 10 ma. at 220 volts for the plates of the tubes and 2 amperes at 2.5 volts for the heater will be satisfactory." The third sentence in the second paragraph under the heading "Variable Resistor" in the same column should read: "The settings of R_3 and R_4 have no bearing on the accuracy or sensitivity of the titrimeter, but the values of R_3 and R_4 for maximum sensitivity depend on the effective resistance of the tubes and of the meter. . . ."

Iodometric Determination of Maltose

A Rapid and Convenient Semi-micromethod for Determining Maltose in Studies of Amylase Action

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THE method briefly presented here for the iodometric determination of reducing sugar formed in the hydrolysis of starch by amylases was developed to meet the special requirements of studies of amylase action in the presence of heavy water (*5*) but has proved convenient for more general use with these enzymes. The method is accurate, precise, and rapid, requires relatively small volumes of solutions and no elaborate apparatus, and is suited to work with different amylases. This is shown by the quantitative recovery of maltose from starch dispersions of different electrolyte concentrations and hydrogen-ion activities adjusted to the conditions which favor the action of pancreatic amylase (*11*) on the one hand and of the amylases of barley malt (*4, 12*) on the other. The method is especially recommended for work with heavy water, in which the recovery of the heavy water is an important consideration, as its dilution with reagents is kept relatively low and its evaporation is decreased by the omission of such steps as boiling and filtering which are encountered in many other procedures.

Previous investigators have emphasized the importance to quantitative interpretation of controlling the hydrogen-ion activity of the solutions during the oxidation of sugar by iodine (*1–3, 6–8*) and have proposed the use of suitable buffers (*2, 3, 7, 8*). This principle has been successfully applied in the micromethod recently developed by Linderstrøm-Lang and Holter (*7*) for the determination of minute amounts of reducing sugar in microstudies of amylase action and has been incorporated in the method described here. The present report does not introduce new theoretical principles but unites in one convenient procedure conditions which have been found important by different workers.

Determination of Reducing Sugar

Reagents. A buffer solution (*7*) was prepared by mixing 5 volumes of 0.2 *M* sodium carbonate and 1 volume of 0.4 *M* hydrochloric acid. The sodium carbonate was purchased in the form of a highly purified and analyzed product and used without further purification.

0.05 *M* iodine in 2.4 per cent potassium iodide (*14*), 0.6 *M* sulfuric acid, 0.05 *M* sodium thiosulfate, and 1 per cent starch dispersion as indicator.

Procedure. Five cubic centimeters of the buffer solution are pipetted into a 250-cc. glass-stoppered Erlenmeyer flask. One cubic centimeter of the sugar solution (starch-hydrolysis mixture) to be analyzed is pipetted into the buffer solution in the flask and immediately treated with 2 cc. of 0.05 *M* iodine solution which is added from a long-tipped automatic buret graduated to 0.01 cc. After gentle rotation to insure thorough mixing, the solution is allowed to stand in the tightly stoppered flask in the dark at room temperature for 30 minutes for the oxidation of the sugar. Variations in room temperature from 23° to 29° do not appreciably influence the results. The time allowed for the oxidation of the sugar is, however, important and should be kept constant. At the end of 30 minutes, 5 cc. of 0.06 *M* sulfuric acid are added from a buret in such a manner as to wash down the sides of the flask and mix gently but thoroughly with the solution. The excess iodine is immediately titrated with 0.05 *M* thiosulfate which is added from an automatic long-tipped buret graduated to 0.02 cc. If no starch is present, 1 or 2 drops of a 1 per cent starch dispersion are added as indicator. The difference between the volume of thiosulfate required to reduce 2 cc. of the original iodine solution, treated as described above, and that required for the iodine which remains after the oxidation of the sugar represents the iodine reduced by the sugar and, hence, gives the equivalent of maltose present in the solution.

The data presented here indicate that the maltose is quantitatively oxidized under the prescribed conditions (pH approximately 9.9) to the corresponding monobasic acid according to the following equation:

$$C_{12}H_{22}O_{11} + I_2 + 3NaOH \longrightarrow C_{12}H_{21}O_{12}Na + 2NaI + 2H_2O$$

With the type of buret suggested, approximately 1 minute is required to combine the sugar solution with the buffer and the iodine, while 2 minutes are sufficient for the addition of the sulfuric acid and the titration with the thiosulfate. This makes it possible to obtain measurements of maltose at frequent intervals, 2 or 3 minutes apart, and enables one to follow the course of the formation of maltose throughout the hydrolysis of starch by amylase or to obtain strictly comparable measurements of the action of a given enzyme solution upon different substrates hydrolyzed side by side. In cases where frequent sampling of hydrolysis mixtures is desired, the aliquots of the buffer solution are pipetted into the glass-stoppered Erlenmeyer flasks before the enzyme hydrolyses are started.

Accuracy. The accuracy of the method was established by the use of a purified sample of maltose. It was found to contain 94.9 per cent of maltose when examined by the gravimetric copper-reduction method of Quisumbing and

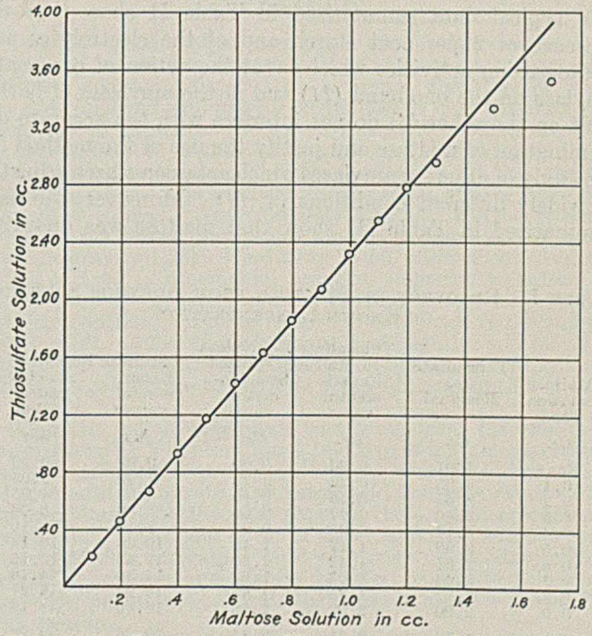

FIGURE 1. RECOVERY OF MALTOSE FROM ITS AQUEOUS SOLUTIONS

Data represent thiosulfate equivalent to the iodine reduced by the maltose. Circles show experimental values; solid line, the stoichiometric values.

The maltose solution contained approximately 20 mg. of anhydrous maltose per cc. The thiosulfate solution was 0.0516 *M* (1 cc. was equivalent to 0.0877 mg. of anhydrous maltose).

Thomas (*9*); 95.1 per cent of maltose when examined for specific rotatory power, $[\alpha]^{20}_{D} = 131.29°$ (*10*); and 94.9 per cent of maltose when examined by the method outlined here.

PRECISION. The precision or reproducibility of the method is shown by the following typical data: Eight aliquot portions of 1 cc. each of a maltose solution which contained approximately 20 mg. of maltose per cc. were treated as described above. The 0.05 *M* thiosulfate required to reduce the excess of iodine which remained after the oxidation of the sugar in the different aliquots was 2.11, 2.11, 2.11, 2.11, 2.10, 2.11, 2.11, and 2.11 cc. (0.01 cc. of the thiosulfate solution used was equivalent to 0.085 mg. of anhydrous maltose).

LIMITS OF CONCENTRATION OF MALTOSE. The stoichiometric relationship between maltose and iodine given above was established with 1-cc. portions of aqueous solutions of maltose which contained approximately 20 mg. of maltose per cc. By taking the experimental thiosulfate equivalent of 1-cc. portions of such maltose solutions as 100 per cent recovery of maltose, it was found that the method outlined here may be used for the quantitative determination of maltose up to 25 mg. This is shown by the experimental data and calculated values given in Table I and in Figure 1. When not more than 25 mg. of maltose are considered, the average deviation of the differences between the experimental and stoichiometric values (columns 3 and 4, Table I) is 0.01 cc. of the thiosulfate solution, equivalent to 0.0877 mg. of anhydrous maltose. Therefore the method is suitable for the determination of the amounts of maltose which are theoretically obtainable from 1-cc. portions of reaction mixtures resulting from the hydrolysis of 1 or 2 per cent starch.

DETERMINATION OF MALTOSE IN THE PRESENCE OF STARCH AND ITS HYDROLYSIS PRODUCTS. In the study of amylase action it is important to use a method for the determination of reducing sugar which gives quantitative results in the presence of starch and its other hydrolysis products, which may be present in the reaction mixtures in any proportions depending upon the conditions of the amylase experiments. The procedure outlined above fulfills these requirements. The typical data summarized in Table II show that the presence of 2 per cent starch and of the electrolytes and hydrogen-ion activities which favor the action of pancreatic amylase on the one hand (*11*) and of the amylases of barley malt on the other (*4*) do not interfere with the accurate determination of maltose and justify the use of the method for the study of different amylases which act upon starch adjusted to widely different conditions (*4*, *11*). Moreover, the data summarized in Table III show that maltose was quantitatively accounted for when it was superimposed upon reaction mixtures obtained at different stages of the hydrolysis of starch, in the presence of different concentrations and proportions of its hydrolysis products. This justifies the use of the method to follow the course of the formation of maltose from starch throughout its hydrolysis by amylase.

TABLE I. RECOVERY OF MALTOSE FROM AQUEOUS SOLUTIONS OF KNOWN CONCENTRATION

Maltose Solution Used	Thiosulfate for Residual Iodine	Thiosulfate Equivalent to Maltose Oxidized		Maltose Recovered	
		Experimental value	Stoichiometric value	Experimental value[a]	Stoichiometric value
Cc.	*Cc.*	*Cc.*	*Cc.*	*Mg.*	*Mg.*
None	4.07	0.00	0.00	0.00	0.00
0.1	3.85	0.22	0.23	1.93	2.03
0.2	3.61	0.46	0.46	4.03	4.05
0.3	3.40	0.67	0.69	5.88	6.08
0.4	3.14	0.93	0.92	8.16	8.10
0.5	2.90	1.17	1.16	10.26	10.13
0.6	2.65	1.42	1.39	12.45	12.16
0.7	2.44	1.63	1.62	14.30	14.18
0.8	2.22	1.85	1.85	16.22	16.21
0.9	2.00	2.07	2.08	18.15	18.14
1.0	1.76	2.31	2.31	20.26	20.26
1.1	1.52	2.55	2.54	22.36	22.29
1.2	1.30	2.77	2.77	24.29	24.31
1.3	1.12	2.95	3.00	25.87	26.34
1.5	0.75	3.32	3.47	29.12	30.39
1.7	0.55	3.52	3.93	30.87	34.44
1.9	0.42	3.65	4.39	32.01	38.49
2.1	0.30	3.77	4.85	33.06	42.55

[a] 1 cc. of the thiosulfate solution was equivalent to 8.77 mg. of maltose anhydride.

TABLE II. DETERMINATION OF MALTOSE IN PRESENCE OF 2 PER CENT STARCH ADJUSTED TO CONDITIONS WHICH FAVOR ACTION OF DIFFERENT AMYLASES

(Data expressed in cc. of 0.05 *M* thiosulfate required for reduction of excess iodine)

	a	*b*	
1 cc. of maltose solution, alone			1.89
1 cc. of 2 per cent starch, alone	4.36	4.36	..
1 cc. of 2 per cent starch + 1 cc. of maltose solution	1.88	1.88	..
0.5 cc. of maltose solution, alone	..	..	3.15
1 cc. of 2 per cent starch + 0.5 cc. of maltose solution	3.08	3.07	..

[a] 2 per cent starch adjusted to pH 7.1; 0.01 *M* phosphate; 0.025 *M* sodium chloride; conditions which favor the action of pancreatic amylase (*11*).

[b] 2 per cent starch adjusted to pH 4.5; 0.01 *M* acetate; conditions which favor the action of the amylases of barley malt (*4*).

In this connection, it is of interest to note that there is good agreement in the values obtained for reducing sugar (calculated to maltose) formed in the hydrolysis of starch by amylase when comparable reaction mixtures are analyzed by the method described above and by the gravimetric copper-reduction procedure heretofore generally employed in this laboratory (*11*, *13*). In a typical case, proportionate volumes of a solution of pancreatic amylase reacted with 100-cc. and 5-cc. portions of 2 per cent buffered (*11*) starch. At the end of 30 minutes, the 100-cc. digestion mixtures, when examined by the gravimetric method, yielded 270 mg. of maltose, while 1-cc. aliquots of the 5-cc. reaction mixture gave 2.79 mg. of maltose per cc. when analyzed by the procedure described here.

TABLE III. RECOVERY OF MALTOSE

(When superimposed on reaction mixtures at different stages of the hydrolysis of starch by pancreatic amylase)

Time of Hydrolysis of Starch by Amylase	Thiosulfate for Residual Iodine		
	Reaction mixture alone	Reaction mixture plus 1 cc. of maltose soln.[a]	Difference[a]
Min	*Cc.*	*Cc.*	*Cc.*
10	3.00	1.96	1.04
20	2.77	1.76	1.01
45	2.59	1.58	1.01
60	2.52	1.51	1.01
120	2.48	1.43	1.05

[a] 1 cc. of this maltose solution alone was equivalent to 1.01 cc. of the thiosulfate solution.

DETERMINATION OF MALTOSE IN PRESENCE OF HEAVY WATER. Equal weights of maltose were dissolved in 100 per cent purified heavy water (*5*) and in redistilled ordinary water and analyzed by the above procedure with the following results, given in cubic centimeters of 0.05 *M* thiosulfate required for the excess iodine in each case:

Reagents alone plus 1 cc. of ordinary water (blank)	4.07, 4.07
Reagents alone plus 1 cc. of 100 per cent heavy water (*5*) (blank)	4.07, 4.07
1 cc. of a solution of maltose dissolved in ordinary water	2.13, 2.13
1 cc. of a solution of maltose dissolved in 100 per cent heavy water (*5*)	2.13, 2.12

These data make it evident that the method outlined here may be used for the determination of maltose in the presence of heavy water.

Summary

A rapid and convenient method for the quantitative determination of reducing sugar (maltose) formed in the hydrolysis of starch by amylases is briefly described. It is especially recommended for studies of amylase action in the presence of heavy water.

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Determination of Phosphorus in Stainless Steels

A Rapid Method Using Perchloric Acid

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IN THE course of recent months, the materials testing laboratories of the Tennessee Valley Authority have been called upon to make a large number of analyses of stainless steels. Particular stress was placed upon the rapidity with which the analyses could be made. The analysis in general presented no unusual difficulties, but since time was an important factor, a more rapid method for the determination of phosphorus was sought to replace the one now in general use. The method now used requires the action of hydrochloric-nitric acid mixture to effect solution of the sample, oxidation of phosphides to phosphate, and the subsequent removal of hydrochloric acid, at best a time-consuming operation fraught with many difficulties.

Perchloric acid (60 per cent) was found to be suitable for replacing the above-mentioned acid mixture, thus eliminating the necessity of removal of hydrochloric acid. It is known that perchloric acid interferes neither with the precipitation of ammonium phosphomolybdate nor with its estimation by alkalimetric methods (*6*). It is shown below that phosphides in steel are completely oxidized to phosphate by the action of hot 60 per cent perchloric acid. The use of weaker concentrations of perchloric acid is not recommended. Lundell advises that from 10 to 15 per cent of the phosphorus may be lost if a 50 per cent acid is used (*5*).

The speed of the method lies in obviating the necessity of removing chlorides and in circumventing oxidation by nitric acid and potassium permanganate as practiced in the normal phosphorus procedure (*4*). It is known that perchloric acid may be used for the removal of chlorides, when present, as hydrochloric acid in phosphorus determinations (*7*), but the power of perchloric acid to oxidize phosphides to phosphate has apparently not been described. The authors' conclusions with regard to the accuracy and the precision of the suggested method are based on the results of repeated analyses of several Bureau of Standards samples and a comparison with the certified values given therewith. The data given below show close agreement with Bureau of Standards phosphorus values.

To show that perchlorates do not interfere with the precipitation of ammonium phosphomolybdate, a series of determinations on pure diammonium phosphate was made in the presence of normal concentrations of perchloric acid. The results (Table III) gave close checks with the calculated theoretical phosphorus content of the salt in each case. In the determination of phosphate in iron ore, Willard has substituted perchloric acid for nitric acid in the procedure for the removal of chlorides after silica dehydration. He reports that the presence of perchloric acid introduces no error (*11*).

In this laboratory, this method has resulted in more than 50 per cent saving in operator's time in the analysis of stainless steels. Fewer losses by splattering occur and, in general, greater accuracy has been obtained.

While 60 per cent perchloric acid is among the more expensive analytical reagents, the saving in operator's time more than compensates for the additional cost. The cost of the chemicals for this method amounts to approximately 7 cents per determination.

Experimental

Reagents. The reagents for this method are essentially those required in the normal determination of phosphorus in steel, plus 60 per cent reagent grade perchloric acid (*1*).

Procedure

To a 2.00-gram sample placed in a 500-ml. Erlenmeyer flask, add 20 ml. of 60 per cent perchloric acid and warm to effect complete solution. Cover with a funnel, the stem of which has been removed, and boil for 30 minutes or until the chromium is completely oxidized. Here a modified still head, as described by Smith, may be used to advantage (*8*). The solution should be a deep red to brown color. Cool, dilute to 100 ml., and add ammonium hydroxide (specific gravity 0.90) until a slight precipitate is formed. Approximately 12.5 ml. will be required. Dissolve the brown precipitate by the addition of nitric acid (specific gravity 1.20). Here 20 to 25 ml. will suffice. Add 1 to 5 ml. of 1 to 10 ammonium bisulfite, sufficient to reduce the chromium and vanadium present (ferrous sulfate may be used for this reduction). Boil to remove nitrous oxide fumes and free chlorine (*2*). Allow the solution to cool slightly, add 50 ml. of ammonium molybdate solution, and agitate for 5 minutes. Allow the precipitate to settle at room temperature for 2 hours or more.

Filter the yellow precipitate and wash from the containing vessel, first with 2 per cent nitric acid five to ten times to remove iron salts, and subsequently with 2 per cent potassium nitrate solution until the filtrate is no longer acid to litmus paper. Place the precipitate with the filter paper in the original precipitation vessel, dilute with about 50 cc. of water, and then add 8 drops of phenolphthalein indicator. Add an excess of standard sodium hydroxide solution and agitate to effect complete solution of the yellow precipitate. Titrate the excess of alkali with standard acid solution.

If the standard solutions are adjusted to 0.149 *N*, 1 ml. of alkali consumed by the yellow precipitate will be equivalent to 0.01 per cent of phosphorus in the original 2.00-gram sample. The alkali was standardized against Bureau of Standards potassium acid phthalate. The acid was then,

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in turn, standardized against the alkali and the theoretical factor (1 to 23) was used in the titrations according to the reaction (*4*)

$$(NH_4)_3PO_4(MoO_3)_{12} + 23NaOH = Na_2MoO_4 + NaNH_4HPO_4 + 11H_2O + (NH_4)_2MoO_4$$

Discussion and Notes on Procedure

The presence of vanadium in quantities up to 0.25 per cent seems to present no difficulty in this method since it appears in the precipitation reaction in the reduced state. If, however, the operator fails to reduce this element, error will be admitted in the form of apparent high phosphorus percentage. Bureau of Standards samples, No. 73 stainless steel, No. 101 18-8 chrome-nickel steel, and No. 30c chrome-vanadium steel, all contain vanadium in appreciable quantities, yet the results in Table I are in keeping with the certified phosphorus values.

The quantity of silicon normally encountered in stainless steels failed to affect the results noticeably when alkalimetric methods were used in the final estimation. Gravimetric procedures, of course, call for the removal of silica before precipitation and this may be readily done when perchloric acid is used for initial solution, since silica appears in its most tractable form when dehydrated with this acid. In fact, silicon may be determined by the Willard and Cake method (*12*) on the same sample originally weighed for phosphorus.

Smith and Goehler have proved that vacuum-distilled perchloric acid is free from phosphorus (*9*). Blank determinations of perchloric acid used in these tests confirmed their findings. It is therefore unnecessary to run blank determinations if it is known that the perchloric acid is purified by vacuum distillation.

For plain carbon steels (Tables I and II) this method may also be applied. The authors' conclusions in regard to its use in the analysis of plain carbon steels have been confirmed in parallel tests by Willard and Delp (*10*). Likewise, high-phosphorus iron may be analyzed. Nothing will be gained, however, by the use of perchloric acid in the analysis of any material which is normally soluble in nitric acid.

An effort was made to eliminate the neutralization of perchloric acid by ammonia and the reacidification with nitric acid by the addition of ammonium nitrate directly to the reaction mixture. The results were not consistently good.

The method seems applicable to phosphorus concentrations over a wide range. Bureau of Standards sample No. 56, brown phosphate rock, was checked by this method and the results were comparable with those obtained by the usual alkalimetric method (*3*).

The analysis of several Bureau of Standards samples indicates that the accuracy and precision of the method using perchloric acid is good. Table I shows results obtained with the perchloric acid method using acid-alkali titration.

TABLE I. RESULTS WITH PERCHLORIC ACID METHOD

Bureau of Standards Sample	Number of Determinations	Certified Phosphorus Value	Phosphorus Found		
			Average	High	Low
		%	%	%	%
No. 73 stainless steel	4	0.023	0.023	0.024	0.022
No. 101 18-chromium 8-nickel steel	3	0.011	0.011	0.012	0.010
No. 8d bessemer steel	3	0.099	0.097	0.098	0.096
No. 20c A. O. H. steel	3	0.044	0.042	0.043	0.042
No. 30c chrome-vanadium steel	4	0.019	0.019	0.022	0.018
No. 7c cast iron	3	0.78	0.80	0.80	0.80

Table II gives the results of analyses performed in the same manner as given above, except that the phosphorus is determined finally as in the usual gravimetric method by precipitation as magnesium ammonium phosphate and ignition to the pyrophosphate.

TABLE II. DETERMINATION OF PHOSPHORUS

Bureau of Standards Sample	Number of Determinations	Certified Phosphorus Value	Phosphorus Found		
			Average	High	Low
		%	%	%	%
No. 8d bessemer steel	3	0.099	0.105	0.108	0.101
No. 20c A. O. H. steel	2	0.044	0.042	0.042	0.042

The results of several aliquots of pure diammonium phosphate are given in Table III. In each case the aliquot was equivalent to 0.235 mg. of phosphorus, a quantity in the same order as those quantities occurring in the Bureau of Standards samples used in this investigation.

TABLE III. RESULTS WITH PURE DIAMMONIUM PHOSPHATE

Sample	Number of Determinations	Phosphorus Present	Phosphorus Found		
			Average	High	Low
		%	%	%	%
$(NH_4)_2HPO_4$	5	0.235	0.232	0.235	0.226

It is likely that this method may be applied to the analysis of phosphor-bronze with considerable savings in operator's time. Work on such a method is now in progress in this laboratory.

Summary

The phosphorus content of difficultly soluble steels, such as stainless steels, may be quickly determined by dissolving and subsequently boiling the sample in 60 per cent perchloric acid before subjecting it to normal analytical procedures. Perchlorates do not interfere with the determinations of phosphorus either in volumetric or gravimetric methods.

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Bituminous Plastics

Determination of Flow Properties

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The complicated flow properties of bituminous plastics probably cannot be satisfactorily evaluated by any single method discussed. On account of the number of variables encountered and the varying degrees in which each property may appear, absolute values will be difficult or impossible to attain. However, this fact should not discourage the investigator from employing any of the methods of rheology, since only by means of such approaches can a clear understanding of the behavior of bituminous plastics under service conditions be acquired.

AMONG bituminous technologists the terms "plastic" and "plastic cement" are usually reserved for three-phase compounds made up of bitumen, solvent, and filler. In most cases the latter is composed of fibrous material, either alone or in combination with a granular mineral powder. However, in the discussion to follow, a bituminous plastic will be considered as any asphaltic material which shows a definite deviation from viscous flow—i. e., exhibits a curvilinear relationship between flow and shearing stress. These substances may or may not possess an apparent yield value, but they all exhibit, in varying degrees, elasticity, thixotropy, and comparatively great resistance to deformation. The more highly filled materials frequently show the phenomenon of dilatancy (*20*).

Karrer (*12*) in a discussion of plasticity mentions the prevailing tendency to classify materials by the manner in which they may be plasticized. If such a classification is employed, the bituminous materials to be discussed must be described as thermoplastics because they are workable and moldable when hot. Cameron and Lineberry (*4*) suggested, however, that the term "plasticity" be applied only to dispersed systems in which at least one component is a film-forming liquid. This definition describes most bituminous plastics.

Methods for Studying Flow Properties

Several distinctly different methods for obtaining information concerning the flow properties of bituminous materials have been used recently in this laboratory. Although some of the methods were not thoroughly explored, valuable information concerning the nature of the flow of asphaltic materials was obtained by the various approaches.

A parallel-plate plastometer similar to that described by Peek (*17*) was employed to study the flow properties of viscous bitumens filled with large amounts of pulverized minerals. In this machine a constant load is applied to a small briquet of the plastic material, and the rate of movement in the sample is followed by means of an Ames dial. The graphical method of treating the data advocated by Peek was tedious if a large number of mixtures was to be investigated. For some purposes the more rapid method of treatment proposed by Manning (*14*) should be satisfactory.

A mixture made up of 39 per cent by volume of pulverized slate and 61 per cent by volume of a soft bitumen (48 seconds float at 150° F. or 65.6° C.) was cast in the form of a cylinder 2.540 cm. in diameter and 0.793 cm. high. This sample was placed in the parallel-plate plastometer at 25° C. and subjected to a load of 11,500 grams for 336 hours (1,209,600 seconds). By analyzing the data obtained during the first two or three hours by the graphical method mentioned, a yield value of approximately 360,000 dynes per sq. cm. was obtained for this slate-bitumen mixture. However, as shown by the data in Table I, the mixture was still flowing after 336 hours had elapsed and when the sample was 45 per cent of its original height. These results indicate that the yield value ascribed to many bituminous materials may be a fictitious value obtained through the use of insufficient data.

Careful measurement with this instrument indicated that even highly filled compounds, containing as little as 10 or 12 per cent bitumen, do not possess a true yield value. Nevertheless, valuable comparisons of various mixtures may be obtained by calculating an apparent yield value for each compound from the deformations occurring during the course of one or two hours in the plastometer.

The parallel-plate plastometer in a modified form was also used to obtain information concerning the elastic properties of mixtures of sand, mineral powder, and bitumen, in which the latter is present only to the extent of 10 per cent by weight. A rather large force was applied to the briquet of plastic material for a length of time sufficient to cause complete elastic compression without appreciable permanent deformation. The load was then carefully but quickly raised and the instantaneous recovery in sample height noted. After several minutes the upper plate of the plastometer was again lowered into contact with the sample, and the final recovered height was recorded. This procedure was repeated several times, and the average value thus obtained was used in calculating the modulus of elasticity of the paving mixture. The testing loads were applied in decreasing order of magnitude. Moduli of elasticity, for two-sheet asphalt paving mixtures, determined by this method are as follows; the bitumen used in preparing these mixtures was a batch steam-processed oil asphalt of 50 penetration at 25° C., 100 grams, 5 seconds:

TABLE I. FLOW OF SLATE-BITUMEN MIXTURE IN PARALLEL-PLATE PLASTOMETER

Time[a] Sec.	Height of Sample Cm.	Time[a] Sec.	Height of Sample Cm.	Time[a] Sec.	Height of Sample Cm.
0	0.7930	80	0.4022	258,000	0.3622
5	0.4670	210	0.3862	600,000	0.3587
10	0.4480	600	0.3782	885,600	0.3575
15	0.4385	2400	0.3751	950,000	0.3567
20	0.4310	21,800	0.3719	1,209,600	0.3560
40	0.4168				

[a] In order to conserve space, all of the intermediate values are not recorded.

Bitumen	Limestone Dust	Sand	Temp.	Elastic Modulus	
—Per cent by weight—			° C.	Dynes/sq. cm.	Lb./sq. in.
12	10	78	24.7	5.9×10^8	8.5×10^3
9	10	81	25.0	6.5×10^8	9.5×10^3

In addition to the parallel-plate plastometer, a Baldwin-Southwark compression testing machine was used to obtain preliminary data concerning the flow of asphalt paving mixtures under compression. The moduli of elasticity were determined on a variety of paving mixtures, and values were obtained for the yield point, ultimate strength, and mobility. At the present time the amount of data available using this machine is limited, and all its possibilities have not been fully explored.

The alternating stress method described by Bingham and Stephens (*3*), which utilizes a cylinder of the material cast in a glass tube, was used to investigate the flow characteristics of viscous bitumens (*18*, *21*) as well as some air-blown asphalts and a large number of rather soft, mineral-filled compounds which possess only moderate plastic properties. Apparent viscosities at 60° C. and at different shearing stresses are given in the following table for a mineral-filled air-blown bitumen possessing a penetration of 15 at 25° C., 100 grams, 5 seconds:

Shearing Stress *Dynes/sq. cm.*	Apparent Viscosity at 60° C. *Poises* $\times 10^{-6}$	Shearing Stress *Dynes/sq. cm.*	Apparent Viscosity at 60° C. *Poises* $\times 10^{-6}$
104,200 (out)	9.30	62,240 (out)	6.44
104,200 (in)	6.28	62,240 (in)	6.41
91,600 (out)	4.75	52,750 (out)	7.99
91,600 (in)	4.58	52,750 (in)	7.77

These data give considerable information concerning the flow properties of the compound. Structure within the bituminous material is rapidly destroyed by the mechanical working to which the sample is subjected. This explains the large decrease in apparent viscosity which occurs between the first and second "out" determinations—the material is thixotropic. Presence of elasticity in the sample is evident from the fact that the "out" values are always higher than the "in" values. Finally, the increase in viscosity with decreasing shearing stress indicates that the material is not purely viscous. If the determinations had been made at a lower temperature, all of the above effects would have been amplified.

The consistencies of bituminous materials increase with age, rapidly at first and then more slowly, as a longer time elapses since the material was in a molten condition. This increase in consistency is not due to the loss of volatile constituents because careful remelting and cooling will effect a return to the original value. Time-hardening in bituminous materials, which is being studied at present by means of the falling coaxial cylinder type of viscometer (*19*), appears to be due to the development of some type of structure within the material. Seven falling coaxial cylinder viscometers were filled with a soft air-blown bitumen (90 penetration at 25° C., 100 grams, 5 seconds). One sample was brought to 25° C. and a determination was made 4 hours after pouring. The remaining loaded viscometers were placed in a constant-temperature cabinet maintained at 25° C. and left undisturbed at that temperature until removed for testing. The times and experimentally determined viscosities for the air-blown asphalt are as follows; a shearing stress of 17,000 dynes per sq. cm. was used for each determination:

Time *Hours*	Viscosity at 25° C. *Poises* $\times 10^{-6}$	Time *Hours*	Viscosity at 25° C. *Poises* $\times 10^{-6}$
4	12.3	171	21.7
25	15.1	507	24.9
52	16.3	700	31.4
100	18.8		

A similar set of experiments was performed using six viscometers filled with an asphalt (55 penetration at 25° C., 100 grams, 5 seconds) produced from Mexican petroleum in a vacuum still. The data for this vacuum-refined asphalt are as follows:

Time *Hours*	Viscosity at 25° C. *Poises* $\times 10^{-6}$	Time *Hours*	Viscosity at 25° C. *Poises* $\times 10^{-6}$
4	5.13	171	5.94
24	5.51	507	6.52
72	5.71	1012	6.71

Steam- and vacuum-refined asphalt do not show as rapid an increase of viscosity with time as do the air-blown bitumens. The structure which probably accounts for this time-hardening can be destroyed by heating above the softening point but begins to return immediately upon cooling. Mechanical working is also capable of eliminating the hardening influence of time to some extent.

The application of the falling coaxial cylinder viscometer to the study of plastic materials is limited in about the same way as the alternating stress method, in that the material cannot be sheared continuously for any appreciable length of time. Also, the rates of shear cannot be varied over a wide range. These criticisms cannot be raised against the rotating cylinder type of viscometer (*7*, *16*) since by the use of such an instrument it may be possible to break down the structure to a greater degree than is possible in either the tube or falling cylinder viscometer, thus giving values for the consistencies of bituminous plastics in the worked condition. However, the practical value of any bituminous plastic may bear very little relationship to its consistency in the worked state, since the material usually serves its purpose in the unworked condition.

Plasticity of Filled Bitumens

Green and Haslam (*9*) concluded, from a study of the relationship between yield value and particle size, that plasticity was influenced by the interfacial area and number of points of contact of the dispersed phase per unit cross-sectional area. These effects and relationships have been found to hold in general for bituminous plastics. Also, the amount of elasticity, thixotropy, and dilatancy, as well as the plasticity, exhibited by the system will depend on the characteristics of the solid and liquid, and the ratio of the volumes of the two phases. Some bituminous plastics, which contain only a small amount of dispersed phase, may acquire the characteristics of a viscous liquid after being subjected to prolonged working. In those with appreciable amounts of filler the structure cannot be completely eliminated, and thus their flow properties are anomalous under all conditions of test.

When a viscous bitumen is filled with a mineral powder, the consistency increases gradually until a concentration is reached, depending on the characteristics of the bitumen and the powder, where nonviscous flow begins to appear. The degree of "plasticity," elasticity, and in fact all phenomena dependent upon structure within the material becomes more conspicuous as the concentration of filler increases. A number of measurements are given below to illustrate the appearance of plastic or nonviscous properties with an increase in the amount of dispersed phase in a bituminous mixture. The compounds employed were prepared using various proportions of an asphalt produced by the vacuum distillation of California petroleum and a finely ground pumice. The asphalt had a penetration of 55 at 25° C. (77° F.), 100 grams, 5 seconds, and a Ball and Ring softening point of 47° C. (116.5° F.). Measurements made by the Bingham-Stephens alternating stress method at 25° C. gave the same viscosity values for different shearing stresses, and thus the bitumen was assumed to be a viscous liquid. Viscosity data on this vacuum-refined asphalt are as follows:

Shearing Stress *Dynes/sq. cm.*	Viscosity at 25° C. *Poises* $\times 10^{-6}$	Shearing Stress *Dynes/sq. cm.*	Viscosity at 25° C. *Poises* $\times 10^{-6}$
33,382	3.17	22,057	3.09
33,086	3.14	18,132	3.13
28,677	3.13	15,437	3.09
25,484	3.03		

Mixtures were prepared using 90, 80, and 70 per cent by volume of this bitumen combined with 10, 20, and 30 per cent by volume, respectively, of pulverized pumice. The consistencies of the mixtures were measured at 25° C. by the method used for the bitumen. Table II gives the data obtained.

TABLE II. VISCOSITY DATA ON BITUMEN-PUMICE MIXTURES

90% Bitumen 10% Pumice		80% Bitumen 20% Pumice		70% Bitumen 30% Pumice	
Shearing stress	Apparent viscosity at 25° C.	Shearing stress	Apparent viscosity at 25° C.	Shearing stress	Apparent viscosity at 25° C.
Sq. cm.	*Poises* $\times 10^{-6}$	*Dynes/sq. cm.*	*Poises* $\times 10^{-6}$	*Dynes/sq. cm.*	*Poises* $\times 10^{-5}$
52,305	4.77	66,490	10.11	64,270	29.62
51,791	4.75	66,490	9.16	64,147	24.72
46,358	4.79	59,480	8.77	63,993	22.80
41,441	4.69	52,784	8.66	55,763	22.08
36,585	4.72	46,088	8.36	47,193	21.15
31,564	4.80	39,967	8.65	42,076	20.13
26,214	4.86	33,794	8.40	34,278	19.40

The data indicate that the mortar containing 10 per cent by volume of pumice was essentially a viscous liquid. However, when 20 per cent of this particular filler was present, a small amount of structure appeared and had to be worked out of the sample before even approximately constant values for viscosities at different shearing stresses were obtained; thus, these values illustrate the type of data obtained on materials which are thixotropic. When the concentration of pumice was increased to 30 per cent by volume, the deviations from viscous flow became very definite and even prolonged working in the viscometer did not completely eliminate the effects due to structure in the mass. From these facts it is evident that appreciable amounts of dispersed material must be added to viscous bitumens in order to create sufficient structure within the system to give even mild plastic properties.

Paving Mixtures

Using the definitions given at the beginning of this paper, all asphalt paving mixtures may be considered as plastics. According to Horsfield (*10*), the resistance of an asphaltic paving mixture to deformation depends on the interlocking and friction developed between the particles of mineral aggregate and to the viscous resistance of the bitumen. Thus, a close-packed aggregate is necessary in order to obtain a high frictional resistance. "The asphalt mixture at first has no internal frictional resistance and is a liquid, but by the end of the test its structure has so altered in the stressed zone that the bulk of the resistance is frictional and the remainder viscous. In other words, it has become a plastic solid and this change has been effected solely by stressing the mixture." Horsfield thus describes what is probably a manifestation of the phenomenon of dilatancy.

Of the numerous methods devised for estimating the stability of asphalt paving mixtures, one of the most widely used is that described by Hubbard and Field (*11*). In this test a cylindrical briquet 2 inches (5 cm.) in diameter and 1 inch (2.5 cm.) thick is formed from the paving mixture in a standard type of mold under a specified pressure. If hot, the briquet is allowed to cool and age for a short time; then after warming to 60° C. (approximately the maximum temperature of a pavement under a summer sun), it is placed in a testing mold. The test consists in measuring the maximum load required to force the mixture through a circular orifice 1.75 inches (4.4 cm.) in diameter. This load is recorded as the stability value of the mixture.

The Hubbard-Field test measures the initial resistance to shear and not the mobility of the paving mixture. This initial resistance to deformation depends to a great extent upon the closeness of packing of the mineral aggregate; thus, the degree to which the sample is compressed before the test is made becomes important.

Milburn (*15*), Emmons and Anderton (*8*), Wilson (*2*), Chatillon (*5*), and Skidmore (*1*) have devised methods and apparatus for estimating the stability, plasticity, and resistance to shear of bituminous paving materials. Reference should be made to the original descriptions for details concerning the construction of the various instruments and the preparation and testing of the samples. Of these methods, that of Skidmore which measures the resistance to shear of the mixture is the most widely used.

Roofing Asphalts

Roofing asphalts, which are usually prepared with air-blown bitumen, are another important class of bituminous plastics. Resistance to disintegration by exposure to sun, air, and water, elasticity at low temperatures, and absence of deformation at summer temperatures are the prime requisites of a plastic to be used in the production of roofing materials. Fiber-filled plastic cements are used extensively in repairing bituminous and metal roofs, and in constructing flashings, sealing laps, and closing or filling the valleys around vents and other objects. Certain types may also be used under heavy roofing tiles.

An apparatus based on the principle of the falling ball and falling cylinder viscometers and used for measuring the "worked" consistencies of roofing putties and fibrous roof coatings prior to the evaporation of the solvent has been developed by Clarvoe (*6*). Either a ball or a cylinder attached to a rod is permitted to sink through the plastic mass under constant load, and the rate of fall is taken as a measure of the consistency. The cylinder is used with heavy putties and the ball with materials which are so thin that they are usually applied with a brush.

Flooring Materials

Highly filled asphalts are moldable into tiles, slabs, or planks which may be laid as a floor covering over some strong but less flexible or elastic foundation. In mastic floors the bituminous plastic is placed over the foundation in a continuous sheet. The resiliency of such floors makes them desirable where workers are on their feet all day.

McBurney (*13*) has developed and described a portable instrument for measuring the ease of indentation of asphaltic tile and other materials by means of a metal sphere. His method of test should be given careful consideration because it can be applied to plastic materials *in situ*, whereas most other methods treat them in the form of a small sample and usually in a worked condition. The evaluation of most bituminous materials (e. g., paving mixtures) after they have been put into position would be valuable since there is always present the danger of drawing false conclusions concerning the behavior of a material under actual conditions of use from tests made in the laboratory under entirely different conditions and environment. McBurney has developed an empirical formula which relates the depth of indentation to the load and diameter of sphere, and to the time during which the loaded sphere acts upon the material.

Acknowledgment

The writer is indebted to several of his colleagues for suggestions and criticisms and especially to F. B. Burns, H. E. Schweyer, and C. E. Coombs for the experimental data.

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Preparation and Storage of Standard Chromous Sulfate Solutions

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THE preparation and storage of standard chromous reducing solutions are of special importance, for this reagent is the most powerful of any of the well-known reducing agents which can be used as an aqueous solution. The change from Cr^{++} to Cr^{+++} has a molal oxidation-reduction potential of -0.41 volt (*5*). Its reaction with the oxygen of the air is extremely rapid. Hence, like titanous solutions, the chromous reagent must be protected from the atmosphere at all times. The lack of an entirely satisfactory method of preparation and the difficulty involved in excluding the air from the reagent have greatly curtailed its use. The present work describes both a simple efficient method of preparing the chromous sulfate reagent and an improved method of protecting it from the atmosphere.

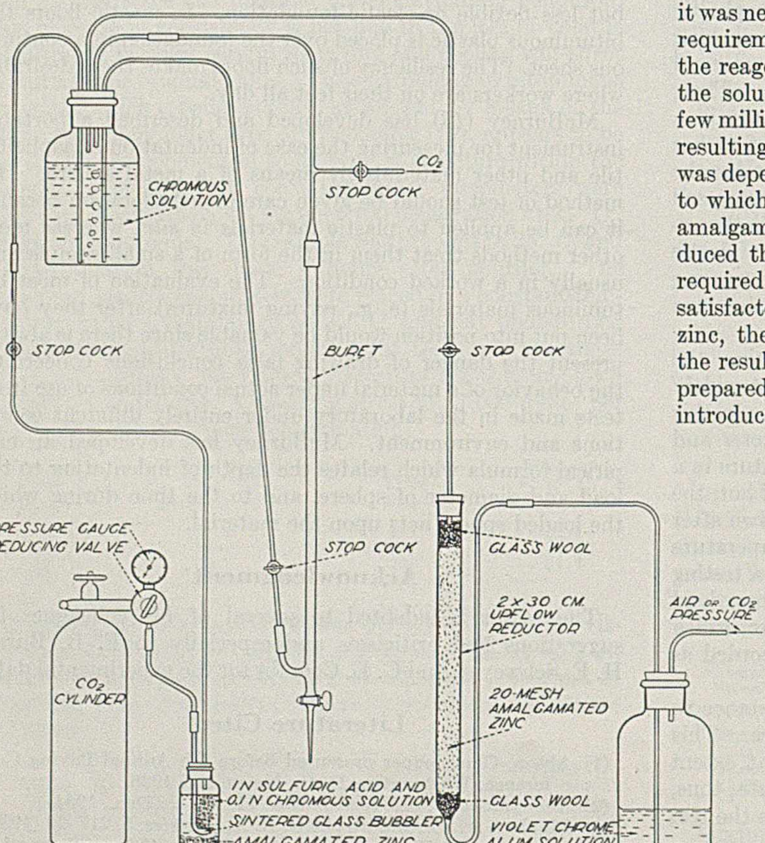

Figure 1. Diagram of Apparatus

Thornton and Sadusk (*9*) report preparation of the chromous reagent—by a reduction of an acid solution of potassium dichromate with zinc amalgam in a Jones reductor. A 0.067 *N* solution of chromous sulfate was obtained by them which was not over 0.18 *N* in sulfuric acid, representing a 67 per cent yield. The rate of reduction was 40 ml. of solution per minute. Carbon dioxide was used to exclude the air during the preparation. Apparently, the reagent was stored under hydrogen from a Kipp generator (*10*).

When this method was used by the authors, the concentrations of the resulting chromous solutions varied so greatly that it was necessary to start with two or three times the theoretical requirement of dichromate to insure a given concentration of the reagent. During certain experiments, the rate of flow of the solution through the Jones reductor was reduced to a few milliliters per minute by the buoyant effect of the hydrogen resulting from the action of the acid on the zinc. This effect was dependent on the concentration of the acid and the extent to which the zinc had been amalgamated. A more complete amalgamation of the zinc eliminated the hydrogen but reduced the yield. A considerable concentration of acid was required to enable the zinc to reduce the potassium dichromate satisfactorily. Because of the reaction of the acid with the zinc, there was always an uncertainty as to the acidity of the resulting solution. Solutions of low acidity could not be prepared by this method. The quantity of nonessential ions introduced into the solutions was large.

The use of violet chrome alum solutions, in place of the strongly acid potassium dichromate solutions in the preparation of the chromous reagent, has been found to eliminate the acid difficulties and to reduce the unavoidable ions in the final solutions by at least 40 per cent. In addition to this, yields of from 90 to 100 per cent of the chromium in the chromous form were obtained at from two to five times the rate of reduction used by Thornton and Sadusk (*9*).

A list of references on the subject of the preparation and use of chromous solutions in analysis is given by Brennecke (*2*).

Influence of Complex Chromic Salts

The fact that chromic salts exist in solution in both violet and green modifications is of importance in this work. At room temperatures these forms are at equilibrium and when the equilibrium is disturbed it is adjusted rather slowly. The authors found that the violet solutions were more rapidly reduced than the green ones. Three factors which were observed to favor the rapid reduction are also known to promote the formation of the violet complex in the solution. A chrome alum solution that has been freshly prepared, that is made up in dilute sulfuric acid solution, and that is held at room temperature or below, is violet in color and rapidly reduced by the zinc amalgam in a Jones reductor. If the solution is allowed to stand, if acid is not added, or if the solution is heated, there is a shift to the green color and the rate of reduction is less. The effect of the acid on the color has been shown by Orlova and Petin (*8*). The fact that higher temperatures and aging of the solution tend to favor the green form is proved by the work of Montemartini and Vernazza (*7*).

The violet color in chrome alum solutions is thought to be due to complex groups in which six water molecules are coördinated with chromium as in $[Cr(H_2O)_6]^{+++}$, while the change to the green color involves the replacement of two or more of the water molecules in the complex with sulfate ion. $[Cr(H_2O)_4SO_4]^+$ represents one of several possible complex ions of the green type. This situation is complicated by the fact that these groups are hydrolyzed in the solution and by the fact that they exist as condensed aggregates. Graham (*4*) gives a comprehensive bibliography of this subject.

Experimental Work

The amalgamated zinc was prepared by stirring 240 grams of 20-mesh C. P. zinc in 100 ml. of 3 *N* hydrochloric acid for 30 seconds. Then 100 ml. of 0.013 *M* mercuric chloride solution (5 ml. of a saturated solution at 25° C. diluted to 100 ml.) were added to the zinc acid mixture. Soon after the addition of the mercuric chloride the evolution of hydrogen practically ceased. The stirring was continued for 3 minutes longer, after which the amalgamated zinc was washed thoroughly with distilled water by decantation.

The reductor shown in Figure 1 was then filled with the amalgamated zinc. In this device, the customary Jones reductor was modified so that air pressure was used in place of hydrostatic pressure to force the solution through the reductor. Moreover, the usual direction of flow through the reductor was reversed, causing the liquid to flow up through the amalgamated zinc. The use of air pressure permitted the investigation of much higher rates of flow. The reversal of the direction of flow took advantage of the buoyancy of any hydrogen liberated in the reductor. The hydrogen aided the flow of the liquid instead of hindering it, as is the case in the usual form of reductor.

The drawing (Figure 1) of the arrangement used in preparing the chromous reagent, and in protecting it from the air during the determination of its concentration, requires little explanation. Before starting the preparation of the chromous reagent, the air was flushed from the system by a stream of carbon dioxide from the cylinder. The gases escaped through the outlet above the buret. While the stream of gas was maintained, the stopcock above the reductor was opened and the chrome alum solution was forced through the amalgamated zinc. When sufficient chromous reagent had been prepared, the line from the reductor was cut off, and the chromous solution was thoroughly agitated by a stream of carbon dioxide bubbles. After about 15 minutes of such agitation the outlet above the buret was closed and the reagent was ready for titration.

The air was effectively excluded from the stored reagent by means of a small pressure of carbon dioxide. The use of the pressure reducing valve and gage made it possible to reduce the high pressure from the liquid carbon dioxide to the fairly constant low pressure required to exclude the oxygen of the air from the reagent. This low pressure was comparable to that obtained from a Kipp generator. The pressure could be maintained without the escape of gas and without the building up of pressure in the system. This method was far more satisfactory than the use of a Kipp generator, such as has been recommended by Zintl and Rienäcker (*11*) and Thornton and Wood (*10*). Moreover, the valve and gage, which cost about $7, were no more expensive than the Kipp generator which they displaced. The cylinder of carbon dioxide involves no extra expense, since in using such a reducing agent a cylinder of inert gas is usually required for flushing out the titration beaker. The usual arrangements for anaërobic work have been modified to meet the requirements of repeated preparation and testing of the concentration of the reagent. Readers desiring details of methods for the storage and use of such reagents are referred to the authors mentioned above (*10*, *11*), and particularly to Crowell and Baumbach (*3*). It would seem that wherever standard solutions are to be protected from the oxygen of the air by the pressure of an inert gas, the use of the pressure reducing valve and cylinder of gas would be desirable.

Although liquid carbon dioxide is usually free from oxygen or other impurities which might oxidize the chromous ion, the precaution was taken of purifying the gas used. As shown in Figure 1, the carbon dioxide entered the wash solution through a Jena sintered-glass distribution tube. This insured a thorough mixing of the gas with the chromous sulfate–sulfuric acid solution which is capable of absorbing oxygen very rapidly. The amalgamated zinc, in the bottom of the bottle, served to regenerate any chromous ion which may have been oxidized.

Because it has been reported that hydrogen may be liberated from acid solutions by the chromous ions, the authors considered this possibility carefully and found no evidence of such a reaction under the experimental conditions of this work. There can be no doubt as to the stability of chromous sulfate–sulfuric acid solutions with respect to this reaction, in view of the fact that Thornton and Sadusk (*9*) and Crowell and Baumbach (*3*) reported no appreciable change in the titer of such solutions over a period of a month. Asmanoff (*1*) found that chromous sulfate did not liberate hydrogen even from 10 *N* sulfuric acid, but that it did react slowly with 4 *N* hydrochloric acid, and that ammonium salts and platinum catalyzed the liberation of hydrogen from sulfuric acid by chromous sulfate. That no change of titer was observed in this work with the solutions containing hydrochloric acid may be explained by the fact that the concentration of the hydrochloric acid never exceeded 0.1 *N* and that the period of storage was never more than a few hours at the most.

The titer of the chromous reagent was determined by siphoning the solution, under carbon dioxide pressure, into the buret from which it was delivered below the surface of an excess of standard potassium triiodide solution. After dilution and acidification, the excess of triiodide was determined by titration with sodium thiosulfate solution. Each yield in the tables represents an average of two or more closely agreeing duplicate determinations on each sample prepared. Any possible effect of oxygen dissolved in the potassium triiodide solution was neglected. The percentage yield was based on the assumption that the C. P. chrome alum was indeed pure.

The authors did not attempt to determine why 100 per cent yields of the chromous reagent were not regularly obtained when the recommended conditions for the preparation were used. Since Lundell and Knowles (*6*) have already shown that chromium solutions can be quantitatively reduced by zinc amalgam in a Jones reductor, it seems sufficient to state that the values reported are strictly comparable with each other.

Experimental Results

The experiments of Table I indicate that with an efficient zinc amalgam one may force the solution through the reductor at any convenient rate and obtain satisfactory yields of the chromous reagent. The high rate of 200 ml. per minute, used in experiment 39S, is about as rapid as it is practicable to force a liquid through such an apparatus. The apparent decrease in yields with the increase in rate, brought out by comparing experiments 21B through 25B, has not been observed in other cases. It might be explained by a decrease in the efficiency of the amalgam, a point discussed later.

TABLE I. RELATION BETWEEN RATE OF FLOW THROUGH REDUCTOR AND YIELD OF CR^{++}

(Concentration of violet Cr^{+++}, 0.1*M*)

Expt. No.	Acid	Age of Cr^{+++} Solution	Rate of Reduction	Yield of Cr^{++}
		Hours	*Ml./min.*	%
21B	0.01 *N* HCl	0.5	40	100
22B	0.01 *N* HCl	0.5	40	99
24B	0.01 *N* HCl	0.5	150	93
25B	0.01 *N* HCl	0.5	150	91
37S	0.1 *N* H_2SO_4	2	50	97
40S	0.1 *N* H_2SO_4	19	120	96
38S	0.1 *N* H_2SO_4	2.25	135	98
39S	0.1 *N* H_2SO_4	0.5	200	97

TABLE II. EFFECT OF VARIATIONS IN ACID AND CR^{+++} CONCENTRATIONS ON YIELD OF CR^{++}

Expt. No.	Acid	Concn. of Violet Cr^{+++}	Age of Cr^{+++} Solution	Rate of Reduction	Yield of Cr^{++}
		M	*Hours*	*Ml./min.*	%
13S	None	0.01	0.5	50	90
41S	None	0.01	0.5	140	92
39S	0.1 *N* H_2SO_4	0.1	0.5	200	97
22B	0.01 *N* HCl	0.1	0.5	80	99
28S	0.1 *N* H_2SO_4	0.4	0.75	17	96

TABLE III. EFFECT OF AGE OF SOLUTION, WITH AND WITHOUT ACID, ON YIELD OF CR^{++}

Expt. No.	Acid	Concn. of Violet Cr^{+++}	Age of Cr^{+++} Solution	Rate of Reduction	Yield of Cr^{++}
		M	*Hours*	*Ml./min.*	%
28S	0.1 *N* H_2SO_4	0.4	0.75	17	96
29S	0.1 *N* H_2SO_4	0.4	27	17	93
38S	0.1 *N* H_2SO_4	0.1	2.25	135	98
40S	0.1 *N* H_2SO_4	0.1	19	120	96
41S	None	0.01	0.5	140	92
43S	None	0.01	4	100	84
44S	None	0.01	4.5	150	72

Table II offers evidence that the yield is less where no acid has been added to the chrome alum solution, that satisfactory yields can be obtained with either sulfuric or hydrochloric acid, that a change in concentration of the acid from 0.01 *N* to 0.1 *N* does not change the yield materially, and that variations in the Cr^{+++} concentration of the chrome alum solution up to 0.4 *M* Cr^{+++} do not alter the yield greatly. Though the yield with hydrochloric acid is as good as with sulfuric acid, the hydrochloric acid solutions are known to be less stable.

Experiments 41S, 43S, and 44S show that the longer a chrome alum solution stands, the lower the yield of chromous ion obtained upon reduction. When acid was added to the chrome alum solutions, this reduction in yield with age was much less. The explanation lies in the fact that the violet chromium complex gradually changed to the more slowly reduced green complex. The shift from the violet to the green form was retarded by the presence of acid, hence the age of the solution was only a small factor where acid had been added.

A solution made from green chromic sulfate crystals was 89 per cent reduced at a rate of 20 ml. per minute and only 44 per cent reduced at a rate of 120 ml. per minute. Similar reductions in yield, in cases where the chrome alum solution had been changed to green by heating, have shown that the rate of reduction is a factor to be considered where the green form is being reduced.

Certain preparations of zinc amalgam, which at first were entirely satisfactory, suffered a loss of efficiency that could not be explained. An example of such an amalgam is found in one preparation which, after having previously been satisfactory, so decreased in efficiency that a chromous yield of only 64 per cent was obtained. By replacing this amalgam with a fresh preparation and keeping all other factors constant, the yield was returned to nearly 100 per cent. This difficulty of low efficiency on the part of the zinc amalgam was met only where the amalgamated zinc had been used and stored under water for a period of not less than several days.

Conclusions

Certain difficulties arising in the use of the Thornton and Sadusk method of preparing standard chromous sulfate solutions have been pointed out. A method of eliminating these difficulties by the use of violet chrome alum solutions in place of potassium dichromate solutions has been given. A study of the factors involved in the preparation has shown that those things which tend to change the violet complex in the alum solution to the green complex, also tend to reduce the yield of the desired reagent. An improved method of protecting the reagent from the oxygen of the air has been described.

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Accelerated Method for Determining Wear Caused by Abrasion

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Equipment was designed to measure the comparative rate of wear of travertine and an artificial travertine flooring. A silicon carbide block fastened to a reciprocating arm was loaded to a weight of 3000 grams and operated at 30 cycles per minute. Observation shows that after the surface skin is removed from the stone a steady rate of wear is obtained with the particles of fine dust from the stone as the actual wearing agent. The silicon carbide block does not contact the stone. By replacement of the block with a blackboard eraser liberally supplied with chalk the equipment was used for measurement of the rate of wear of a glass blackboard. A miniature machine operating on the same principle was designed and used for comparison of efficiency of tooth pastes in removal of mucin plaques. The equipment appears to be of rather general applicability.

DETERMINATION of the effect of wear on a given surface over a period of time is a problem similar in many ways to estimating the effect of aging or of weathering on a product. Choice must be made between observing the material actually in use over an extended period of time or of devising a method whereby the action can be accelerated so as to obtain substantially the same effect in a shorter period of time. An accelerated method is preferable and in many cases essential. The usual uncertainty then arises as to how well the artificial conditions imposed correspond to the actual conditions of use.

In starting accelerated wearing tests on flooring materials several years ago, the apparatus that had already been proposed for such a purpose seemed to have a number of disadvantages. In an effort to make the determination correspond more closely to conditions of normal use, a different type of apparatus was set up and the problem approached from a different viewpoint. The apparatus so developed was found later to apply to the study of abrasion on other types of surfaces also. With simple modifications it is believed applicable to shoe leather, the enamel of compacts, linoleum finishes, and other articles receiving frictional wear. The illustrations given are of three typical applications. Similar equipment is known to be in use in industry but no details of design have been published so far as the authors know. It is therefore given as a method which may be found applicable to diverse problems and which is believed to have advantages over the methods already in print.

Of the various methods for determining hardness, only a few measure the type of abrasive action occurring on floors. The Dorry apparatus (*6*) for testing road materials measures the hardness of a cylindrical sample by abrading it against a steel disk with crushed quartz under a weight of 1250 grams. The duration of the test is for 1000 revolutions of the disk and the results are expressed in terms of hardness where hardness equals 20 minus one-third the loss in weight of the sample in grams. This apparatus has been modified (*7*) for application with specimens cut from flooring.

Another apparatus, rather similar in principle, but designed particularly for application to flooring, was developed by Kessler (*5*). In this method, three specimens of the material are abraded against a disk which revolves at 45 r. p. m. A weight of 2000 grams is applied on each specimen and No. 60 artificial aluminum oxide is fed constantly onto the disk as the abrasive. The disk is rotated for 5 minutes and the specimens are weighed in terms of hardness where hardness equals the reciprocal of the loss in volume times a factor. Correlation with service measurements was only fair, but is believed adequate to permit prediction of service wear.

Still another method designed especially to test flooring is that used by the Dow Chemical Company (*1*) on magnesia cement composition flooring. In this case the essential feature of the apparatus is a horizontal blade mounted on a vertical shaft so that the blade revolves just above the sample, pushing six steel cubes around and around over its surface. At the same time silica stucco sand is fed onto the surface of the sample. The abrasive is changed three times during the wearing operation, which is ordinarily for 6000 revolutions of the blade. The results are expressed in terms of the depth of wear obtained as measured by a micrometer mounted in a movable block on a bridge.

Other apparatus has more general application but is based on the same principle of exerting abrasion by revolving the abrading element against the sample. One design (*3*) consists of an upright leather wheel which rolls with constant slippage on a path of test samples mounted on a horizontal revolving disk. Sand is fed as the abrasive. Another (*9*) measures wear of leather, tires, etc., against a rotating abrading member in terms of loss of material per unit of abrading powder. Another (*2*), which has been made the subject of a patent, rotates blocks of the materials to be compared under predetermined pressure around a raceway constructed of the desired abrading agent.

There seemed to be two disadvantages common to all these methods. With respect to flooring particularly, observation shows that the wear that occurs very seldom results from rotary motion of an abrading surface. The tread of feet on a floor or stairway in general produces reciprocating motion. With respect to any surface, the abrasive action occurring naturally will only in rare cases be as harsh as that imposed in these accelerated tests. There may be other fundamental differences between the abrasives as well. Undoubtedly the wear on flooring varies as to the nature of the materials causing it. In the extreme case it is partially due to sharp particles. In the normal case examination shows that it is caused by particles of the material itself or of very fine dirt, which, in most cases, are neither sharp nor hard. In setting up a different type of abrasive measurement apparatus, therefore, two specifications were established: (1) that the motion of the abrading element should be in a straight line rather than circular; and (2) that the abrasive action used should correspond as closely as possible to that which would cause the normal wear when the material being studied was in use and therefore consist of only fine, relatively nonabrasive particles such as those derived from the material under test. For general applicability it must be possible to vary the abrasive used.

The use of fine particles of the material under test as the abrasive, in place of other miscellaneous dirt, is believed to introduce no serious variable so long as the material under test is of a fine-grained structure. It does not seem to be an unreasonable extension of Kessler's work (*5*) to assume that, if the use of coarse abrasive correlates with service results, the correlation with service will be as good or better when fine abrasive is used. Further there is nothing inherent in the

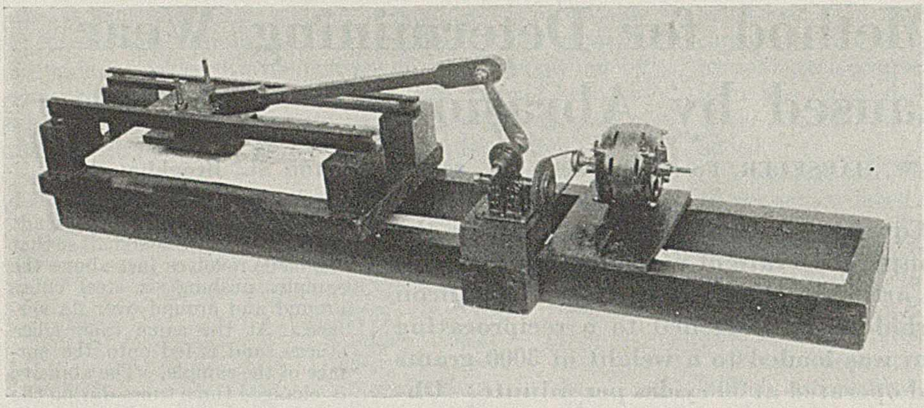

FIGURE 1. APPARATUS USED ON FLOORING

equipment which prevents the use of sharp particles such as silica sand if extreme conditions are to be measured. The equipment is, however, primarily for measurement of normal rather than for abnormal wear.

Naturally, when the second specification is adopted, the duration of the test period must be considerably greater than Kessler's 5-minute period, in order to obtain an appreciable effect. However, the action is still an accelerated one, since the motion can be made continuous as contrasted with actual use, where the impact of an abrading element, such as a footstep on flooring, occurs only intermittently and at irregular intervals.

Tests on Flooring

The apparatus as originally set up for tests on flooring and shown in Figure 1 was as follows:

> A 0.75-horsepower motor operating through a speed reducer was set up to produce reciprocating motion of an arm, operating at 30 cycles per minute. The arm carried the abrading element with an additional weight imposed so that the total weight of the abrading element was 3000 grams. The abrading element itself consisted of a block of appropriate material, the surface of which measured 15 cm. (6 inches) long and 2.5 cm. (1 inch) wide. This moved lengthwise over the face of the specimen being tested. The machine gave a stroke of 30 cm. (12 inches), so that abrasion occurred over a strip about 45 cm. (18 inches) long with the center of this strip receiving the greatest amount of wear. If desired this strip might be composed of two materials of not vastly dissimilar hardness in order to compare their rate of wear at the same time, such as of black and of white marble to be laid in alternating blocks.

The selection of the weight is a compromise. The weight to be used must not be so great as to cause active contact of the abrading element with the flooring. Rather it should be cushioned by the fine dust resulting from the wear, or by abrasive supplied. Observation shows that the movement of a shoe over the flooring, which is believed to be the time of greatest wear, is before the major portion of the weight is applied and as the foot is being lifted. For those reasons a weight slightly over 1 pound per square inch was used instead of the estimated 10 pounds per square inch present when the weight is all on one foot. Naturally, many variables, such as rubber and leather heels, women's small heels, etc., must be blended into the composite. Except in the case of actual slippage, the foot does not move after the full weight is applied and the heel touches the floor.

It should also be noted that the abrading member passes over the floor being tested at the rate of 60 times per minute, so that even with the lesser weight the rate of wear would be expected to be considerable. In view of these considerations conservatism dictates a tendency towards low rather than high pressure as well as towards mild rather than harsh abrasive for the study of normal wear.

The specimen to be tested was marked off into 5-cm. (2-inch) sections along the 45-cm. (18-inch) strip. The depth of wear after given periods of operation of the abrading arm was measured in each section of the worn strip by a stud micrometer suitably mounted in a frame constructed for the purpose. The micrometer was sufficiently delicate so that measurements were reproducible to 0.0025 cm. (0.001 inch). Any material, such as flooring, on which measurements of abrasive resistance are to be made, generally has different characteristics at the surface than in the body of the stone. Usually the surface is harder, and there are also minor surface irregularities. The same would be the case with nearly any flat solid. Therefore, a firmly bonded silicon carbide block was used as the abrading element. This caused the initial cut in the surface to be obtained quickly, as desired. The space between the abrasive crystals in the block soon become filled with powder derived from the specimen and thereafter the abrasive action is similar to that obtained in actual wear. Examination shows that the abrading member is not in contact with the flooring after this initial period, but is riding on a layer of dust particles derived from the flooring which are in turn the actual abrading agent, just as in stepping on the floor the abrading agent is the fine dirt, not the shoe.

The rate of wear at the very beginning of the test is not representative and would not be, even if the abrading element were already filled with debris from the specimen. The rate of wear in the remainder of the test is substantially constant and the abrasive action then occurring may be reasonably assumed to have a constant ratio to the rate of natural wear. After some time the silicon carbide block becomes impeded by excessive accumulated particles on the surface of the specimen, so that it is desirable to brush off this accumulation at regular intervals depending on the nature of the surface. The block itself should not be brushed and thus actual abrasion by the block is avoided. To accelerate the test further and thus measure drastic wearing conditions, the normal detritus from the floor could be replaced by a layer of abrasive such as emery, replaced at suitable intervals as in the Dow apparatus (*1*).

The apparatus may be operated for as long a period as seems desirable for the particular material under study. The study for which the machine was originally designed was a comparison between the wearing qualities of travertine marble and an artificial travertine made of a magnesium oxychloride cement composition. For this purpose the maximum period of operation was a total of 60 hours and the minimum 18 hours, depending on how quickly an appreciable wearing effect was obtained. In all cases the machine was stopped and the surface brushed off at 6-hour intervals, measurements of the depth of wear being made at those times.

Results were expressed in terms of depth of wear per hour as calculated from the micrometer measurements at 6-hour intervals. If preferable, of course, the loss in weight or in volume in a given period could be determined instead. Using the micrometer readings on the center sections of the specimen where the wear was deepest, and eliminating the first readings obtained before the rate of wear became constant, representative values for the two types of flooring material were as follows:

Travertine	0.1067 mm. (0.0042 inch) wear per hour
Artificial travertine compared	0.0254 mm. (0.0010 inch) wear per hour

Accumulation of extensive data showing the rate of wear at various points on the stone was found unnecessary after adequate data for interpretation had been assembled. Correlation between different determinations was very satisfactory, considering the type of determination. The results quoted have, of course, no general applicability but refer only to relative values on the types of material compared.

These results, obtained several years ago, have been confirmed qualitatively by observations on floors in use. No method of exact measure of rate of wear has been applicable to floors under our observation.

Kessler (*5*) points out the variable effect of humidity on the abrasive action in his apparatus and specifies that comparative tests should be run at the same relative humidity. No attempt was made to control the humidity in this study, and minor irregularities in the results may have been due to this cause. Since the authors' machine was operated for a period of 18 to 60 hours in comparison with Kessler's test period of 5 minutes, variation in humidity was not as important and the average rate of wear over the entire test period was consistent. As another comparison this equipment performed 30,000 to 100,000 complete cycles as compared with 225 to 6000 for the other types of equipment referred to.

The effect in wet wear would be expected to be less than when dry, because the water film would interfere with the contact between the finely divided particles and the stone. This was substantiated. For determinations of wet wear a separatory funnel was arranged to drip water continuously on the surface of the specimen, so that it was kept wet throughout the test period. The results under these conditions showed that after the rate of wear became constant it amounted to less than 0.00254 mm. (0.0001 inch) per hour for both travertine and the artificial travertine.

Glass Blackboard Tests

While this apparatus was originally developed for use on flooring materials, it was found to have more general applicability. As an example, the apparatus has been used to study the behavior on wearing of a composition glass blackboard. In that case, it was possible to exert abrasive action corresponding very closely to that occurring in use. In place of the silicon carbide block, an ordinary 6.25 × 15 cm. (2.5 × 6 inch) blackboard eraser was mounted at the end of the arm. The eraser was filled with chalk beforehand and chalk powder was spread on the surface of the piece of blackboard being tested. The eraser was loaded with a weight of 2 kg. and a pad of cloth placed under the sample to take up any irregularities in pressure. The excess chalk on the surface of the sample was removed and a fresh supply added every 6 hours throughout the test. No quantitative measurement of the results was made in these tests, as the primary interest was in the appearance and writing surface of the boards after an extended period of use. Instead, the macroscopic and microscopic appearance of the blackboard surface, with and without chalk, were recorded photographically as previously published (*8*). Micrometer measurements might be made in the same way as on the flooring if desired. On the basis of an estimate of the average amount of erasing a blackboard receives in schoolroom use, it was calculated that an hour's operation of the machine corresponded to approximately 2 years of actual service.

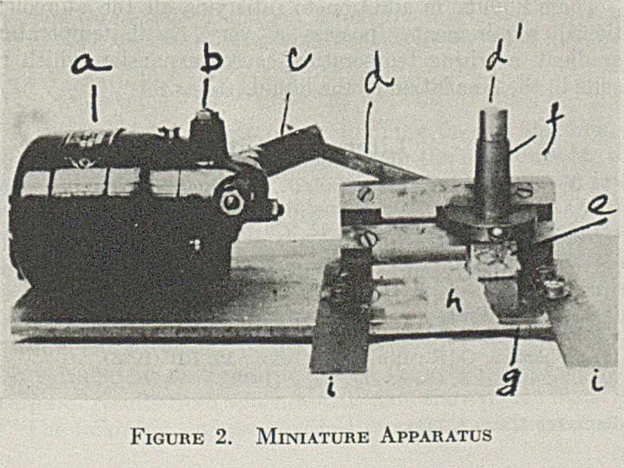

Figure 2. Miniature Apparatus

Abrasive Efficiency of Tooth Pastes

Still another application of the apparatus, and one certainly far removed from tests on flooring, was its use to compare the relative abrasive efficiency of tooth pastes. In this instance, the interest was in comparison of different abrasives against a standard surface, rather than comparison of the resistance of different surfaces to a standard abrasive. A much smaller machine was built for this purpose, following the same principles as those already described for the larger machine. The miniature apparatus is illustrated in Figure 2.

A 0.25-horsepower motor, *a*, is attached to the gear-reducing unit, *b*. Through the eccentric, *c*, and connecting rod, *d*, the abrading element is given a reciprocating motion of about 100 strokes per minute. The steel plunger, *d'*, fits snugly into the metal shoe, *e*, the bottom of which is surfaced with a plate glass. The plunger is guided by a brass tube, *f*. A glass plate, *g*, carrying the surface to be abraded, *h*, is held in place by two iron clamps. The combined weight of the plunger and metal shoe gives a load of 160 grams.

Abrasives are present in tooth pastes in order to remove the film of mucin which builds up on the teeth. They must be sufficiently abrasive to be effective but not so drastic as to injure the teeth. The standard surface against which the tooth pastes were compared consisted of a mucin plaque prepared as follows. A suitable quantity of mixed human saliva was collected and centrifuged to throw down the mucin (*4*). This mucin was then spread upon a thoroughly clean flat glass plate as evenly as possible. When nearly dry, it was subjected to the vapors of formaldehyde for several hours in order to form a hard, tough film, corresponding closely to the mucin films formed on the teeth. The plaques so produced were about 10 cm. (4 inches) square, and each was marked into four equal sections.

In order to simulate conditions of use exactly, the abrading element would have to be a brush, corresponding to a toothbrush. However, use of a brush would introduce the complication of having varying amounts of the different tooth pastes run up into the bristles and out of contact with the mucin plaque. A glass surface was therefore used as one offering no variables.

In carrying out the tests, definite quantities of tooth paste were intimately mixed with fresh human saliva and the mixture was deposited on one section of the mucin plaque. Similar mixtures of other tooth pastes to be compared were deposited on the other sections of the plaque. The plaque was then set in place in the machine and abrasion applied to the extent of 100 strokes of the arm on each of the four sections. At the end of the operation the plaque was removed, rinsed gently, and the four sections compared as to relative degree of removal of the film and presence or absence of striations. The results obtained showed definite and reproducible differences between the tooth pastes compared.

In terms of any one accepted as standard, greater or lesser abrasion can be obtained and recorded photographically.

Summary

The apparatus described presents a method of relative comparison of wear on materials. It is known to be in use in industry but not previously described and has the following advantages:

Normally a mild rate of wear is obtained, but this can be varied if desired.

No special equipment is required for preparation of the specimen.

Adjacent blocks to be laid alternately in the same floor can be compared.

The equipment is easily assembled in any laboratory.

The large number of cycles tends to eliminate accidental variations.

With suitable modification it is applicable to many types of materials.

It has the following disadvantages:

The large number of cycles requires a substantial time for the operation.

A large specimen is required for the full-size machine.

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An Inorganic Liquid Mixture for Temperature Baths in the Range 100° to 250° C.

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IT IS common laboratory practice to employ for temperature baths in the range 100° to 300° C. sulfuric acid, paraffin oils, bath waxes (*5*, *8*), or fusible alloys (*3*, *6*, *7*, *9*), all of which are subject to rather serious limitations. In regard to other materials (*1*, *2*, *4*) which can be used, the literature is indeed meager.

In connection with some work on organic oxidations it was necessary to employ a bath having the following specifications: (1) temperature range 125° to 250° C., (2) relatively high heat capacity, (3) no fuming at the temperature of operation, (4) transparent after long usage, (5) material easy to remove from glassware, and (*6*) offering no fire hazard.

The organic substances which are usually employed in the work do not meet the five latter requirements. Of the inorganic materials, only the fusible alloys and sulfuric acid can be used in this range. Metal baths are objectionable on two counts: their relatively low heat capacities and high specific gravities. Sulfuric acid is rather satisfactory except that, on account of fuming, its use is limited to the hood, and some danger is entailed in handling it while hot.

Since the usual fusible salts cannot be employed in this range, other inorganic substances were investigated. Of these, ortho- and metaphosphoric acids appeared to have many desirable properties. Metaphosphoric acid forms a clear liquid above 150° C. which solidifies on cooling. A series of experiments was conducted using 85 per cent orthophosphoric acid as a diluent.

Experimental

Mixtures containing various amounts of 85 per cent orthophosphoric acid to a given weight of metaphosphoric acid were prepared. Before being employed in the bath, each was given an initial heat treatment, which consisted of raising the temperature slowly to 260° C. and holding until rapid evolution of steam had ceased. After this treatment, the solutions appeared to possess constant thermal properties.

Test runs were made on various mixtures which had received this treatment, to determine which were most suitable for use over the given temperature range. The results are tabulated in Table I.

TABLE I. TEST RUNS

No.	Composition by Weight		Maximum Temperature		State at Room Temperature
	85% H_3PO_4	HPO_3	Before H_2O evolved on second heating ° C.	Before fuming ° C.	
1	1	1	Above 250	340	Solid
2	2	1	Above 250	340	Viscous
3	3	1	Above 250	340	Less viscous
4	4	1	Above 250	340	Mobile
5	6	1	Above 250	340	Mobile

For most purposes No. 4 seemed highly satisfactory, in that it is liquid at room temperature. No. 2 can be used more satisfactorily in the higher temperature ranges up to 340° C. but is solid at 20° C. A bath such as No. 3 has been used for over a month in this laboratory with no apparent change in properties.

These liquids, in addition to satisfying all the aforementioned requirements, possess a very small temperature gradient, as rising temperature causes expansion which results in the circulation of the liquid.

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Volumetric Determination of Sulfate in Water

The Barium Chromate Method

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THE barium chromate method for the volumetric determination of sulfate was proposed in 1889 by Andrews (*1*), who stated "The process depends upon the following series of reactions: First, to the solution of a sulfate is added an excess of a solution of barium chromate in hydrochloric acid; second, the solution is neutralized with ammonia or calcium carbonate and filtered; third, the filtrate is acidified with hydrochloric acid, potassium iodide added, and the free iodine titrated with decinormal sodium thiosulfate solution."

This description implies exact equivalence between the chromate determined by titration and the sulfate originally present in the sample. Under the conditions of the determination, however, barium chromate is slightly soluble. Several investigators (*2*, *3*) have recommended the use of a blank obtained by carrying a definite portion of the reagent solution through the procedure used by them, to correct for the barium chromate dissolved under the conditions of the determination and, therefore, once determined, applicable in all subsequent determinations of sulfate by the method. This is true if the reagent is free of impurities. Most of the barium chromate available on the market, however, contains either soluble barium salts or soluble chromates, usually the latter. In order to eliminate error from these sources it is necessary to determine the thiosulfate requirement of each new reagent solution made up, or first to free the barium chromate of impurities and then apply a correction for the barium chromate dissolved under the conditions of the determination. As the use of a blank is necessary in either case, it has been found more practical in this laboratory to purify the barium chromate partially before the preparation of the reagent solution by a simple process, in order to reduce the quantity of soluble chromate or soluble barium salts present, and then to determine the blank on each new reagent solution made up. The blank represents in this case barium chromate soluble under the conditions of the determination plus soluble chromate in the reagent or minus an amount of soluble chromate equivalent to soluble barium salts in the reagent.

Purification and Preparation of Reagent

Dissolve 25 grams of barium chromate in *N* hydrochloric acid, make the volume up to approximately 2 liters with distilled water, precipitate the barium chromate with ammonium hydroxide, wash three or four times by decantation with distilled water, and redissolve in as little *N* hydrochloric acid as possible. Determine the strength of the solution iodometrically (using 5 ml.) and dilute so that 1 liter contains approximately 7.5 grams of barium chromate. A dilution of four times is usually necessary to obtain a solution of this strength, making the acidity 0.25 *N*.

Determination of the Blank

Carry a series of samples containing known amounts of sulfate (5, 10, 15, and 20 mg.) through the procedure for the determination of sulfate. The difference between the thiosulfate titration for the 5-mg. SO_4 sample and that for the 10-mg. sample represents the amount of thiosulfate required by chromate equivalent to 5 mg. of SO_4. This volume, subtracted from the titration obtained on the 5-mg. sample, gives the volume of thiosulfate solution required for dissolved barium chromate and soluble chromate in the reagent. Similar calculations for the titrations on the other samples give a series of results from which to calculate the average blank.

The following slightly modified procedure, with the use of a blank determined as described, has been found to give results consistent with those obtained gravimetrically.

Procedure

Measure 100 ml. of the water sample into a 250-ml. Erlenmeyer flask and make just acid to methyl orange (1 drop) with *N* hydrochloric acid, added dropwise. Add, at room temperature, 10 ml. of barium chromate solution (7.5 grams of barium chromate in 1 liter of 0.25 *N* hydrochloric acid). Allow the sample to stand 10 minutes, swirling the flask several times during this period. Precipitate the excess barium chromate with ammonium hydroxide, adding 3 drops in excess of the amount necessary to change the color from orange yellow to lemon yellow (a total of 6 drops is usually sufficient when 10 ml. of the chromate reagent are used for the precipitation), and again allow the sample to stand 10 minutes, swirling and shaking several times as before. The swirling accelerates coagulation, so that the subsequent filtration is rapid and clean. Filter, catching the filtrate in another 250-ml. Erlenmeyer flask, and wash the precipitate several times with a fine stream of distilled water. Add to the filtrate 10 ml. of 10 per cent potassium iodide solution and 2 ml. of hydrochloric acid (sp. gr. 1.18 to 1.19) and mix carefully with a glass stirrer. After 10 minutes titrate, while rotating the flask gently, with 0.05 *N* sodium thiosulfate (1 ml. = 1.64 mg. of SO_4), using starch solution as indicator. From the milliliters of thiosulfate required for the titration subtract the blank, previously determined, and multiply the remainder by 16.4 (if a 100-ml. sample has been used) to get parts per million of SO_4.

One hundred water samples on which the sulfate had been determined gravimetrically in the course of regular complete analysis were tested by the procedure and the use of a blank determined as described in this paper. The samples tested contained from 2 to 1786 parts per million of SO_4, but for each test a volume of the sample containing not more than 25 mg. of SO_4 was used. The results obtained, compared with the gravimetric results on the same sample, are shown in Figure 1. The value (in mg. of SO_4) used for plotting was the SO_4 content of the sample taken for the test. With few exceptions the results obtained by the barium chromate method check those obtained gravimetrically within ±0.2 mg.

The interfering effects of aluminum, zinc, nickel, and iron have been mentioned by various investigators. Natural waters, however, rarely contain more than a few tenths of a part per million of aluminum, zinc, or nickel, and an examination of more than 650 analyses of waters from all parts of the United States shows that in practically all alkaline waters iron in excess of 0.1 part per million is precipitated within a few hours after the waters come from the ground. These constituents might, however, be present in other substances tested in quantities sufficient to affect the results. Calcium,

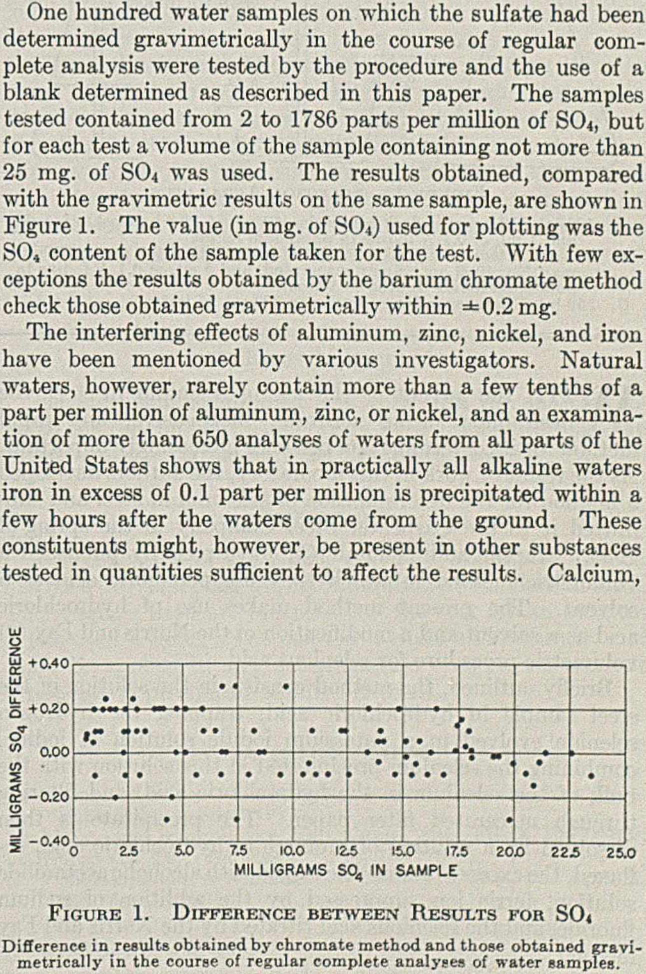

FIGURE 1. DIFFERENCE BETWEEN RESULTS FOR SO_4

Difference in results obtained by chromate method and those obtained gravimetrically in the course of regular complete analyses of water samples.

if present in large amounts as the sulfate, is occluded in the barium sulfate precipitate in sufficient quantity to cause an appreciable error. Because of the high SO_4 content of such waters, however, small volumes of the sample are usually taken for the volumetric determination and diluted to 100 ml., thus minimizing the chance of occlusion. The result then obtained is comparable to that obtained gravimetrically on a similarly diluted sample. High results are obtained if phosphate is present in excess of 5 mg. in the sample tested. Boiler waters are almost the only waters that contain phosphate in quantities approaching this magnitude. They may contain 50 parts of phosphate to more than 1000 parts of sulfate and consequently the amount of phosphate present in the sample used for the sulfate test would be negligible. Of the other acidic constituents, nitrite is the only one that might have disturbing effects, and this is seldom present in natural waters in quantities sufficient to affect the results, because it is so readily oxidized to nitrate after exposure of the sample to air.

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Determination of Selenium in Steel

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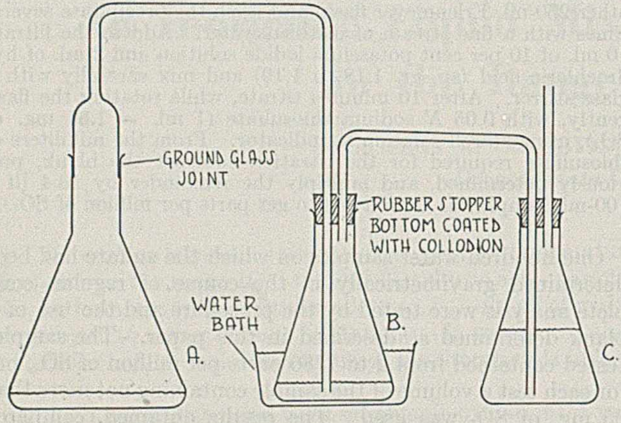

Figure 1. Solution Apparatus

A. 500-ml. Erlenmeyer flask containing 50 ml. of 1.18 hydrochloric acid and 1 ml. of 0.1 *N* iodine in potassium iodide
B. 250-ml. Erlenmeyer flask containing one-fourth filter paper (Whatman No. 40, 9 cm.) finely macerated, and 5 ml. of 0.1 *N* iodine in potassium iodide diluted to 100 ml.
C. 250-ml. Erlenmeyer flask containing 200 ml. of water.

With the advent of the use of selenium in steel, the desirability of an accurate, inexpensive, and rapid method for its determination becomes increasingly important. As the result of work in this laboratory, the authors developed a method for the determination of selenuim in steel and submitted it to the Carpenter Steel Company in the spring of 1935. Marvin and Schumb (*2*) have recently published a volumetric method in which they use perchloric acid as a solvent. The present method makes use of hydrochloric acid as a solvent and a modification of the Norris and Fay (*3*) volumetric procedure for selenious acid.

Briefly outlined, the method consists in the solution of the steel sample in hydrochloric acid, trapping the hydrogen selenide evolved in a potassium iodide solution of iodine, combining the selenium precipitated in this solution with the bulk of the selenium in the hydrochloric acid, and filtering through macerated filter paper. The precipitate is then dissolved by a solution of bromine in hydrochloric acid, refluxed, the excess bromine discharged with alcoholic acetanilide solution, ferric ion suppressed by the addition of sodium fluoride, and the selenious acid titrated by the Norris and Fay method.

The apparatus used for the solution of the sample is shown in Figure 1. A 5-gram sample of steel is placed in flask *A*, containing hydrochloric acid and a potassium iodide solution of iodine. The iodine solution prevents the loss of hydrogen selenide while connecting this flask, and iodide insures complete reduction of any selenite. The flask is heated with a microburner, at first gently, and finally with boiling until solution is complete and the volume is reduced to 25 to 30 ml. Flask *B*, containing a potassium iodide solution of iodine for oxidizing hydrogen selenide, is kept cooled in a water bath. Flask *C*, containing water, maintains a desirable back pressure. (The water bath and flask *C*, as well as the refluxing operation following, are refinements that may be omitted where percentages are reported to only two decimal places.)

The contents of flask *A* are carefully transferred to flask *B*, rinsing the connecting tube into this flask, removing any selenium from the end with moist filter paper. The solution, containing the selenium precipitate and macerated filter paper, is digested on a hot plate for 15 minutes, then filtered through a Gooch containing a circle of filter paper over which is a matte made from one-quarter of a macerated filter paper (Whatman No. 40, 9 cm.). A qualitative analysis showed that this precipitate contains nickel, silicon, and iron as impurities.

The precipitate is washed with warm water and then transferred to flask *B* and 5 ml. of bromine in hydrochloric acid (1 ml. of bromine in 100 ml. of 1.12 acid) are added. If, after shaking, the bromine color disappears and black particles still remain, more bromine solution is added, dropwise, until the bromine color is permanent. The mixture is refluxed in a 40-cm. (16-inch) condenser for 5 minutes, with a connecting tube from the top of the condenser dipping into a test tube containing 5 ml. of water to trap bromine. The tube is disconnected at the top of the condenser, the burner removed, and through the condenser tube are poured 50 ml. of water to which has been added 1 ml. of a saturated solution of acetanilide in alcohol. Excess bromine not removed by refluxing is discharged by the acetanilide. (Of several reducing agents tried, acetanilide was found most satisfactory.) After removing the flask, 20 ml. of 2.5 per cent sodium fluoride and starch solution are added, and the solution is cooled to 20°, diluted to 150 ml., and titrated by the Norris and Fay method, using approximately 0.02 *N* solutions of sodium thiosulfate and iodine.

As a means of evaluating this work, a gravimetric method was developed which depends on separating the selenium from the steel by distillation as selenium tetrabromide, its reduction to elemental selenium, and weighing as such. The selenium tetrabromide distillation method was first used by Gooch and Pierce (*1*) and its reliability as an accurate method ably demonstrated by the work of Robinson, Dudley, Williams, and Byers (*4*).

A 5-gram sample of steel is treated with 50 ml. of 1.18 hydrochloric acid in a special distilling flask fitted with a ground-glass funnel tube (Figure 2). A low flame is used until the steel is decomposed and then the flame is increased and acid distilled until only 5 to 10 ml. remain in the flask. The distillate is caught in a flask under bromine water (20 ml. of saturated bromine diluted to 50 ml.). Air is aspirated through the apparatus and bromine added to the cooled distilling flask through the funnel tube until its vapors appear in the delivery tube. Suction is discontinued, and 10 ml. of 1.49 hydrobromic acid are added and distilled down to the former volume. This distillation is repeated two more times using 10 ml. of 1.49 hydrobromic acid and 0.5 ml. of bromine each time. The receiving flask is disconnected, the acidity made 4 to 5 N (adding hydrochloric acid if necessary), and the solution filtered. Bromine is discharged with sulfur dioxide, 2 ml. of 25 per cent hydroxylamine hydrochloride are added, and the flask is placed on a hot plate to digest at 80° overnight. The precipitate is collected on asbestos in a Gooch crucible, washed with warm water and then with ethyl alcohol, dried at 80°, and weighed with a tare. (Besides lowering the temperature of drying, alcohol aids in protecting finely divided selenium from oxidation.)

To test the accuracy of the distillation method, 0.02 mg. of selenium in solution as selenious acid was added to a distillation residue shown to be free from selenium and the distillation method employed. A pink coloration on the subsequent treatment with hydroxylamine hydrochloride showed to the authors' satisfaction that the amount of selenium not removed in an average sample of steel by this method is less than 0.02 mg. By similar experiments Robinson, Dudley, Williams, and Byers demonstrated the accuracy of this method for removing minute amounts of selenium from other materials. Furthermore the insoluble portions of residues from the distillations of selenium steels were carefully tested for selenium with negative results.

A selenium steel with the manufacturer's analysis of 0.254 per cent of selenium was analyzed by the distillation method. A percentage of 0.241 was obtained for each of three determinations when the values were rounded off at the third place. On the same sample the control method used by the Carpenter Steel Company was employed, except that the selenium precipitate formed was redissolved with bromine in hydrochloric acid solution and reprecipitated with hydroxylamine hydrochloride. In the authors' opinion reprecipitation is necessary to free the selenium from impurities. For each of two determinations a percentage of 0.241 was found, which is in excellent agreement with those obtained by the distillation method. The authors' volumetric method was now used on this sample, 50 determinations giving an average of 0.240 per cent with an average deviation less than 0.002 per cent. This method is considerably more rapid than the gravimetric methods, several analyses being easily accomplished in 1.5 hours.

Another specimen of steel, which according to the manufacturer contained 0.230 per cent of selenium, was analyzed by the distillation method. The values obtained—0.216, 0.216, 0.218, and 0.216 per cent—are lower, and in the authors' opinion this is additional evidence that the manufacturer's analyses give results that are consistently too high.

Carefully purified potassium iodate, bromate, and dichromate were used to standardize the thiosulfate solution. It was found that the Norris and Fay method could be modified to the extent of carrying on the titration at room temperature (20°) if the excess of sodium thiosulfate solution was not more than 5 ml. of 0.02 N solution. In all titrations the concentration of hydrochloric acid was 0.2 N in a volume of 150 cc.

Two standard solutions of selenium were used for reference: (1) a solution of selenious acid standardized by precipitating selenium with hydroxylamine hydrochloride and weighing, and (2) a solution of sodium selenocyanate made by dissolving a known weight of highly purified selenium in sodium cyanide and diluting to a definite volume. The selenium precipitated from the selenious acid solution was determined under the same conditions used in the steel analysis and found to vary from the standardization value by less than 1 part per 1000. Again on precipitating the selenium from the standard sodium selenocyanate solution and carrying on the procedure used in the steel analysis, results were obtained agreeing as closely with the standardization value.

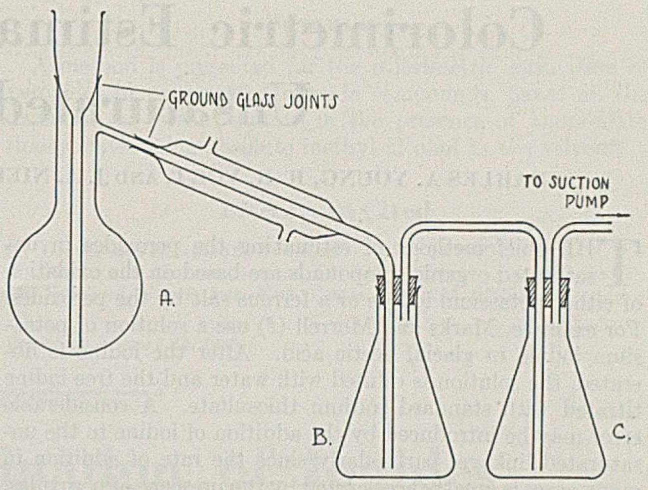

Figure 2. Distillation Apparatus

A. 500-ml. distilling flask
B. 250-ml. Erlenmeyer flask containing 20 ml. of saturated bromine water diluted to 50 ml.
C. 250-ml. Erlenmeyer flask containing 50 ml. of water

In 150 ml. of solution containing 10 mg. of ferric chloride, 20 ml. of 2.5 per cent sodium fluoride, 0.2 N with hydrochloric acid, gave no starch iodine color when 2 grams of potassium iodide were added. This amount of iron is in excess of that always present with the selenium precipitate.

Filtrates were examined for selenium by allowing them to stand for 12 hours and then filtering through filter paper. Appreciable amounts were recovered until the method of digesting for 15 minutes in the presence of macerated filter paper was adopted. Six successive filtrates were then found to be free from selenium. The authors are convinced that small amounts of selenium are commonly lost on filtration unless special precautions are taken. Digestion in the presence of macerated filter paper effectively prevents the loss of colloidal selenium.

Acknowledgment

The steel samples used in this work with the analyses reported by the company's laboratory were supplied through the courtesy of the Carpenter Steel Company, Reading, Pa.

Summary

A modification of the Norris and Fay volumetric method has been developed for the determination of selenium in steel. The reagents used are inexpensive; the cost for an analysis is less than 4 cents. The method is rapid and accurate, and could be applied in any determination of selenium when it is possible to precipitate the free element.

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Colorimetric Estimation of Peroxides in Unsaturated Compounds

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THE chief methods of estimating the peroxides in unsaturated organic compounds are based on the oxidation of either potassium iodide or a ferrous salt by the peroxides. For example, Marks and Morrell (*2*) use a solution of potassium iodide in glacial acetic acid. After the iodine is liberated, the solution is diluted with water and the free iodine titrated with standard sodium thiosulfate. A considerable error may be introduced by the addition of iodine to the unsaturated linkage, particularly since the rate of addition in many cases is greatly accelerated by the presence of peroxides.

Yule and Wilson (*3*) estimate peroxides in cracked gasoline by shaking it with an acidified solution of ferrous sulfate and ammonium thiocyanate in a 50 per cent acetone-water mixture. The ferric thiocyanate which is formed is titrated with a standard titanous chloride solution. Several improvements in this method are desirable. Instead of using as the solvent 50 per cent acetone, in which most hydrocarbons have a limited solubility, it is preferable to use a solvent which is miscible with hydrocarbons. It is also desirable to estimate the ferric thiocyanate formed by the peroxides by some means other than standard titanous chloride, in order to avoid the difficulties inherent in the use of this reagent. Since minute quantities of ferric thiocyanate produce an intense coloration when in solution, it is possible and advantageous to determine the ferric thiocyanate colorimetrically. The convenience and rapidity of colorimetric procedures are well known.

In selecting a solvent there are two important factors to be considered: (1) the solvent should dissolve an appreciable quantity of the inorganic salts used, and (2) the solvent should be miscible with the organic compounds which are to be analyzed. Absolute methyl alcohol meets these requirements.

Preparation of the Reagent

The reagent is prepared by dissolving 5 grams of ammonium thiocyanate and 5 cc. of 6 *N* sulfuric acid in 1000 cc. of absolute methyl alcohol, and then saturating the solution with pure ferrous ammonium sulfate. Shaking the solution with the finely pulverized salt for a few minutes is sufficient. The faint pink color which is formed may be evaluated by comparing it with a suitable color standard. The results of analyses may then be corrected for the trace of ferric thiocyanate present in the reagent. The faint pink color in the reagent does not deepen appreciably over a period of an hour or so. The usefulness of the reagent may be extended to much longer periods by keeping the reagent in an inert atmosphere.

Preparation of the Color Standard

Solutions of ferric thiocyanate in absolute methyl alcohol are used as color standards. In order to make the colorimetric comparisons conveniently and accurately, the concentration of the standard solution should not differ more than two- or threefold from that of the solution whose color is being determined. Furthermore, since solutions of ferric thiocyanate in methyl alcohol fade slowly on standing, the standard solutions should be freshly prepared each day. This may be accomplished by adding ammonium thiocyanate and sulfuric acid, in the same proportions used in preparing the reagent, to standard solutions of ferric chloride in absolute methyl alcohol. For colorimeters of the Duboscq type, it is recommended that the concentrations of the ferric chloride solutions range from 0.00004 to 0.001 mole per liter. Three concentrations are sufficient for ordinary purposes. In case any ferric chloride has been reduced to the ferrous state, a small amount of active peroxide may be added.

Procedure

If the compound being analyzed is a liquid having a moderate peroxide concentration, it is added directly to the reagent by means of a small pipet or buret. Otherwise a solution in absolute methyl alcohol is made, and the concentration so adjusted that, when quantities of the solution ranging from 0.05 to 0.5 cc. are added to 10-cc. portions of the reagent, a color equivalent to 0.00002 to 0.0002 mole of ferric thiocyanate per liter is produced. With many compounds, such as butylacetylene and 1-hexene, the color reaches a maximum intensity within a few seconds, and the solution is then immediately compared with a color standard having approximately the same concentration. Some peroxides, such as the one found in diamylene, react with the reagent rather slowly. In such cases the reaction may be greatly accelerated by heating the solution to just below boiling for 4 or 5 minutes. The quantity of peroxide detected by this method is proportional to the amount present in the solution. The results of an analysis are reproducible.

Discussion

Potassium iodide is more easily oxidized than is ferrous sulfate, as the molal electrode potentials of the ferrous and the iodide ions show. Certain peroxides, such as benzoyl peroxide, readily liberate iodine from potassium iodide, but react extremely slowly, if at all, with ferrous sulfate. Consequently, if some organic material contains a wide variety of peroxides, it is possible that a portion of the peroxides is not determined by a method using a ferrous salt as the reducing agent. Yule and Wilson (*3*) found that after an exhaustive treatment of cracked gasoline with ferrous sulfate, there still remained a small amount of peroxide which oxidized potassium iodide. Nevertheless, since potassium iodide cannot be used with many peroxides of unsaturated compounds, the ferrous sulfate methods are very useful for comparative purposes even where complete reduction of all peroxides is not obtained.

TABLE I. COMPARISON OF METHODS

	Yule and Wilson	Colorimetric
Cracked gasoline	0.025	0.036
Butylacetylene	0.23	0.29
Diamylene	0.30	0.54

The accuracy of the colorimetric method presented here has been studied by means of dilute solutions of hydrogen peroxide of known concentrations and by means of pure preparations of succinyl peroxide ($(HOOC.CH_2.CH_2.COO)_2$). For example, the concentration of a hydrogen peroxide solution as given by the standard potassium permanganate method was 0.0279 mole per liter, while the colorimetric procedure gave 0.028 mole per liter. The succinyl peroxide was prepared by the method of Clover and Houghton (*1*), and was recrystallized twice from acetone. The calculated weight per cent of active oxygen in succinyl peroxide is 6.83 per cent; obtained 7.0 per cent.

For fuller evaluation of the merits of the colorimetric procedure, it was compared with the method of Yule and Wilson (*3*). In calculating the results of an analysis, the reasonable assumption was made that each mole of peroxide reacted with two equivalents of ferrous sulfate. The comparison of the two methods is presented in Table I, the results being reported in terms of gram equivalents of active oxygen per liter of hydrocarbon.

The lower results given by the method of Yule and Wilson are probably due to the incomplete reduction of the peroxides, for the reacting substances are, on the whole, concentrated in two different layers. The more peroxide there is present, the more difficult it becomes to obtain a quantitative reduction. Yule and Wilson have noted that an increase in peroxide concentration does not give a proportionate increase in the quantity of peroxide detected by their method.

Summary

A method is presented for the colorimetric estimation of peroxides in unsaturated organic compounds, based on the oxidation of ferrous sulfate in the presence of ammonium thiocyanate, using absolute methyl alcohol as the solvent.

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Volumetric Determination of Iodides by Ceric Sulfate

An Application of the Indicator *o*-Phenanthroline Ferrous Ion

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THE direct oxidative titration of iodides to a visual end point depends, in most procedures, upon the conversion of the initially liberated iodine to the cationic or covalent state. The end point is the disappearance of iodine, and it is in the manner of determining this disappearance that the various methods differ. Each is subject to certain disadvantages, either of manipulation or of estimating the end point.

In Andrews' method (*1*) an immiscible organic solvent, such as chloroform, must be used to detect the oxidation of the iodine to iodine monochloride. Addition of oxidizing agent, with shaking after each addition, is continued until the violet iodine color is discharged from the layer of inert solvent. Lang's procedure (*6*) is more direct. Titration is continued to the disappearance of the blue starch-iodide color which occurs at the conversion of the iodine to iodine cyanide. To minimize the danger of working with an acid solution of a cyanide, it is necessary to use long, narrow-necked flasks. In Berg's method (*2*) the iodine liberated in the oxidation reacts with acetone to form iodoacetone. Starch is the indicator. As the end point is approached each drop of oxidizing agent produces a blue color which is slowly discharged. The end point is reached when further addition of oxidant no longer produces a blue color. The most common oxidizing agent is potassium iodate, although Swift (*7*) has shown that potassium permanganate, potassium dichromate, and ceric sulfate can be used in the Andrews procedure, and Berg (*3*) has shown the utility of potassium bromate in the cyanide method.

In the method to be described the disadvantages of these methods are eliminated by avoiding the use of an iodine end point. A previous attempt in this direction was made by Hahn and his co-workers (*5*), who proposed titration to a permanganate end point, without, however, eliminating the inconvenience of a two-phase system. The iodine liberated in the oxidation had to be extracted (with ethyl acetate) to permit detection of the end point.

The present method is based upon Berg's procedure for the elimination of iodine by the acid catalyzed iodination of acetone. By the use of ceric ion as oxidizing agent and *o*-phenanthroline ferrous ion as indicator, the titration of iodides can be performed rapidly, precisely, and accurately.

Reagents

Two ceric sulfate solutions were prepared by dissolving ceric ammonium sulfate in *M* sulfuric acid, and were standardized against sodium oxalate by the method of Walden, Hammett, and Chapman (*8*). Solution I was 0.1074 *M;* solution II, 0.09982 *M.*

An approximately 0.1 *M* solution of purified potassium iodide was used throughout these experiments. It was standardized against the ceric sulfate solutions, the end point being determined electrometrically—a procedure shown to be exact by Willard and Young (*9*).

Acetone was of reagent grade and the potassium bromide, sodium chloride, and sulfuric acid were of C. P. grade. Blanks on these materials in the amounts used in the experiments required a fraction of a drop of ceric sulfate to change the color of the indicator.

The solution of *o*-phenanthroline ferrous sulfate was 0.025 *M.*

Method of Analysis

A measured volume of the iodide solution is treated with 25 ml. of acetone, 10 ml. of 9 *M* sulfuric acid, and water to make the volume 100 ml. After adding one drop of *o*-phenanthroline ferrous sulfate solution, the mixture is titrated with the ceric sulfate until the pink color of the indicator changes to a pale blue. The end point is sharp and lasts several minutes.

The rate at which the oxidant is added does not affect the results. At the start of a titration rapid addition of the ceric sulfate may cause the solution to be colored brown by free iodine, which rapidly disappears on interrupting the titration and stirring a few seconds. It is desirable to conduct the titration in flasks, since iodoacetone is a lachrymator.

Results

Table I illustrates the precision with which this titration can be performed. There is no difficulty in obtaining checks better than one part per thousand.

From these results the normality of the iodide solution is found to be exactly twice the molarity as determined potentiometrically. Assuming monoiodination of the acetone, the reaction may be represented as

$$\mathrm{KI + 2Ce(SO_4)_2 + C_3H_6O = KHSO_4 + Ce_2(SO_4)_3 + C_3H_5OI}$$

It is unnecessary to adhere strictly to the conditions for the titration as given above. Equally good results are obtained if 5 or 15 ml. of acid are used or if the solution is diluted. Such changes merely affect the rate of reaction of the iodine

TABLE I. PRECISION ATTAINABLE

Potassium Iodide Ml.	Ceric Sulfate Ml.
	Solution I, 0.1074 M
10.00	18.67
	18.69
	18.70
	18.69
	18.70
	Av. 18.69
	Av. deviation 0.8 part per 1000
	Solution II, 0.09982 M
10.00	20.10
	20.10
20.00	40.20
5.00	10.04
	Av. deviation 0.1 part per 1000

TABLE II. EFFECT OF VARYING CONCENTRATION OF ACID AND VOLUME OF SOLUTION

(10.00 ml. of potassium iodide and 25 ml. of acetone in each titration. Ceric sulfate required, 18.69 ml.)

Volume at Start Ml.	9 M H_2SO_4 Ml.	Ceric Sulfate Used Ml.
100	1	18.75
100	5	18.70
100	15	18.68
100	20	18.61
145	30	18.60
100	30	18.43
200	20	18.69

TABLE III. EFFECT OF BROMIDE

(10.00 ml. of potassium iodide and 25 ml. of acetone in each titration. Ceric sulfate required, 18.69 ml.)

0.1 M KBr Ml.	Volume at Start Ml.	9 M H_2SO_4 Ml.	Ceric Sulfate Used Ml.
5	100	10	18.70
10	100	10	18.72
15	100	10	18.85
10	200	20	18.68
15	200	20	18.71
20	200	20	18.75
30	300[a]	30	18.72
50	300[a]	30	18.76

[a] 35 ml. of acetone.

with the acetone, which is proportional to the concentration of acid and of acetone (*4*). Too little acid is undesirable, since it leads to slightly high results and the titration is time-consuming, while too high a concentration of acid leads to low results and a fleeting end point. The data in Table II show the effect of varying these conditions.

EFFECT OF BROMIDE. Measured volumes of 0.1 M potassium bromide were added to the iodide and the titration was performed as described above. In general, more ceric sulfate is required than for iodide alone. The larger the ratio of bromide to iodide, the greater is the excess of ceric sulfate necessary to reach an end point lasting 1 minute. This interference can be almost entirely eliminated by diluting the solution sufficiently while keeping the acid concentration approximately constant. Within the limits investigated it was possible to titrate the iodide with an accuracy of 3 to 4 parts per thousand when the bromide-iodide ratio was 5 to 1. The results of several of these titrations are given in Table III.

EFFECT OF CHLORIDE. Moderate amounts of neutral chloride do not interfere. Titrations in the presence of 0.5, 1.0, and 5.0 grams of sodium chloride required 20.10, 20.16, and 20.23 ml. of ceric sulfate, compared to 20.10 ml. for iodide alone. In the titration with 5.0 grams of chloride present, precipitation of the salt occurred. The excess ceric sulfate required with the larger amounts of chloride may be due to the formation of hydrochloric acid, since titrations of iodide alone in which hydrochloric acid was substituted for the sulfuric acid used excess ceric sulfate.

Summary

In the presence of acetone and sulfuric acid iodides may be titrated quantitatively with ceric sulfate to a visual end point, using *o*-phenanthroline ferrous ion as indicator. The effect of bromides and chlorides on this titration has been determined.

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Standardization of Sodium Thiosulfate Iodometrically against Copper

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THE method of standardizing sodium thiosulfate against copper and of determining copper in samples which are soluble in nitric acid as outlined by Gooch and Heath (*1*) requires long evaporations. Kendall (*2*) has pointed out that these evaporations eliminate nitrous acid. The use of urea for the elimination of nitrous acid was worked out independently by the author. Afterwards, in a careful study of the literature it was found that Koelsch (*3*) suggested a procedure essentially the same as that given below and that Pozzi-Escot (*4*) also suggested the use of urea, employing, however, a much longer procedure. It is felt that this simple method has been overlooked and should be called to the attention of the analytical chemist. Results with this method agree with those of Gooch and Heath (*1*) within one part per thousand.

Procedure

Weigh a sample of pure copper, 0.2 to 0.3 gram. Dissolve the sample in 2 to 5 ml. of concentrated nitric acid. Add 0.5 gram of urea and heat to boiling. Cool, adjust the acidity by adding 6 N ammonium hydroxide until a white precipitate is formed, dissolve the precipitate with 6 N acetic acid, and add 5 ml. in excess. Add 3 grams of potassium iodide, allow to stand 2 minutes, and titrate the liberated iodine with sodium thiosulfate solution. Starch is used as an indicator (2 ml. of 1 per cent solution) and should be added about 1 ml. before the end point is reached.

Variations in concentration of NO_3^- and NH_4^+ have no effect on the final precision.

Literature Cited

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Microdetermination of Ammonia Nitrogen in Eggs

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A method for the determination of ammonia nitrogen in eggs without aëration is described. The ammonia is absorbed in standard acid from a thin layer of an alkaline solution of the sample in a modification of the Conway-Byrne cell. It has many advantages over the troublesome aëration methods in that larger numbers of samples may be run simultaneously and the operation, control, and equipment are simpler. Data are presented to show the reliability and accuracy of the procedure. Directions are given for the fabrication of the modified Conway-Byrne cell.

INTERIOR quality of shell eggs is commonly and most conveniently determined in commerce upon the unopened egg by means of candling. Physical methods that measure quality more precisely have been described for eggs which may be broken out (*3*, *4*). Chemical methods have not found application in this field except for comparatively few studies of the loosely bound nitrogen (*2*, *5*). The chemical procedure hitherto followed has been an adaptation of the Folin aëration method for ammonia in urine—that is, aëration of an alkaline solution of the material, absorption of the ammonia by excess standard acid, and its subsequent determination by titration or nesslerization.

The aëration method has many disadvantages, especially when applied to the estimation of the extremely small amounts of ammonia in egg materials. It involves a complicated setup of wash bottles, aëration tubes, absorption tubes, manometers, pressure regulators, and traps, since the volume of air, its rate of flow, and its pressure must be carefully regulated and its freedom from ammonia insured (*2*, *5*). Excessive foaming must be prevented, which is very difficult with egg materials. The time involved for aëration is between 4 and 5 hours, and the attention of the operator is required during this period.

To overcome the inconvenience of the aëration method an attempt was made to use the absorption process described by Conway and Byrne (*1*), but it was found necessary to modify this procedure to adapt it to the purpose at hand. The principle involved is the liberation of ammonia by a saturated potassium carbonate solution and its absorption in standard acid as before, but instead of its removal by aëration, the volatility of the ammonia is employed for this purpose.

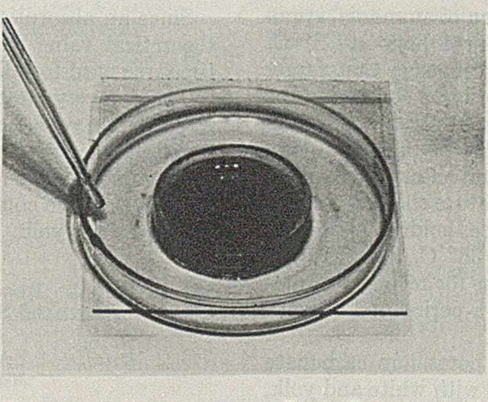

FIGURE 1. ABSORPTION CELL, INDICATING METHOD OF INTRODUCING MATERIALS

Apparatus

Cells were made from tops of 10-cm. Petri dishes. The rims of these dishes were ground to a smooth surface on a piece of plate glass with the aid of fine Carborundum powder and water. Glass rings 5 cm. in diameter and of a height slightly less than that of the side walls were centered in the dishes and sealed in place with de Khotinsky cement, which in turn was coated with beeswax to protect the cement from the alkali used. This wax coating had to be renewed at intervals. An all-glass cell proved very satisfactory but was unduly expensive. Covers were glass plates with a ground surface and when used were coated with a thin film of vaseline to insure a gas-tight seal. By slipping the cover horizontally until there was an opening just large enough for the tip of a pipet, solutions were added to the cell without either absorption of ammonia from the atmosphere or loss of ammonia from the cell. Figure 1 shows the cell and indicates the method of introduction of materials. In washing these cells it was found advisable to rinse them in a 1 to 1 hydrochloric acid solution to remove the last traces of the alkali, especially from the inner chamber. Ostwald-Folin pipets were used to sample the egg material. Tips were adjusted to allow rapid delivery and they were then calibrated to deliver 5 cc. of egg white, yolk, diluted yolk, or mixed whole egg. An electrically heated cabinet kept at 38° ± 1° C. by means of a thermostat was used to heat the cells for the required time.

Solutions Required

The acid used was 0.005 *N* hydrochloric acid, made by diluting 0.10 *N* hydrochloric acid, and contained the indicator. The indicator, adapted from that described by Tashiro and modified by Conway (*1*), was prepared by dissolving 0.08 gram of the sodium salt of methyl red and 0.02 gram of methylene blue separately in alcohol, mixing, and making up to 100 cc. with alcohol. One cubic centimeter of this solution was added to each 100 cc. of the standard acid before making to volume. With this indicator the end point was that point at which the least color was present, the solution having a grayish tinge between the red of the acid and the green of the alkaline colors. The end point was very sharp and readily reproducible, titrations checking within 0.01 cc. The excess acid was determined by titration with 0.0025 *N* sodium hydroxide, also prepared by diluting a 0.1 *N* solution and standardized each day against the acid. A saturated potassium carbonate solution was used to liberate the ammonia from the egg mixtures. Ammonia-free water prepared by distilling distilled water containing a small amount of potassium acid sulfate was used throughout, and it was found advisable to carry out the determinations in an ammonia-free atmosphere. Suitable blanks were run.

Method

This method was used for whites and yolks separately and for mixed whole eggs. The eggs to be examined were broken out into Petri dishes and samples taken as described below.

Egg White. Place in the inner chamber 5 cc. of 0.005 *N* hydrochloric acid from a calibrated pipet and in the outer chamber approximately 2 cc. of ammonia-free water. Cover the cell. Slip the cover horizontally slightly to provide a narrow opening and add to the outer chamber 5 cc. of the liquid white from the pipet calibrated for this purpose. Close the cell and mix the contents by gently tilting and rotating. Introduce approximately 2 cc. of saturated potassium carbonate solution into the outer chamber and again mix the contents as before. Place the cells in stacks with a kilogram weight on top in the cabinet kept at 38° C. for 1.5 hours. At the end of this period, titrate the excess acid with 0.0025 *N* sodium hydroxide solution, and calculate the ammonia to milligrams of ammonia nitrogen per 100 cc. of egg white.

Egg Yolk. This procedure has been slightly modified by a preliminary dilution of yolk, since undiluted yolk does not mix properly with the carbonate solution under the conditions specified for egg white.

After removing the sample of white, slit the yolk membrane slightly with a small scalpel at the top of the yolk without removing the firm white. Thrust the Ostwald-Folin pipet with an enlarged tip through the opening, remove 5 cc. of yolk, and add to 3 cc. of ammonia-free water in a test tube. The yolk can be conveniently blown out by means of a rubber bulb attached to the pipet. After thoroughly mixing, introduce a 5-cc. aliquot with the pipet calibrated for diluted yolk into the outer chamber of a cell containing 5 cc. of the standard acid in the inner chamber. Add 3 cc. of the saturated potassium carbonate solution to the diluted yolk, close the cell, mix with the same rotary and tilting motion, and place in the cabinet with a weight for 1.5 hours at 38° C. As before, titrate the excess acid with 0.0025 *N* sodium hydroxide and calculate the ammonia to milligrams of ammonia nitrogen per 100 cc. of yolk.

Mixed Whole Egg. Mixed whole egg was prepared by breaking an egg in a 6-ounce wide-mouth glass-stoppered bottle and shaking it with four large glass beads. The procedure then used was practically the same as for egg yolk.

Deliver 5 cc. of mixed whole egg with the Ostwald-Folin pipet calibrated for mixed whole egg into the outer chamber of a cell which contains 5 cc. of the standard acid in the inner chamber. Add 3 cc. of the saturated potassium carbonate solution, close the cell, mix by tilting and rotating, and place in the cabinet for 1.5 hours at 38° C. Titrate the excess acid and calculate in terms of milligrams of ammonia nitrogen per 100 cc. whole egg.

Experimental

Conway and Byrne (*1*) have suggested alternative sets of conditions for the quantitative absorption of ammonia, stipulating 1.5 hours at room temperature or 1 hour at 38° C. The ammonia nitrogen is so low in fresh eggs that larger samples are required than can satisfactorily be handled in the Conway-Byrne unit. With the modification of the unit suggested in this paper the interrelationships of time, temperature, and linear dimensions of the inner and outer chambers require a longer period or a higher temperature than that specified by Conway and Byrne. In practice, holding periods at room temperature up to 3 hours or at 38° C. less than 1.5 hours did not provide suitable conditions for recovery of ammonia from egg materials. As a result a period of 1.5 hours at 38° C. was chosen.

The volume of saturated solution of potassium carbonate required was determined by experiment with white and yolk, keeping other factors constant.

From Table I it was evident that the quantity of saturated solution of potassium carbonate could be varied considerably without changing the amount of ammonia liberated. Since it was desirable to keep the volume in the outer chamber as small as possible and there was no advantage in using larger volumes, it was deemed sufficient to use for the white 2 cc. of the saturated solution of potassium carbonate and for the yolk, 3 cc.

Table I. Saturated Solution of Potassium Carbonate Required for Complete Expulsion of Ammonia

K_2CO_3 Solution Used	Ammonia Nitrogen White	Ammonia Nitrogen Yolk
Cc.	*Mg./100 cc.*	*Mg./100 cc.*
1	..	2.30
2	0.49	2.63
3	0.52	2.60
4	0.45	2.58
5	0.46	2.63

The possibility that ammonia might be liberated from yolk alone during the period of heating was investigated and the results are given in Table II.

Table II. Effect of Holding Yolk at 38° C. for 1.5 Hours without Addition of Carbonate Solution

	0.005 *N* Alkali Required to Titrate Acid
	Cc.
NH_3-free water	4.52
	4.54
NH_3-free water + yolk	4.58
	4.54
	4.54
	4.52

Since titration values of the standard acid were the same with and without the yolk, it is certain that no ammonia was liberated by the yolk itself when held for the required time without the carbonate addition. This is probably due to the fact that yolk is naturally slightly acid, having a pH of approximately 6.0 when fresh which increases to about pH 6.8 after long periods of storage.

The absorption period was established as the time required for the recovery of ammonia from a standard ammonium sulfate solution at 38° C.

Table III. Time Necessary for Complete Removal of Ammonium Nitrogen from Ammonium Sulfate Solution

(Results expressed as milligrams of ammonia nitrogen in 100 cc. of solution.)

Time at 38° C.	Concentration of Solution Used	Concentration of Solution by Actual Determination
Hours		
0.5	4.11	2.45
1.0	4.11	3.56
1.5	4.11	4.07
2.0	4.11	4.03

Since an absorption period of 1.5 hours gave practically the theoretical value for the ammonia nitrogen recovered, this time was used for all the experiments.

The recovery of ammonia from a standard ammonium sulfate solution replacing yolk or when added to yolk was found to be satisfactory. Varying quantities of a standard ammonium sulfate solution were used in a series of determinations to produce concentrations similar to what might be expected in egg yolk.

Table IV. Recovery of Ammonia Nitrogen from a Standard Solution of Ammonium Sulfate

No. of Detns.	Ammonia Nitrogen Added	Ammonia Nitrogen Recovered	Standard Deviation
	Mg./100 cc.	*Mg./100 cc.*	
7	2.05	2.04	0.143
10	4.11	4.06	0.145
7	5.00	5.24	0.080
7	6.16	5.97	0.365

A comparison of the amounts added and recovered in Table IV shows satisfactory agreement.

When definite amounts of ammonia nitrogen were added to yolk and determinations made before and after the additions, the results shown in Table V were obtained.

In Table V three different quantities of ammonia nitrogen were added to aliquots of two lots of pooled yolk. The recovery of the ammonia nitrogen was deemed satisfactory in all cases. The period of 1.5 hours at 38° C. was used for the experiments reported in Tables IV and V and for results reported below.

TABLE V. RECOVERY OF AMMONIA NITROGEN FROM EGG YOLK CONTAINING VARYING ADDITIONS OF AMMONIUM SULFATE

(Results expressed as milligrams of ammonia nitrogen per 100 cc.)

No. of Detns.	Determined on Yolk Alone	Added to Yolk	Calculated Total	Actually Determined
4	3.47	1.81	5.28	5.23
4	2.49	1.81	4.30	4.40
4	3.47	3.38	6.85	6.76
4	2.49	3.38	5.87	5.80
4	3.47	4.73	8.20	8.23
4	2.49	4.73	7.22	7.39

In the procedure for egg white described above, the directions specify the use of liquid white. Firm white could also be used, but the liquid white is much easier to pipet and mix with the carbonate solution than the firm white and has the same percentage of ammonia nitrogen for the same egg. This is shown in Table VI, where the values for the three distinct layers of egg white for four eggs are given. All the results are within experimental error. In practice it was found satisfactory to slit the firm white envelope and pipet from the mixture of outside and inside liquid white.

TABLE VI. DISTRIBUTION OF AMMONIA NITROGEN IN EGG WHITE

(Results expressed as milligrams of ammonia nitrogen per 100 cc.)

Egg	Outside Liquid White	Firm White	Inside Liquid White
1	0.12	0.10	0.11
2	0.14	0.18	0.21
3	0.12	0.18	0.12
4	0.20	0.21	0.20

In a large number of eggs of similar history the ammonia nitrogen was determined for both white and yolk by the aëration and absorption methods. Both methods were not applied on the same samples. Reference to Table VII shows that in general there was satisfactory agreement between the values obtained by the two methods for both white and yolk on material of similar nature.

TABLE VII. COMPARISON OF RESULTS OF THE ANALYSIS OF EGGS BY AËRATION AND ABSORPTION METHODS

Method	Material	No. of Samples	Ammonia Nitrogen	Standard Deviation
			Mg./100 cc.	
Aëration	White	83	0.24	0.086
	Yolk	83	2.30	0.287
Absorption	White	16	0.35	0.137
	Yolk	301	2.41	0.280
	Mixed whole egg	6	0.87	0.003

Acknowledgment

The eggs used in this study were kindly supplied by the Poultry Section of the Experiment Station.

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Estimation of Oleomargarine in Ice Cream

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A method for determining the percentage of oleomargarine and butter fat in ice cream is given, which consists of a modified Roese-Gottlieb extraction procedure combined with a modified Reichert-Meissl procedure. Formulas are derived for calculating the percentage of oleomargarine in the extracted fat, the fat being calculated in the usual manner.

THE lower price of oleomargarine as compared to butter fat at present has led some manufacturers of ice cream to substitute oleomargarine to some degree for butter fat. This may soon bring about serious consequences; it is illegal in many states and some investigators (*3*) have shown that ice cream made of oleomargarine is deficient in certain vitamins. It would seem obviously unfair to sell as ice cream a product that is not made of butter fat, but any ruling of fair trade competition must first have some basis for classification. This problem led the authors to work on a method for determining the relative amounts of oleomargarine and butter fat in ice cream with a reasonable degree of accuracy. The problem is more difficult than it first seemed. Modern homogenizing equipment has made microscopic examination and staining almost useless as a means of detecting oleomargarine, and refractive index and specific gravity gave no suitable quantitative data. The iodine value gave qualitative indication, but because of the diversity of oleomargarines on the market did not give quantitative confirmation. The Kirschner-Flanders (*4*) method did not give quantitative results when tried on the authors' samples. The usual Reichert-Meissl method (*1*) was also somewhat unsatisfactory and gave erratic results.

However, it was found that if the Roese-Gottlieb extraction procedure and the Reichert-Meissl procedure were slightly modified, a precise method was obtained.

Experimental

APPARATUS. The usual apparatus for determining the fat percentage in butter was used (*2*).

REAGENTS. Oleomargarine was furnished by the Joseph Costa Co., Athens Ga., and had the following composition:

	%	%
Total fat		83
Oleic oil	34	
Neutral oil	34	
Cottonseed oil	15	
Moisture		12
Salt		3
Milk solids		2

Ammonium hydroxide, ethyl alcohol, diethyl ether, and petroleum ether as given by the method of the Association of Official Agricultural Chemist (*2*).

Sulfuric acid: 31.5 cc. of acid (sp. gr. 1.83) per liter.

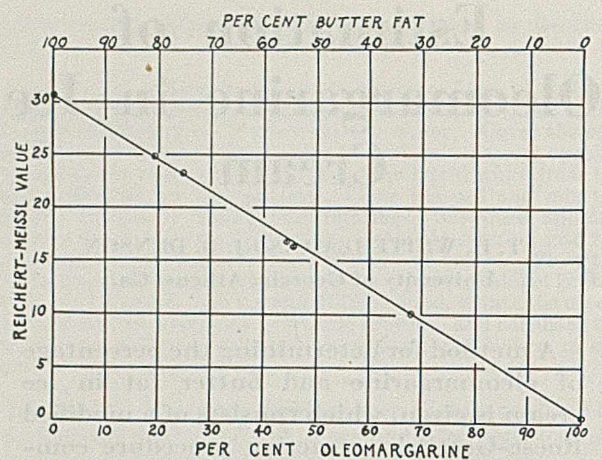

FIGURE 1. RELATION OF REICHERT-MEISSL VALUE TO PERCENTAGE OF OLEOMARGARINE AND BUTTER FAT IN ICE CREAM

Procedure

EXTRACTION OF FAT FROM ICE CREAM. The ice cream is allowed to soften at room temperature. The fat soon separates and rises to the top, and the sample is then thoroughly mixed with an egg beater or other mechanical stirrer.

Aliquot portions of about 100 grams each are accurately weighed and the fat is extracted by using 12.5 cc. of ammonium hydroxide solution, 50 cc. of ethyl alcohol, 100 cc. of diethyl ether, and finally 100 cc. of petroleum ether. After the addition of each the mixture is thoroughly agitated in the separatory funnel for 30 seconds, and is then allowed to stand for 20 minutes, before separating the layers. As much as possible of the ether-fat solution is drawn off into a flask through a small, quick-acting filter. A second extraction, with 100 cc. of each ether, is necessary to insure complete removal of fat. The clear solution is drawn off through a small filter into the same flask; and the tip of the separatory funnel, the filter, and the funnel are washed with a few cubic centimeters of a mixture of equal parts of the two ethers, free from suspended water. The greatest portion of ether is distilled off, and the fat is dried in an oven at 90° C. to constant weight. The flask is weighed with a similar flask as a counterpoise. The fat is now ready for use, and can conveniently be handled at about 40° C. (A volume of about 5.5 cc. at this temperature weighs about 5 grams.) After samples have been taken from the flask, the fat is completely removed with petroleum ether. The weight of the dried flask with residue is deducted to obtain the weight of the fat.

Determination

Weigh out accurately a sample of about 5 grams of extracted fat in a tared glass vessel, add 10 cc. of ethyl alcohol and 2 cc. of sodium hydroxide solution, and saponify on a water bath (usually 1 hour).

Allow the flask to cool to room temperature after all alcohol has evaporated, taking care to prevent any loss of soap. The last traces of alcohol can be removed by waving the cool flask to and fro, mouth down. Dissolve the soap in 100 cc. of recently boiled distilled water and transfer to a 250-cc. distilling flask. Heat the flask up to 60° to 70° C. and add 40 cc. of sulfuric acid solution. Drop in a few pieces of pumice stone and connect to the condenser. Warm the flask until the fats separate as a clear layer, then continue the heating until 110 cc. of distillate have been collected in a graduated cylinder. The time of distillation should be between 28 and 32 minutes. Titrate a 100-cc. portion of the distillate with standard 0.1 N sodium hydroxide solution, using phenolphthalein as indicator. The Reichert-Meissl value is calculated from the usual formula.

$$\text{Reichert-Meissl value} = \frac{\text{cc. of NaOH} \times 1.1 \times 5}{\text{grams of sample}}$$

The procedure followed was to make up samples of ice cream varying from 100 to 0 per cent of butter fat and from 0 to 100 per cent of oleomargarine, and to analyze these according to the procedure outlined above. The results are given in Table I and Figure 1.

TABLE I. REICHERT-MEISSL VALUES OF EXTRACTED FAT

Sample	Butter Fat %	Oleomargarine %	Reichert-Meissl Value
1	100.0	0.00	30.96
2	80.72	19.28	24.96
3	75.74	24.26	23.24
4	55.67	44.33	16.65
5	55.33	44.67	16.45
6	32.36	67.64	10.02
7	0.00	100.00	0.38

Duplicate determinations on butter fat varied ±0.1 in the Reichert-Meissl value and ±0.03 on oleomargarine duplicates. Taking 30.96 and 0.38 as reliable averages and the slope of the curve in Figure 1 as 0.31, it was possible to obtain a formula by substitutions in the classical equation for a straight line, $y = mx + b$, where m is the slope and b a constant.

$$\text{Per cent of oleomargarine in fat} = \frac{30.96 - \text{Reichert-Meissl value}}{0.31} \quad (1)$$

$$\text{Per cent of butter fat in fat} = 100 - \text{per cent of oleomargarine} = \frac{\text{Reichert-Meissl value} - 0.38}{0.31} \quad (2)$$

Since the variation in 0.38 is greater than that in 30.96, it is safer to subtract from 100 per cent to get butter fat.

To test this formula, samples of varying composition were prepared and submitted for analysis to Mr. Dunson, who did not know their composition. The results are shown in Table II.

TABLE II. ANALYSES OF UNKNOWN SAMPLES

	Sample	Reichert-Meissl Value	Calculated Percentage	Theoretical Percentage	Deviation
Oleomargarine	1	5.57	82.0	83.0	−1.0
Butter fat	1	5.57	18.0	17.0	+1.0
Oleomargarine	2	13.25	57.1	57.2	−0.1
Butter fat	2	13.25	42.9	42.8	+0.1
Oleomargarine	3	27.45	11.3	12.0	−0.7
Butter fat	3	27.45	88.7	88.9	+0.7

The percentage of fat may be calculated as usual.

$$\text{Per cent of fat in ice cream} = \frac{\text{grams of fat} \times 100}{\text{grams of ice cream}}$$

The composition of this fat is then calculated by Formulas 1 and 2. The grams of oleomargarine and butter fat can be calculated easily and the percentage of oleomargarine in the original ice cream sample found by substituting grams of oleomargarine for grams of fat.

Discussion

Although this paper offers no new qualitative differentiation between butter fat and oleomargarine, it does offer a more exact quantitative determination, accomplished by standardizing the extraction method for ice cream, and by increasing the strength of the sulfuric acid in the usual Reichert-Meissl procedure. In this way more reliable results were obtained.

Only vanilla ice cream was used, but the method should apply to other flavors, particularly chocolate, caramel, and nut flavored ice cream.

The precision and accuracy are evident from the data presented.

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The Buffer Capacity of Tomato Juice

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THE capacity of various biological fluids to resist changes in hydrogen-ion concentration upon the addition of strong acid or base has been subject to much investigation, and has been studied quantitatively and developed mathematically by Van Slyke (*6*). Using the Van Slyke expression β or $\frac{dB}{dpH}$ expressing the relationship between the increment in gram equivalents of strong base added to the buffer solution and the resultant increment in pH, one of the authors measured β for solutions of gums (*1*), tincture of digitalis (*2*), carbohydrate of burdock (*4*), and oyster liquor (*3*).

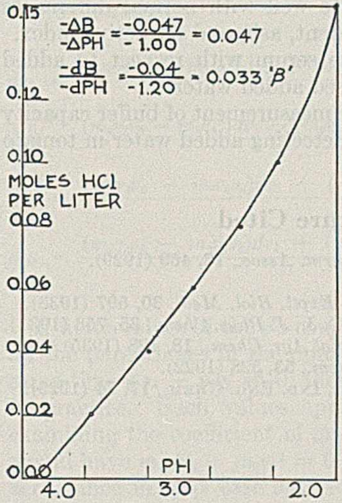

FIGURE 1. BUFFER CAPACITY OF TOMATO JUICE "ACID"

It occurred to the authors that it might prove of interest to measure the buffer capacity of tomato juice, and that this measurement might serve as a trustworthy index to added water or purposeful sophistication.

Experimental

Six standard grades of tomato juice, one juice prepared in this laboratory from sound, ripe tomatoes, and certain samples of tomato pulp were investigated. Samples of the juice (10 cc.) were treated with varying quantities of 0.1 *N* hydrochloric acid and sodium hydroxide solutions, respectively. The pH at 25° ± 1° C. of the various solutions was determined with a Wilson-type (*7*) hydrogen electrode.

After the addition of acid to one sample and subsequent pH measurements, another portion was filtered and the serum treated in the same manner. The measurements made on the whole juice were practically identical with those made on the serum, indicating that the buffer capacity of the juice resides in the soluble constituents and not in the pulp.

The buffer capacities of the various serums to acid were studied individually and observed to be remarkably uniform. The juice prepared in this laboratory and the six commercial samples were practically identical in this respect. The buffer capacity of a composite sample is shown in Figure 1. The pH values of untreated juices obtained agree well with those determined by Mitchell (*5*) using the glass and hydrogen electrodes.

The addition of strongly dissociated alkali to the same tomato juice serums gave variable results, as shown by Table I.

TABLE I. EFFECT OF ADDITION OF ALKALI

No.	0.1 *N* NaOH	pH of Serum						
	Cc.	No. 64	No. 65	No. 66	No. 67	No. 68	No. 69	Fresh
1	0.0	4.09	4.11	4.14	4.18	4.09	4.13	4.14
2	2.0	4.51	4.55	4.60	4.76	4.67	4.65	4.64
3	4.0	5.05	5.29	5.34	5.74	5.35	5.47	5.44
4	6.0	5.94	7.17	7.80	8.58	6.57	7.97	6.86
5	8.0	8.28	9.10	9.03	9.33	8.93	8.96	8.88
6	10.0	9.24	9.32	9.55	9.89	9.74	9.53	9.57

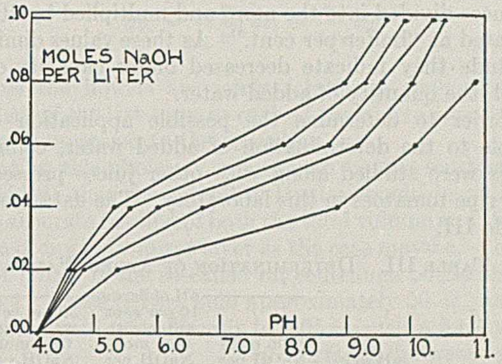

FIGURE 2. ACTION OF 0.1 *N* SODIUM HYDROXIDE ON TOMATO JUICE

As the buffer capacity of these samples varied so widely with respect to added alkali, it occurred to the authors to study the influence of added water on the buffer capacity of the serum with respect to added alkali. This was tested first on serum filtered from concentrated commercial pulp, and then after dilution of this with water. A marked diminution in the buffer capacity was observed when water was added.

Figure 2 shows the buffer capacity of the composite sample of serum upon the addition of strong alkali prior to and after the addition of varying quantities of water.

Other physical factors on the commercial juices were determined and are set forth in Table II.

TABLE II. COMMERCIAL JUICES

No.	Solids	Ash	NaCl
	%	%	%
64	6.08	1.22	0.84
65	6.44	1.05	0.66
66	6.80	1.13	0.76
67	6.40	1.20	0.80
68	6.52	1.08	0.70
69	5.39	0.90	0.63
Fresh	4.70	0.53	0.06

There seems to be little correlation between these data and the buffer capacity to alkalies. However, when these values are modified by sophistication in the form of added water the buffer capacity to alkali is markedly influenced. This condition did not obtain in respect to the addition of acid to the various serums. This is due in all probability to the citric acid content in the form of primary and secondary alkali citrates. The addition of alkali completely neutralizes the acid and thus destroys the naturally occurring buffer mixture. On the other hand, in the presence of added strongly dissociated acid, the buffer mixture is not markedly disturbed.

In order to represent graphically the effect of added water on the buffer capacity with respect to alkali, Figure 3 was constructed from the data in Figure 2. The ordinates designated

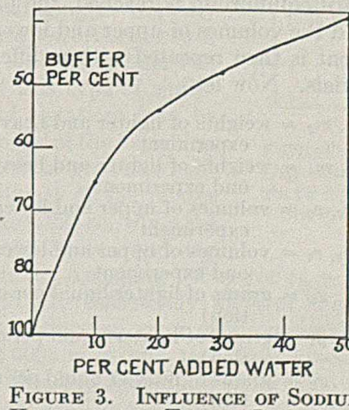

FIGURE 3. INFLUENCE OF SODIUM HYDROXIDE ON TOMATO JUICE WITH ADDED WATER

as "buffer per cent" were calculated as follows: The pH of the composite serum and the change caused by the addition of 0.06 mole of sodium hydroxide per liter were determined. The difference in pH between these two values was considered as the norm. With the sample diluted with water this difference successively increased. These increased differences divided into the norm and multiplied by 100 were designated as "buffer per cent." As these values diminish in magnitude they indicate decreased buffer capacity or, as a parallel, the quantity of added water.

In order to determine the possible application of this principle to the determination of added water, commercial samples were studied along with other juices pressed from sound, ripe tomatoes in this laboratory. The data are shown in Table III.

TABLE III. DETERMINATION OF ADDED WATER

No.	pH of Serum	pH of Serum: 0.06 mole NaOH per liter	pH of Serum: 10 per cent water with 0.06 mole NaOH per liter	pH of Serum: 30 per cent water with 0.06 mole NaOH per liter
Commercial Samples				
1	4.11	8.60	9.09	9.85
2	4.20	8.56	9.07	9.95
3	4.18	8.60	9.03	9.73
4	4.07	8.67	9.06	9.75
5	4.13	8.15	8.60	9.56
6	4.05	6.46	8.00	9.00
7	4.03	6.59	8.11	9.12
8	4.09	8.15	8.75	9.45
9	4.12	7.95	8.75	9.57
10	4.17	8.32	8.84	9.43
11	4.22	8.86	9.40	10.23
Freshly Prepared Samples				
1	4.24	6.70	8.21	9.37
2	4.38	8.50	9.08	9.78
3	4.44	8.35	8.71	9.29
4	4.25	7.78	9.55	10.81
5	4.35	8.63	9.14	9.92

Table III confirms the finding of marked diminution in buffer capacity to alkali of both commercial and freshly prepared tomato juices when water is added. Although the juices showed rather great variations in their buffer capacities, it seems reasonable to suspect that should the pH exceed 8.75 on a sample of tomato juice serum after the addition of 0.06 mole of sodium hydroxide per liter, water has been added to the extent of approximately 10 per cent. With a pH between 9.00 and 11.00, when treated with the same quantity of alkali, one might suspect the addition of approximately one-third volume of water.

Summary

The buffer capacity of six commercial samples of tomato juice has been measured with respect to strong acid. The Van Slyke β is 0.033. Added water does not markedly influence this value.

Tomato juices show considerable variation in their capacity to resist change in pH upon the addition of strong alkali. These values do not correlate well with normal differences found in total solids, salt content, ash, and refractive index.

The buffer capacity of the serum with respect to added alkali diminishes with increased added water.

It is possible to employ the measurement of buffer capacity corroboratively as means of detecting added water in tomato juice.

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The Hill Method for Solubility Determinations

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FOR determining the mutual solubilities of a pair of partially miscible liquids several direct experimental procedures are available. Alexejeff (*1*) described the well-known and widely used synthetic or cloud-point method as early as 1886, while in 1923 Hill (*7*) devised a very ingenious method based on phase rule considerations. In the Hill method the procedure is essentially as follows: Weighed amounts of the two liquids are introduced into a suitably graduated flask (a mixing cylinder, for example), shaken until equilibrium is reached, the phases allowed to separate, and the volumes of upper and lower layers read. The experiment is then repeated with a different ratio of starting materials. Now let

m_1, m_2 = weights of lighter and heavier liquids taken in the first experiment
m_3, m_4 = weights of lighter and heavier liquids taken in the second experiment
v_1, v_2 = volumes of upper and lower layers obtained in the first experiment
v_3, v_4 = volumes of upper and lower layers obtained in the second experiment
x_1 = grams of lighter liquid per cc. of upper layer (at saturation)
y_1 = grams of lighter liquid per cc. of lower layer (at saturation)
x_2 = grams of heavier liquid per cc. of upper layer (at saturation)
y_2 = grams of heavier liquid per cc. of lower layer (at saturation)

Then to determine the x's and y's we have

$$v_1x_1 + v_2y_1 = m_1 \qquad v_1x_2 + v_2y_2 = m_2$$
$$v_3x_1 + v_4y_1 = m_3 \qquad v_3x_2 + v_4y_2 = m_4$$

These equations when solved yield

$$x_1 = \frac{m_1v_4 - m_3v_2}{v_1v_4 - v_2v_3} \qquad y_1 = \frac{m_3v_1 - m_1v_3}{v_1v_4 - v_2v_3}$$
$$x_2 = \frac{m_2v_4 - m_4v_2}{v_1v_4 - v_2v_3} \qquad y_2 = \frac{m_4v_1 - m_2v_3}{v_1v_4 - v_2v_3}$$

As Hill has pointed out, this method is simple in application and has the advantage that besides yielding the solubility figures it also gives the densities of the two layers (as grams per cc.):

$$d_1 = x_1 + x_2 \qquad d_2 = y_1 + y_2$$

One of the first questions to arise regarding this method was the proper choice of v_1, v_2, v_3, and v_4 so as to obtain the greatest possible accuracy (*9*). Hill advocated the use of special equipment, so that a total volume of around 400 cc. could be used in each experiment, although he also pointed out that an ordinary 100-cc. mixing cylinder gave good results. For the proper choice of the ratio of v_1 to v_2 Hill and Malisoff (*8*) deduced that the materials should be taken so as to make $\frac{v_1}{v_2} = \frac{v_4}{v_3} = \frac{y_1}{x_1}$ in order to obtain the maximum accuracy in determining x_1, with similar expressions for the other variables. These conclusions were based on certain rather arbitrary assumptions which are not likely to prevail in practice. Briefly, these assumptions require no error in measuring v_2 and v_3, and equal errors in sign and magnitude in measuring v_1 and v_4. Because of the convenience of this solubility method it seems desirable to investigate this point further and determine suitable volume ratios when the errors in measuring the volumes are assumed independent of one another. Such a general choice for the v's may be determined in the following manner:

It is assumed that the accuracy with which the liquids are weighed is sufficiently great so that errors from this or any other source can be neglected in comparison with errors in reading the volumes. In this case the m's can be considered constants. Under these conditions, if v_1, v_2, v_3, and v_4 denote the true volumes, then the changes in the x's and y's produced by small errors dv_1, etc., in reading the volumes are given approximately by

$$dx_1 = \frac{(m_3v_2v_4 - m_1v_4^2)dv_1 + (m_1v_3v_4 - m_3v_1v_4)dv_2 + (m_1v_2v_4 - m_3v_2^2)dv_3 + (m_3v_1v_2 - m_1v_2v_3)dv_4}{(v_1v_4 - v_2v_3)^2}$$

$$dx_2 = \frac{(m_4v_2v_4 - m_2v_4^2)dv_1 + (m_2v_3v_4 - m_4v_1v_4)dv_2 + (m_2v_2v_4 - m_4v_2^2)dv_3 + (m_4v_1v_2 - m_2v_2v_3)dv_4}{(v_1v_4 - v_2v_3)^2}$$

$$dy_1 = \frac{(m_1v_3v_4 - m_3v_2v_3)dv_1 + (m_3v_1v_3 - m_1v_3^2)dv_2 + (m_3v_1v_2 - m_1v_1v_4)dv_3 + (m_1v_1v_3 - m_3v_1^2)dv_4}{(v_1v_4 - v_2v_3)^2}$$

$$dy_2 = \frac{(m_2v_3v_4 - m_4v_2v_3)dv_1 + (m_4v_1v_3 - m_2v_3^2)dv_2 + (m_4v_1v_2 - m_2v_1v_4)dv_3 + (m_2v_1v_3 - m_4v_1^2)dv_4}{(v_1v_4 - v_2v_3)^2}$$

If finite values of the v's could be found which would make all the parentheses in the numerators equal zero, and at the same time $v_1v_4 - v_2v_3 \neq 0$, then such a choice would be best in practice. Such values apparently do not exist. Thus, examining the coefficient of dv_1 in the expression for dx_1, we would have $m_3v_2v_4 - m_1v_4^2 = 0$. Both v_2 and v_4 cannot equal zero, since in that case $v_1v_4 - v_2v_3 = 0$. Assuming $v_4 \neq 0$, this condition becomes $m_3v_2 - m_1v_4 = 0$. If absolute accuracy were secured in the experiment then

$$v_4 = \frac{m_4x_1 - m_3x_2}{x_1y_2 - x_2y_1} \qquad v_2 = \frac{m_2x_1 - m_1x_2}{x_1y_2 - x_2y_1}$$

Substituting these values we have

$$\frac{x_1(m_1m_4 - m_2m_3)}{x_1y_2 - x_2y_1} = 0 \text{ or } \frac{m_1}{m_3} = \frac{m_2}{m_4}$$

Hence the requirement that the coefficient of dv_1 be zero is satisfied only under conditions such that the original equations do not define the x's and y's uniquely. (The previously cited conclusions of Hill and Malisoff may be derived easily from the foregoing equations. For example, it is necessary to assume in the expression for dx_1 that $v_2 = v_3$, $v_1 = v_4 = kv_2$, $dv_2 = dv_3 = 0$, $dv_1 = dv_4$, and then set the numerator of the fraction equal to zero.)

While it is impossible to choose the conditions such that the dx's and dy's are zero for all values of the dv's, nevertheless a suitable choice of the v's may suffice to make the dx's and dy's relatively small. Inasmuch as the dx's and dy's are expressed as fractions, and all the fractions have the same denominator, it seems plausible that if the v's are chosen so as to make this denominator a maximum the most suitable general choice of the v's will have been made. This may be accomplished by making both v_1 and v_4 (or v_2 and v_3) as small as is experimentally possible, and the other volumes correspondingly large. Under these conditions, as v_1 and v_4 both approach zero, the errors introduced by small errors in reading the volumes become roughly the following:

$$dx_1 = -\frac{m_3}{v_3^2}\,dv_3 - \frac{m_1}{v_2v_3}\,dv_4$$

$$dx_2 = -\frac{m_2}{v_2v_3}\,dv_4 - \frac{m_4}{v_3^2}\,dv_3$$

$$dy_1 = -\frac{m_3}{v_2v_3}\,dv_1 - \frac{m_1}{v_2^2}\,dv_2$$

$$dy_2 = -\frac{m_2}{v_2^2}\,dv_2 - \frac{m_4}{v_2v_3}\,dv_1$$

Unless the liquids are fairly soluble in each other, the coefficient of the last term in each of the above expressions is small in comparison to the preceding one.

Granting this choice of volumes to be the most suitable, it is evident that the solubility bottles should be such as to permit accurate reading of both the total volume and the small volume of upper or lower layer as the case may be. One such type of bottle is the so-called oil centrifuge bottle shown in Figure 1. These bottles hold approximately 50 cc., and have their necks graduated directly to 0.05 cc. over a 5-cc. volume, the distance between graduations being approximately 1.3 mm. Consequently, by calibrating the graduations it is possible to read both the total volume and a small upper layer volume to about 0.025 cc. For the other measurement, involving a small lower layer, the standard centrifuge tubes with tapered bottoms might be used, except that they afford poor accuracy in the total volume determination. Consequently it seems best to use the same oil centrifuge bottle, with the modification of introducing about 0.5 cc. of mercury originally. As before, the total volume is readily secured, while by inverting the tube the volume of lower layer may be determined, since the mercury seals off the uncalibrated portion of the tube. Another similar type of bottle, known as the Babcock bottle, has a slightly smaller neck which is graduated for a volume of 1.8 cc. in 0.02-cc. divisions. A special bottle may obviously be constructed having a small graduated well in the bottom, which should be very suitable for this type of measurement.

The advantages of using this type of bottle are (1) the bottle is a standard, inexpensive article of manufacture; (2) relatively small quantities of liquid are required for fair precision, and (3) the bottle may be readily centrifuged, thus giving a quick and complete separation of the phases. With the larger, specially built flasks centrifuging is virtually impossible and phase separation often difficult.

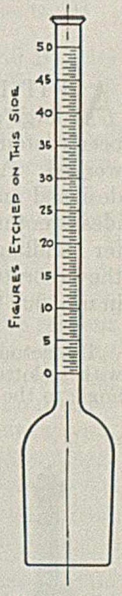

FIGURE 1. OIL CENTRIFUGE BOTTLE

To give an idea of the accuracy which can be attained by the use of this type of equipment the preceding set of equations may be evaluated for different choices of the variables. Using the oil bottle which is graduated directly to 0.05 cc., the volumes of the phases should be accurate to within 0.025 cc., while the larger phase will be about 50 cc., and the smaller about 1 cc. in volume. Assuming values for x_1, y_1, x_2, and y_2 of 0.6, 0.2, 0.2, and 0.7, respectively, an error in each volume of 0.025 cc. can introduce an error of approximately 0.0004 in x_1 and y_1, and 0.0005 in x_2 and y_2. Consequently the solubility percentages obtained should not differ from the true values by over 0.1 per cent in absolute value, and the density should be accurate to within 0.001. If the individual volumes are in error by as much as 0.05 cc., then the solubility figures can differ from the true values by 0.2 per cent and the density be incorrect by 0.002. This assumes, of course, that the starting materials are pure, that there are no handling losses, and that equilibrium is reached, so that only errors in measurement need be considered. This degree of accuracy is sufficient for many purposes, and consequently this method can be used conveniently in these cases.

Table I. Water Solubility Measurements

Substance	Water Saturated with Substance at 20° C.		Substance Saturated with Water at 20° C.	
	% A	d_4^{20}	% A	d_4^{20}
Secondary butyl alcohol[a]	18.5	0.971	64.4	0.880
Methyl ethyl ketone[b]	26.7	0.962	87.9	0.836
Methyl *tert*-butyl ether[c]	4.8	0.990	98.5	0.745
Methyl *tert*-amyl ether[d]	1.25	0.995	99.3	0.771
Chloroform[e]	0.8	1.001	99.8	1.486

[a] Clough and Johns give the values 17.85, 0.9732, 64.17, 0.8797 (*3*). Earlier work by Timmerans gives percentages of 20.2 and 63.8.

[b] A plot of Marshall's data gives methyl ethyl ketone saturated with water as 88.0 per cent ketone (*10*).

[c] Bennet and Philip give percentages of 5.83 and 97.46. Their sample of ether was less pure than that used here, boiling lower and having a higher density, indicating the probable presence of alcohol (*2*).

[d] Determinations by the synthetic method have given percentages of 1.15 and 99.4 (*4*).

[e] Gross and Saylor, using an interferometer method, give values for water saturated with chloroform of 0.77 per cent at 30° C. and 0.84 per cent at 15° C. (*6*). Gibby and Hall by the synthetic method found chloroform saturated with water to contain 99.93 per cent of chloroform (*5*).

As examples of the results obtained using the apparatus described above, the data in Table I are presented. They represent water solubility measurements for several types of organic compounds ranging from a fairly soluble material such as secondary butyl alcohol to a fairly insoluble one such as chloroform. Wherever available the corresponding data obtained by other methods are given for comparison. The agreement is generally satisfactory, and where there are discrepancies these seem to be due in part to differences in the purity of the starting materials.

Summary

The Hill method for solubility determinations has been investigated and a suitable general choice determined for the volume ratios employed. A simple and inexpensive apparatus is described for carrying out the determinations and experimental results obtained with this apparatus are given.

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A Manipulator for Glass Blowing

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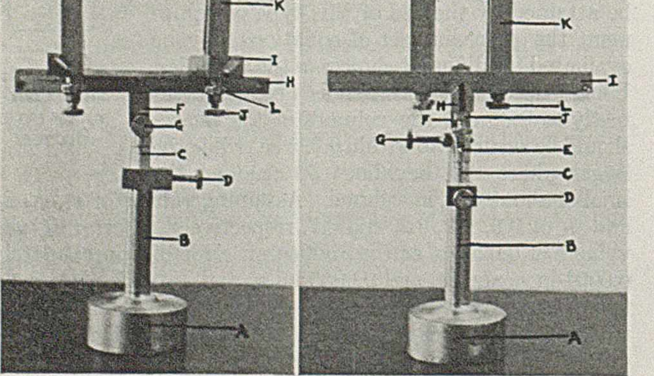
As it is extremely awkward and tiring to manipulate large and bulky pieces of glass in glass blowing, it has been customary to employ some sort of rest for the object being worked. After some experience of this kind the author has designed and constructed the device illustrated. While the idea is not new, the design is and has been found ideally suited for handling any type of apparatus ordinarily constructed in the laboratory. This manipulator offers extreme flexibility in use, due to its wide range of adjustment.

The actual working parts are mounted on a solid brass rod, *C*, with a slotted hinge joint, *E*, which permits adjustment at any angle to the horizontal. This rod works in a hollow brass tube, *B*, with a set screw, *D*, so that it may be adjusted for height. The hollow rod is mounted in a heavy base, *A*. In the author's instrument the hollow tube is 11 cm. high, but this, of course, depends upon the size of the blast lamp being used. The solid brass rod, which should fit snugly into the hollow one, is 12.5 cm. from the bottom to the axis of the hinge joint, which is made by slotting the solid rod and rounding off the top surface. A 2.5-cm. piece of brass, *F*, 13 mm. square, is worked down to fit the slot and the two pieces are then drilled and tapped to take a set screw, *G*. To the top of this square piece of brass another piece of brass, *H*, 13 mm. square and 15 cm. long, is joined by two screws in the center, to form a runner for the two carriages, *I*. It is grooved all the way through except for about 2 cm. in the center where the screws attaching it to the upright pass through. It was necessary to place a screw at each end to keep it from warping. The top surface is milled down at an angle to fit into a cross groove in the bottom of each carriage.



The carriages, made of two 15-cm. pieces of brass 13 × 20 mm. are held on the runner by set screws, *J*. They are grooved all the way through except for 1.5 cm. in the center and are fastened at each end with a screw to prevent warping. The carriages are then milled to carry the uprights, *K*, which are made of 7.5-cm. pieces of brass 13 mm. square.

The bottoms of the uprights are milled to fit snugly into the carriage groove where they are held in place by set screws, *L*. The tops of the uprights are slotted to carry Bakelite or fiber wheels, *M*, with a diameter of 2.5 or 3 cm. These wheels, which carry the glass, should be free to rotate easily.

When constructed in this manner it is possible to carry any diameter of tubing. The wheels on which the tubing rests permit it to be rotated easily and at any desired speed without tiring the hand by supporting. The carriages may be set close together to carry short pieces of glass or far apart to support longer and heavier pieces. The whole instrument may be tilted and used at any angle desired.

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A New Reagent for Potassium

I. Qualitative

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THE solubility of the disodium salt of 2,4-dinitro-1-naphthol-7-sulfonic acid as compared with the dipotassium salt has suggested its use as a reagent for the detection of potassium. The present investigation is a study of its applicability for this purpose. Both the disodium and dipotassium salts are known as naphthol yellow S, but the product usually found on the market is the disodium salt and is the compound designated in this paper as naphthol yellow S.

Naphthol yellow S reacts readily with potassium to form a very bulky, flocculent, orange-yellow precipitate. The rate at which precipitation occurs is dependent upon the concentration of the reagent and of potassium.

General Procedure

To determine the sensitiveness of naphthol yellow S as a qualitative reagent for potassium, it was dissolved in water, and concentrations of 5 and 2 per cent and a solution saturated at room temperature were used. The 5 and 2 per cent solutions were prepared by heating 5 and 2 grams, respectively, in 100 ml. of water until all the naphthol yellow S was dissolved and then keeping these solutions at a temperature of 50° C. or more. This was necessary since the concentration of a solution saturated at room temperature is less than 1.5 per cent. In each series of experiments the same volume of test solution was used with varying concentrations of potassium as potassium sulfate. To each was added the same volume of reagent of a given concentration, and the mixtures, after shaking, were allowed to stand at room temperature.

SENSITIVENESS OF NAPHTHOL YELLOW S AS A TEST FOR POTASSIUM. The following experiments show the sensitiveness of the reagent in the absence of all other cations: (1) three milliliters of a 5 per cent solution of the reagent were added to 10 ml. of test solutions of various concentrations of potassium. (2) This was repeated using a 2 per cent solution. (3) Five milliliters of a solution of the reagent saturated at room temperature were added to 1 ml. of test solution of various concentrations of potassium. The results are given in Table I.

TABLE I. SENSITIVENESS OF NAPHTHOL YELLOW S AS A TEST FOR POTASSIUM

Experiment	Potassium in Reaction Mixture	Time Elapsed before Appearance of Precipitate		
		5 per cent reagent	2 per cent reagent	Saturated solution of reagent
	Mg./ml.	*Min.*	*Min.*	*Min.*
1	7.87	0	1	
2	3.94	Less than 1	4	
3	3.15	1	10	
4	2.36	2	15	
5	1.57	3	30	9
6	0.79	8	65	40
7	0.39	16	4 hours	5 hours
8	0.03	More than 6.5 hours	No ppt. formed	No ppt. formed
9	0.00	More than 6.5 hours	No ppt. formed	No ppt. formed

Using a 5 per cent solution, a blank test should be run, since this concentrated reagent crystallizes out on long standing. To avoid the necessity of running a blank, a more dilute solution was used. The reaction of a solution saturated at room temperature was too slow for practical use.

The use of a 2 per cent solution is recommended, since it obviates the necessity of running a blank, although its sensitivity is less than the 5 per cent solution, as shown by the increase in time required to cause precipitation. Using a 5 per cent solution, the bulk of the precipitate and the length of time required for its formation will enable one to differentiate between the blank and the potassium precipitate where the amount of potassium is 0.4 mg. or more per ml. of reaction mixture.

EFFECT OF SODIUM IONS. Ten milliliters of sodium chloride solution containing 0.1030 gram of sodium were mixed with 10 ml. of potassium sulfate solution and 6 ml. of naphthol yellow S were added. The concentrations of the potassium sulfate solutions were varied and all other factors kept constant. The results, compared to other solutions containing only the reagent and potassium sulfate of the same concentrations, are shown in Table II.

TABLE II. EFFECT OF SODIUM ON DETECTION OF POTASSIUM BY NAPHTHOL YELLOW S

Experiment	Potassium in Reaction Mixture	Sodium in Reaction Mixture	Ratio of Na to K	Time elapsed before Appearance of Precipitate
	Mg./ml.	*Mg./ml.*		*Min.*
1A	3.93	3.96	1:1	1
1B	3.94	..	....	Less than 1
2A	1.96	3.96	2:1	4
3A	1.57	3.96	2.52:1	8
3B	1.57	..	....	2
4A	1.18	3.96	3.35:1	15
5A	0.79	3.96	5.03:1	30
5B	0.79	..	....	8
6A	0.39	3.96	10:1	65
6B	0.39	..	....	16
7A	0.19	3.96	20:1	Less than 24 hours
8A	0.02	3.96	26.4:1	No ppt. formed
9B	..	3.96	....	No ppt. formed

The amount of precipitate obtained in the A and B series was much the same, but there was a marked difference in physical appearance. The solution containing sodium produced an orange precipitate of a finer texture, which settled much more readily. The most noticeable effect of the sodium was that about four times as long was required to produce a precipitate. Increasing the ratio of sodium to potassium appeared to have little or no effect.

OTHER INTERFERENCE. Ten milliliters of test solution containing 80 mg. of one of the cations commonly associated with potassium and 3 ml. of a 2 per cent solution of the reagent were mixed and set aside at room temperature. The cations tested were the chlorides of lithium, sodium, and ammonium, and sulfate of magnesium. At the end of 24 hours no precipitate was formed, but the test containing ammonium gave a slight precipitate in 48 hours.

Rubidium and cesium, the other two alkali metals associated with potassium, are so infrequently encountered that interference from these elements is not likely to occur.

DETAILS OF PROCEDURE. To 10 ml. of the aqueous solution to be tested, containing only the soluble group, add 3 ml. of a 2 per cent solution of naphthol yellow S and set aside at room temperature. The appearance of a precipitate in 65 minutes or less will indicate the presence of 0.79 mg. of potassium or more per ml. of reaction mixture. As an alternative procedure, 3 ml. of a 5 per cent solution of the reagent may be used, with a blank test run under the same conditions. The appearance of a precipitate in 20 minutes or less at room temperature will indicate the presence of 0.39 mg. or more of potassium per ml. of reaction mixture.

Discussion

The salts of potassium are very soluble in water and so the number of reagents that will detect 1 part of potassium in

2500 parts of solution are comparatively few (*1*). They are phosphotungstic acid, sodium 6-chloro-5-nitro-*m*-toluene sulfonate, and sodium cobaltinitrite.

Phosphotungstic acid easily forms supersaturated solutions and so is unreliable. The other two react readily with ammonium, which necessitates its removal before the test is made. Sodium cobaltinitrite, the most sensitive reagent for potassium, easily decomposes and as such is useless for the test.

Naphthol yellow S is a stable reagent which will detect at least 1 part of potassium in 2500 parts of solution and the presence of sodium and ammonium ions does not interfere with the test.

Summary

A 2 per cent solution of naphthol yellow S, used in the ratio of 3 ml. of reagent to 10 ml. of test solution, is recommended for general use as a test for potassium.

For test solutions containing less than 0.79 mg. of potassium per ml., 3 ml. of a 5 per cent solution of the reagent to 10 ml. of test solution should be used. This necessitates running a blank.

The reagent will detect 1 part of potassium in 2500 parts of solution.

The presence of sodium does not interfere with the test but does increase the length of time before precipitation occurs.

Ammonium and other cations commonly associated with potassium do not interfere with the test.

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Action of 4-Nitrocatechol as a Titration Indicator

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BENEDIKT (*1*), who first mentioned 4-nitrocatechol, obtained it by the action of dilute sulfuric acid upon a dilute solution of a mixture of catechol and potassium nitrite. He stated that this substance was yellow under acid conditions and red under alkaline conditions, and should be an excellent indicator for acid-base titrations.

The object of this investigation was to ascertain if 4-nitrocatechol could be used in titrations and the type of titrations in which it could be employed.

Preparation of Reagents. The 4-nitrocatechol was prepared by the method of Benedikt (*1*), and was further purified by distilling the solid in a vacuum of 2 mm. and collecting the portion which came over between 190° and 210° C. The distillate was dissolved in ether and filtered, and the ether allowed to evaporate. A light yellow product which melted at 174° C. was obtained.

Approximately 0.1 *N* solutions of hydrochloric, nitric, acetic, and oxalic acids, sodium hydroxide, sodium carbonate, and ammonium hydroxide were prepared.

Color Changes and Constants of Indicator. The indicator changes from very light straw color under distinctly acid conditions to lemon yellow and finally to red as alkali is added to a solution containing it. The change from straw color to lemon yellow is sharp and that from lemon yellow to red gradual.

The ionization constants were determined by using a Bausch and Lomb hydrogen-ion colorimeter and checking the pH of the buffer solutions employed by means of a Queen potentiometer, using the customary hydrogen-calomel combination. The pKa for the first hydrogen was found to be 6.56 and for the second hydrogen 11.33 at 25° C. Gilbert, Laxton, and Prideaux (*2*) found the pKa for the first hydrogen to be 5.56 and for the second hydrogen 10.96 by employing a similar method.

The ranges of the color changes were obtained by observing the colors produced in a series of buffer solutions. The pH range for the change from straw color to red was found to be 3.92 to 10.57, and from straw color to lemon yellow 3.92 to 6.34 at 25° C.

Titrations. Titrations of acids with bases were made by using the appropriate indicator in each case. These were compared with similar titrations made by employing a 1 per cent aqueous solution of 4-nitrocatechol as the indicator. The color change used to designate the end point when this indicator was employed was from straw color to lemon yellow. In the case of sodium carbonate the salt was treated with a slight excess of hydrochloric acid, boiled to free the solution from carbonic acid, and then back-titrated with sodium hydroxide solution when the 4-nitrocatechol was used as the indicator.

Table I. Titrations of Acids with Bases[a]

Acid *Ml.*	Base *Ml.*	Ratio (Acid/Base)	Indicator
HCl	NaOH		
25.0	20.8	1.20	Methyl orange
25.3	21.2	1.19	Phenolphthalein
26.68	22.22	1.20	4-Nitrocatechol
HCl	NH_4OH		
25.06	25.44	0.985	Methyl orange
25.02	25.34	0.987	4-Nitrocatechol
HNO_3	NaOH		
25.0	20.69	1.208	Phenolphthalein
25.0	20.60	1.214	4-Nitrocatechol

[a] The values are the averages of several titrations.

Discussion

The authors feel that the differences between the constants which they have obtained and those obtained by Gilbert, Laxton, and Prideaux (*2*) were due to a difference in the purity of the two compounds. Their compound was described as being light brown and melting at 173° C., whereas the authors' compound was light yellow and melted at 174° C., and the product obtained before vacuum distillation was light brown. During the distillation a light brown product came over first and then a yellow distillate which was collected and used in the authors' study.

The 4-nitrocatechol is useful for titrations of strong acids with strong bases and strong acids with weak bases, but cannot be used in titrations of weak acids. A strong oxidizing acid like nitric did not affect its operation, but on the other hand it did not function well in a solution containing much carbon dioxide.

Summary

A 1 per cent aqueous solution of 4-nitrocatechol has been employed for titrations of nitric acid with sodium hydroxide, hydrochloric acid with ammonium hydroxide, hydrochloric acid with sodium hydroxide, and sodium carbonate with hydrochloric acid.

The action of the indicator is affected by carbon dioxide, but not by a strong oxidizing acid like nitric.

The indicator changes from a very light straw color under acid conditions to lemon yellow and finally red as alkali is added, the first change being sharp and the second gradual.

The pH range for the change from straw color to red was found to be 3.92 to 10.57 and for the change from straw color to lemon yellow 3.92 to 6.34 at 25° C.

The pKa for the first hydrogen was found to be 6.56 and for the second hydrogen 11.33 at 25° C.

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Determination of Small Amounts of Potassium by Means of Silver Cobaltinitrite

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THE determination of small quantities of potassium is of prime importance in the study of biological fluids, soil extracts, and fresh waters. Because of incomplete precipitation when there is less than 0.100 mg. of potassium per ml., the widely used method based on precipitation with sodium cobaltinitrite leaves much to be desired (*7*, *11*). Even when the potassium concentration is 0.150 mg. per ml. or more, satisfactory results are obtained only because of compensation of errors of rather large magnitude (*7*, *13*). Taylor (*14*) has shown that the sensitivity of the method is increased with an alcoholic precipitation medium. Reported below are preliminary experiments with the sodium cobaltinitrite reagent establishing the lower limit of each of these procedures. From these data it is apparent that neither method possesses the sensitivity necessary for the direct determination of extremely small amounts of potassium, such as are found in most lake and river waters. Since concentration by evaporation in quartz or platinum is time-consuming and requires expensive equipment, a direct determination would be most desirable for water analysis. The silver cobaltinitrite method of Breh and Gaebler (*2*) appeared to offer the most promise for such a direct determination. Using a modification of this method, smaller amounts of potassium than reported elsewhere in the literature have been determined.

Colorimetric Determination of Nitrite

Heretofore the most sensitive method for the determination of potassium has been based upon the precipitation of $(Na,K)_3Co(NO_2)_6$ with subsequent determination of the cobalt or nitrite colorimetrically (*7*). The extremely sensitive Greiss method has been extensively used for the colorimetric estimation of the nitrite content of this precipitate (*5*).

PROCEDURE. A solution containing 0.0005 to 0.0050 mg. of NO_2 (*1*), which is equivalent to approximately 0.0001 to 0.0010 mg. of potassium, respectively, was diluted to 50 ml. in a Nessler tube, and was treated with a mixture of 2 ml. of sulfanilic acid and 1 ml. of 1-naphthylamine (*1*). Comparison was made with standards after the color had developed 20 minutes. To determine 0.005 to 0.100 mg. of NO_2 the solution was diluted to 100 ml., the color developed and the comparison with standards made in a Klett colorimeter.

OBSERVATIONS ON THE COLORIMETRIC TECHNIC. From investigations of the colorimetric technic, the authors draw the following conclusions: First, to obtain strictly reproducible results the sulfanilic acid and 1-naphthylamine should first be mixed and then added to the nitrite solution. When the Greiss reagents are added separately, the color is, within certain limits, more intense the longer the time interval between the addition of the sulfanilic acid and the 1-naphthylamine. This observation has been noted by others (*7*, *9*), though most investigators fail to heed this precaution. The mixture of reagents was found to be stable for at least 2 weeks in the absence of light (*9*). Secondly, confirming the work of Taylor (*14*) it was found that the use of a 10 per cent acetic acid medium prevents the formation of a reddish brown precipitate with large quantities of nitrite. Furthermore, when acetic acid and sodium acetate are used, they must be present in the same concentration in both standard and unknown (*16*). Thirdly, Beer's law is valid over a range of 0.0001 to 0.0010 mg. of NO_2 per ml. of solution, which is equivalent to 0.00002 to 0.00020 mg. of potassium per ml.

Determination of Potassium with Sodium Cobaltinitrite Reagent

For the purpose of ascertaining the sensitivity of the sodium cobaltinitrite reagent, the authors employed a modification of the method (*15*) which Tischer had claimed to be more sensitive than previous methods. More recent work indicates that the Kramer-Tisdall (*6*) reagent may be somewhat more sensitive, though surely not less than 0.025 mg. of potassium per ml. can be determined with accuracy (*12*).

In the present investigation the modifications of the Tischer method were: (1) the precipitate was separated by centrifuging; (2) the precipitate was dissolved in 0.1 *N* sodium hydroxide; and (3) the nitrite was determined with the Greiss reagents. The first two modifications were recommended by Lewis and Marmoy (*7*), while Herzner (*5*) showed that the Greiss reagents may be used satisfactorily for the determination of nitrite.

The results with this modified procedure were corrected for a blank which ranged from 0.00002 to 0.0007 mg. of potassium. No precipitation was observed when the potassium concentration was less than 0.040 mg. per ml., although a precipitate of $(Na,K)_3Co(NO_2)_6$ containing 0.001 mg. of potassium may be seen easily in the centrifuge tube. Moreover, seeding the reagent just before use did not increase the sensitivity of the reagent. It was found that a minimum of 0.120 mg. of potassium per ml. may be determined with accuracy when calculating the potassium from a potassium-nitrite factor based on the $NaK_2Co(NO_2)_6$ formula as Tischer did, whereas somewhat less than 0.080 mg. may be estimated quantitatively if potassium standards are carried through simultaneously with the unknowns for the colorimetric comparison.

Taylor (*14*) obtaind an increased sensitivity with the sodium cobaltinitrite reagent by the use of a precipitation medium containing about 30 volume-per cent ethyl alcohol. Recently Lohse (*8*) reported results for Taylor's procedure when the precipitation was made at low temperatures. However, the smallest concentration of potassium reported by Lohse was 0.100 mg. per ml. and, other than this, the effect of cooling upon the sensitivity was not given. In Table I the sensitivity with the Taylor procedure is given for both room temperature and 4° to 6° C. The colorimetric comparison and estimation were made against standard potassium solutions treated simultaneously with the unknowns.

TABLE I. POTASSIUM RECOVERY WITH TAYLOR'S PROCEDURE

Potassium at Room Temperature			Potassium at 4° to 6° C.		
Present	Found	Difference	Present	Found	Difference
Mg./ml.	*Mg./ml.*	*Mg./ml.*	*Mg./ml.*	*Mg./ml.*	*Mg./ml.*
			0.0020	0.0000	−0.0020
				0.0000	−0.0020
				0.0000	−0.0020
0.0030	0.0000	−0.0030	0.0030	0.0037	+0.0007
	0.0000	−0.0030		0.0019	−0.0011
	0.0000	−0.0030		0.0030	0.0000
0.0060	0.0060	0.0000	0.0060	0.0056	−0.0004
	0.0065	+0.0005		0.0061	+0.0001
	0.0060	0.0000		0.0060	0.0000
0.0120	0.0121	+0.0001	0.0100	0.0100	0.0000
	0.0120	0.0000		0.0091	−0.0009
	0.0120	0.0000		0.0112	+0.0012
0.0300	0.0300	0.0000	0.0200	0.0201	+0.0001
	0.0290	−0.0010		0.0200	0.0000
	0.0300	0.0000		0.0190	−0.0010

On the basis of these results it can be stated that cooling enables the determination of smaller amounts of potassium. At 4° to 6° C., 0.0030 mg. of potassium was determined with fair accuracy while at room temperature no precipitate was formed at all. Furthermore, a comparison of the sensitivity of this method with that of the Tischer method confirms the conclusions of Taylor that an alcoholic precipitation medium increases the sensitivity of the procedure.

Formulas ranging from $KNa_2Co(NO_2)_6$ to $K_2NaCo(NO_2)_6$ have been reported as representing the composition of the precipitate, but the composition is now generally agreed to be a mixture of these two forms whose ratio varies, depending upon the conditions of precipitation, and is well represented by the formula $(K,Na)_3Co(NO_2)_6$. However, with careful regulation of conditions the composition is fairly reproducible from one time to another. The formula which best represented the product in the above determinations was calculated to be $K_{1.35}Na_{1.65}Co(NO_2)_6$, assuming that all the potassium was precipitated. Using standard nitrite solutions for the colorimetric comparison, and a potassium-nitrite factor based on the latter formula, the weight of $(K,Na)_3Co(NO_2)_6$ precipitated is readily calculated. When this was done the increased recovery of potassium at the lower temperature of precipitation was evident. By this method not less than 0.030 mg. of potassium could be accurately estimated at room temperature while as little as 0.006 mg. of potassium per ml. could be determined at the lower temperature.

Precipitation with Silver Cobaltinitrite

Silver cobaltinitrite reagent is the most sensitive of all precipitants of potassium (*3*, *10*), yet, with the exception of Breh and Gaebler's (*2*) investigation in blood serum, there have been no attempts to apply this reagent to quantitative work. They stated that, with their procedure, it is possible to precipitate as little as 0.083 mg. of potassium from 5 ml. of blood serum filtrate and by using a calibration curve to obtain the results with an accuracy of 3 to 5 per cent.

Although it has been reported (*3*) that silver potassium cobaltinitrite has a pronounced tendency to become colloidal in the absence of alcohol and electrolytes, Breh and Gaebler used distilled water as the wash liquor. In the following experiments acetone was the wash solution; alcohol was also tried but acetone was superior. An all-glass wash bottle was essential for use with either alcohol or acetone, as unsaturated compounds were often leached from the rubber connections with subsequent reduction of the silver in the precipitate.

STANDARDS AND REAGENTS. In all instances the reagents were prepared from purified C. P. chemicals.

Alcohol and acetone were of such purity that neither gave a perceptible precipitate when treated with silver nitrate, allowed to stand for 3 hours at room temperature, and then centrifuged.

Silver cobaltinitrite reagent containing 1.0 per cent of silver nitrate was prepared by dissolving 25 grams of sodium cobaltinitrite in 150 ml. of sodium nitrite solution, containing 50 grams of sodium nitrite, and adding with stirring 5 ml. of silver nitrate solution, containing 2.0 grams of silver nitrate. The solution was diluted to 200 ml., 2 ml. of glacial acetic acid were added, and air was passed through the cold solution for 5 minutes. After standing for about 12 hours at 4° to 6° C., the reagent was filtered through a No. 42 Whatman filter paper.

Fresh reagent was prepared at least once every 2 weeks and was preserved at 4° to 6° C. when not in use. Just before use a portion was centrifuged and the supernatant solution used for precipitation of the potassium.

A stock solution of potassium sulfate was prepared to contain 1.000 mg. of potassium per ml. Standard solutions were prepared by proper dilution.

Synthetic hard water, potassium-free, had the following composition in parts per million: Ca^{++}, 195; Mg^{++}, 53.3; Na^+, 780; Fe^{+++}, 35; SiO_3^{--}, 150; Cl^-, 1080; SO_4^{--}, 582. The solution was 0.17 *N* in respect to acetic acid.

PROCEDURE. One milliliter of a standard potassium solution was measured into a 15-ml. centrifuge tube and 1.00 ml. of the silver cobaltinitrite added. The precipitate and solution were allowed to stand for 3 hours and then centrifuged at 3000 r. p. m. for 15 minutes. The supernatant liquid was carefully removed through a siphon. The first washing was made with 5 ml. of water, the second with the same volume of 60 volume-per cent acetone, and subsequent washings with the same volume of 99.5 per cent acetone. After centrifuging 5 to 10 minutes, the wash liquid was removed by siphoning. The precipitate was finally dissolved in 1 ml. of 0.1 *N* sodium hydroxide. Solution was quickly completed by immersing the tube in a boiling water bath for 10 to 15 minutes. The Greiss reagents were added and the colorimetric comparison was made against potassium standards that had been treated identically. When the amount of potassium was believed to be under 0.001 mg. the comparison was made in a colorimeter, using an aliquot containing 0.001 to 0.020 mg. of potassium.

Following this procedure, known amounts of potassium in distilled water were precipitated both at room temperature and at 0° C. to determine the sensitivity and the accuracy of the method at the two temperatures. These results are shown in Table II.

TABLE II. POTASSIUM RECOVERY WITH THE SILVER COBALTINITRITE REAGENT

Potassium at Room Temperature			Potassium at 0° C.		
Present	Found	Difference	Present	Found	Difference
Mg./ml.	*Mg./ml.*	*Mg./ml.*	*Mg./ml.*	*Mg./ml.*	*Mg./ml.*
			0.0010	0.0000	−0.0010
				0.0000	−0.0010
				0.0000	−0.0010
			0.0020	0.0021	+0.0001
				0.0020	0.0000
				0.0019	−0.0001
0.0050	0.0000	−0.0050	0.0050	0.0050	0.0000
	0.0000	−0.0050		0.0050	0.0000
	0.0000	−0.0050		0.0047	−0.0003
0.0100	0.0091	−0.0009	0.0100	0.0100	0.0000
	0.0113	+0.0013		0.0109	+0.0009
	0.0100	0.0000		0.0092	−0.0008
0.0500	0.0486	−0.0014	0.0400	0.0400	0.0000
	0.0507	+0.0007		0.0404	+0.0004
	0.0500	0.0000			
0.1000	0.1000	0.0000			
	0.0993	−0.0007			
	0.1030	+0.0030			

With this reagent cooling assisted precipitation greatly and increased the sensitivity. When standard potassium solutions were carried through simultaneously with the unknowns a minimum of 0.010 mg. of potassium per ml. could be determined with precipitation at room temperature, whereas 0.002 mg. per ml. could be determined at 0° C. Moreover, precipitation was completed within 2 hours at the lower temperature. The composition of the precipitate was found to be best represented by the formula $K_{1.35}Ag_{1.65}Co(NO_2)_6$. Using standard nitrite solutions for the colorimetric comparison, and a potassium-nitrite factor based on the latter formula, the potassium content of the unknown was calculated. In this manner a minimum of 0.050 mg. of potassium per ml. could be determined with precipitation at room temperature and 0.002 at 0° C. Although an alcoholic precipitation medium increases the sensitivity of the sodium cobaltinitrite reagent, neither alcohol nor acetone was found to exert a beneficial influence upon the sensitivity of the silver cobaltinitrite reagent.

Determination of Potassium in Water

Ammonium and chloride (*3*) are the only commonly occurring ions in water that interfere with the qualitative silver cobaltinitrite test. In view of the previous satisfactory results by this method, precipitation of the potassium without first concentrating appeared feasible when the potasssium occurred in quantities greater than 0.002 mg. potassium per ml.—that is, 2 p. p. m. Less than 0.002 mg. per ml. necessitated concentrating in an acid solution. Acetic acid was satisfactory for this purpose and concentrations as great as 0.08 *N* did not interfere materially with the precipitation.

The effect of the excess silver ion upon the recovery of potassium was determined by using reagents containing 1 and 2 per cent of silver nitrate. For practical purposes the concentration of the excess silver ion in the precipitation medium was twice as great with the second silver nitrate solution as with the first because, in either case, only an extremely small amount of silver was removed by precipitation. When using the more concentrated solution, somewhat larger amounts of potassium were apparently recovered; this was believed to be due to a higher silver-potassium ratio in the precipitate. Preferably but a slight excess of silver ion should be present from the precipitation of the chloride and, what is more important, the same concentration of excess silver should occur in both standard and unknown.

In the analysis of naturally occurring waters, if the water sample is very soft, distilled water is satisfactory for the dilution of the potassium standards; while for accurate analysis of waters of greater hardness a synthetic water of the same hardness as the unknown should be used for this purpose. The previous work with the silver cobaltinitrite reagent indicated the accuracy which may be expected with very soft water samples.

Table III. Potassium Recovery from Hard Water

Potassium Present	Potassium Found	Potassium Difference
Mg./ml.	*Mg./ml.*	*Mg./ml.*
0.0020	0.0021	+0.0001
	0.0020	0.0000
0.0060	0.0067	+0.0007
	0.0060	0.0000
	0.0055	−0.0005
	0.0061	+0.0001
0.0100	0.0100	0.0000
	0.0094	−0.0006
	0.0102	+0.0002
	0.0097	−0.0003
0.0200	0.0201	+0.0001
	0.0200	0.0000
	0.0190	−0.0010
0.0400	0.0400	0.0000
	0.0402	+0.0002
	0.0392	−0.0008

The applicability of the method to hard waters was demonstrated by the recovery of potassium from a synthetic water of extreme hardness. A potassium-free synthetic water was prepared which contained the maximum concentration of each substance ordinarily found in hard waters (*4*). The magnesium and calcium for this solution were weighed as the carbonates and then dissolved in an excess of acetic acid; the excess acid prevented hydrolysis and precipitation of iron, etc. This solution was 0.17 *N* in respect to acetic acid, but after the addition of potassium and removal of chloride the acidity of the final potassium standards had been reduced to 0.05 *N*.

For the determination of potassium from the synthetic water medium, 30 ml. of standard potassium solution were added to 10 ml. of 8.3 per cent silver nitrate solution and then enough synthetic water was added to make a final volume of 100 ml. After thoroughly mixing, the precipitate was removed from a portion of the solution by centrifuging. Remaining in the supernatant solution was 0.55 per cent silver nitrate and 0.6 per cent acetic acid. The potassium content of this solution was determined with the silver cobaltinitrite reagent. The standards possessed the same ionic concentrations as the unknowns and were accorded the same treatment. The results are shown in Table III.

The recovery of potassium from the hard water medium was remarkably good, considering the small quantity of potassium and the large quantity of other ions involved. Moreover, the analyses were made with greater rapidity and accuracy than could be expected with the normal evaporation procedure.

Summary

When a 10 per cent acetic acid medium is used in the Greiss method for the determination of nitrite, Beer's law is valid over a wide range. Since the intensity of the color is somewhat dependent upon the time interval between the addition of the sulfanilic acid and 1-naphthylamine, the accuracy of the method is improved by mixing the reagents before use.

The Tischer method for potassium is not applicable to the determination of less than 0.120 mg. per ml. of solution. Somewhat less than 0.080 mg. per ml. may be determined if comparison is made with potassium standards that have been given an identical treatment. By precipitating from a 30 volume-per cent alcoholic medium at 4° to 6° C., the minimum quantity of potassium determinable may be decreased to about 0.003 mg. per ml. of solution.

By employing a silver cobaltinitrite precipitating reagent, and running potassium standards simultaneously, the minimum quantity of potassium determinable is reduced to about 0.002 mg. Precipitation should be allowed to take place near 0° C., and an acetone wash liquor used. This method was found to be applicable to the determination of potassium in fresh water.

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The Design of a Precision Photoelectric Colorimeter

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AMONG the first applications of the modern photoelectric cell was its use to replace the human eye in photometric measurements. Many circuits and cell arrangements for specialized types of photoelectric photometry have been proposed in the literature (*4, 8, 13, 17*). The earlier photometers were of the direct-reading type and employed a single photoelectric cell. In 1919, Gibson (*8*) of the Bureau of Standards described the null method for photometric measurements, using it for the routine photometry of lamps. The null method with two photoelectric cells eliminates many of the inaccuracies entering through direct reading.

More recently the photoelectric cell has received attention as a means of minimizing the human element as a factor in colorimetry. Müller (*11*) in 1928 described a photoelectric colorimeter of the direct-reading type and discussed its application to automatic titration and pH control. Since that time a large number of papers have appeared describing colorimeters which employ various circuit arrangements and types of photoelectric cells (*1, 10, 12, 14, 15, 16*). While these papers have adequately discussed the detailed features of each colorimeter in question, there seems to be lacking in the literature a discussion of certain fundamental principles especially applicable to the general design of photoelectric colorimeters.

The design of a photoelectric colorimeter is determined largely by the inherent limitations of the photoelectric cell type employed and of the optical system. The following discussion will deal, first, with the manner in which these elements influence the characteristics of a precision photoelectric colorimeter and, second, with the general details of design of a precision instrument.

Photoelectric Cell Characteristics

RECTIFIER TYPE.[1] The rapid progress made in photoelectric colorimetry since 1932 has been due largely to the development of the rectifier type of photoelectric cell which is very rugged, sensitive, and capable of generating its own e. m. f. It requires no batteries or external source of electrical energy for satisfactory operation.

The complicated manner in which the internal resistance changes with light intensity, temperature, and time prevent the rectifier cell from being entirely suitable for the most precise colorimetric work. If the external circuit resistance is low (less than 100 ohms) in comparison to the internal cell resistance, so that the shunting effect of the latter is relatively small, the response becomes a linear function of light intensity to within 1 or 2 per cent.

The internal resistance also has a positive temperature coefficient for low external resistances and low intensities of radiation. Therefore precautions must be taken in the design of a colorimeter employing these cells to eliminate heating effects due to the light source. Further precaution should be made to allow sufficient time for each reading, since several minutes are required for the internal resistance to come to complete equilibrium for each change in radiation intensity. The relatively low and variable internal resistance precludes the adaptability of these cells to vacuum tube amplification.

In Figure 1 is shown the spectral response curve of a typical rectifier cell. The sensitivity is high throughout most of the visible spectrum. The relatively low sensitivity in the red is of little consequence when the cell is used with incandescent lamps in which the peak of the spectral energy distribution curve occurs in the near infrared (900 millimu for projection lamps).

A circuit employing two rectifier cells in a bridge arrangement is presented in Figure 2. The arrangement is such that the external resistance for each cell under conditions of balance for the galvanometer, *G*, is always constant and equal and of a sufficiently low value that the response is essentially linear. R_1 and R_2 are a pair of dial decade resistances, so connected that if the system is balanced with the absorption cell out of the beam of light to P_1, then the balance which is obtained with the absorption cell in the path of light to P_1 will be in direct proportion to the resistance included between the two contact arms. Thus such a dial decade may very readily be made to read in terms of percentage transmittancy of the absorbing medium. Such a colorimeter in simplified form has been satisfactorily used by the authors for work requiring accuracies of from 1 to 2 per cent. As discussed below this arrangement may be made to be fully compensating for fluctuations in the light source.

PHOTOEMISSION TYPE.[2] The characteristics of the photoemission type of photoelectric cell have been adequately described by Ives and Kingsbury (*9*) and others (*2, 17*). These cells in the vacuum type are almost exclusively used in laboratory precision photometry. Those commonly employed have either potassium hydride or cesium oxide cathodes. The gas cell is not generally suitable for accurate

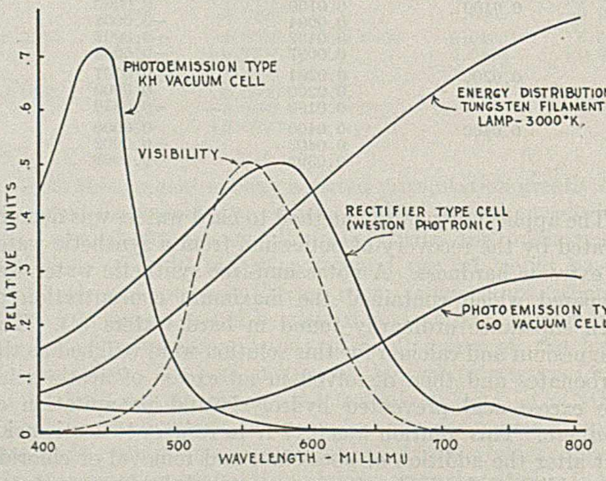

FIGURE 1. SPECTRAL RESPONSE CURVES OF PHOTOELECTRIC CELLS

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[1] The rectifier type of cell consists essentially of a metal disk, upon one side of which is a surface of cuprous oxide or selenium, specially treated for maximun sensitivity to visible radiation. These cells have been referred to in the literature by such various terms as photogalvanic, photovoltaic, photoelectric, photronic, and rectifier.

[2] The term photoemission is applied to those cells which depend upon the emission of photoelectrons from a sensitized cathode, generally of an alkali metal surface of the halide, oxide, sulfide, etc., in an evacuated envelope (vacuum type) or in a rarefied atmosphere of inert gases (gas type).

quantitative work, owing to its relatively unstable current-voltage characteristic and the lack of a strictly linear relationship between light intensity and cell current.

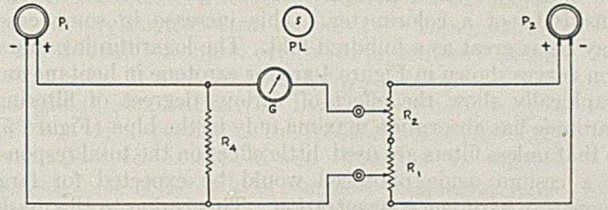

Figure 2. Bridge Circuit for a Pair of Rectifier Cells (Photronic)

R_1. Dial decade 10 × 10 ohms, accuracy −0.1 per cent
R_2. Dial decade 10 × 1 ohms, accuracy −0.1 per cent
R_4. 100 ohms wire-wound fixed resistor

The modern vacuum cell has very stable electrical characteristics with a high internal resistance of the order of hundreds of megohms and a linear relationship of response to light intensity. The current sensitivity is low in comparison to that of the rectifier cell, but the high internal resistance makes these cells especially suited to vacuum tube amplification. By applying a saturating voltage to the vacuum cell it can be made relatively independent in response to small voltage fluctuations as may occur because of IR drop in the load resistance or line voltage. For a typical cesium oxide cell (Cetron) this saturation point is about 40 volts. An applied voltage above this point may vary 10 per cent without affecting the cell current by more than 1 per cent. In general, it may be stated that the load or external circuit resistance should not introduce an IR drop of more than one volt for accurate determinations based upon the cell retaining a linear response.

Ives and Kingsbury (*9*) present evidence to show that it is not safe to assume that the spectral sensitivity of an emission type of photoelectric cell is the same from month to month or like that of another cell, even though apparently manufactured under identical conditions. The relative instability of the spectral characteristics necessitates the use of narrow band pass light filters for precision colorimeters and nephelometers. The same considerations probably hold to the same degree in the case of the rectifier cell.

The spectral response curves in Figure 1 for the potassium hydride and the cesium oxide cells are those of Ives and show to the same scale the relative spectral sensitivity of these two types of cell. The other curves of Figure 1 are not drawn to the same scale. For general use throughout the visible spectrum and especially in the red, the cesium oxide cell is the better type. For the quantitative determination of yellow and red pigments having absorption maxima in the blue, the potassium hydride cell or a cell of similar spectral characteristics is better because of its high sensitivity in the blue and green (Westinghouse SR 51).

In Figure 8 is shown a bridge circuit for use with the vacuum photoemission cell. It operates on the same principle as that shown in Figure 2 for rectifier cells. With the vacuum emission cells, the load resistance need not be constant quantities, provided the total resistance is not high enough to produce an appreciable IR drop. It is possible to use three dial decade resistances in units of multiples of ten, making transmittancy readings possible to 0.1 per cent.

The saturating voltage consists of the alternating current voltage drop in R_6 and R_7 and for a 110-volt supply is 45 volts per cell. Since electrons can pass in appreciable numbers only from the cathode to the anode, the cells may be used to rectify the alternating current and a direct current galvanometer may be used. Only half of the alternating current wave passes through the cell so that the theoretical current efficiency can be only 50 per cent of that of a direct current supply. Actually it is less, being about 45 per cent, owing to the fact that the voltage is too low for electron flow on the low portion of the wave. When the maximum cell sensitivity is required, the resistance R_6 and R_7 may be replaced with a pair of 45- to 90-volt radio B batteries.

Some Optical Systems Applicable to Photoelectric Colorimetry

The optical system of a balanced double photoelectric cell colorimeter may be considered as consisting of a lamp source mounted between and on the same optical axis with two identical optically independent portions, each terminating in a photoelectric cell. Each half of the system, in its most complete form, consists of (1) condensing lenses for concentrating as intense and homogeneous a beam of radiation as possible upon the photocell, and (2) radiation filters for spectrally limiting the radiation as emitted by the lamp source. In most cases condensing lenses are necessary to compensate for the great loss in total radiation occasioned by the use of narrow band pass filters. Without filters it is possible to mount the photocells close enough to the lamp to obtain sufficient radiation without the use of condensing lenses. However, proper filtering offers so many advantages in increased sensitivity, more linear calibration curves, greater stability, and more complete line voltage compensation that the unfiltered precision colorimeter is desirable only for certain specialized applications. In Figure 3 are shown several types of optical systems which may be employed. In diagrams *A* and *B*, the condensing lenses are of the small-diameter, short-focus type used in the small motion picture projectors. In diagram *C* is shown a method of using small precision absorption cells. The lamp source in this case must be small, such as a headlight bulb or strip filament projection lamp.

Systems of lenses often tend to produce an image of the source upon the photoelectric cell cathode, even though the cell may be considerably out of focus. This results in a series of bright bands when filament projection lamps are used. Ives and Kingsbury (*9*) have shown that the cathode of a photoemission cell may vary greatly in sensitivity over its surface. It is well known that these cells have an upper limit of intensity beyond which injury to the sensitive surface may

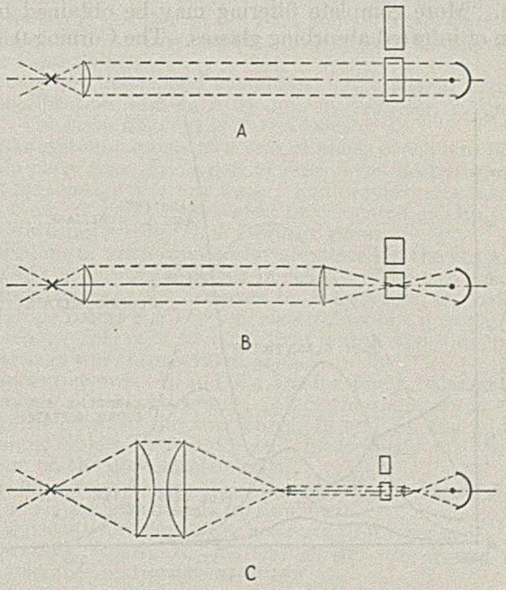

Figure 3. Optical Systems for Photoelectric Colorimeters

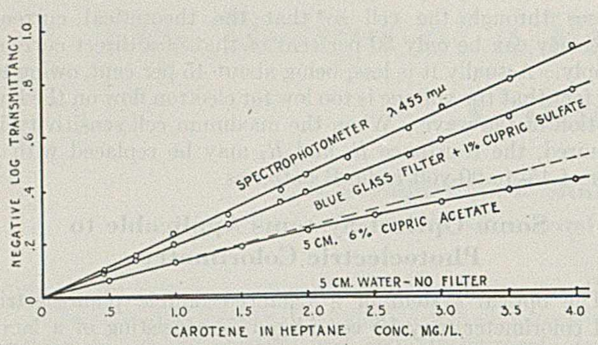

Figure 4. Calibration Curves for Carotene with Various Degrees of Filtering

occur. For these reasons especially, the imaging effects are undesirable. In the case of the rectifier cell, the manner in which the shunting effect of the internal resistance changes with light intensity makes such effects equally undesirable. A diffusing screen of some of the finely molded diffusing window glasses, placed immediately in front of the photocell, adequately eliminates imaging effects without too serious a loss in radiation. In one test it was found that a piece of Diffusex glass scattered the light satisfactorily without incurring a loss of more than 25 per cent in cell response.

Properly spaced diaphragms are necessary to eliminate any scattered extraneous radiation that might reach the photoelectric cell. A diaphragm with an aperture slightly smaller than that of the absorption cell is necessary immediately in front of the absorption cell on the lamp side. Diaphragms having apertures of a wide range of diameters are valuable in limiting the total radiation reaching the photocell to an intensity which is noninjurious to the cell surface. Most small photoemission cells have a maximum safe emission of from 10 to 20 microamperes. The rectifier cell, on the other hand, is claimed by the manufacturers to be uninjured by high radiation intensities.

The radiant energy of the incandescent projection lamp is over 90 per cent infrared which is of no value in most colorimetric work. In order to produce high visible intensities without excessive heating of the absorbing media and photocells, it is necessary to remove the infrared by proper filtering. A water cell will absorb most of the energy beyond 1400 millimu. More complete filtering may be obtained by the addition of infrared absorbing glasses. The Corning 0.32-cm. (0.125-inch) Aklo plate glass (*3*, *7*) is very satisfactory for this purpose.

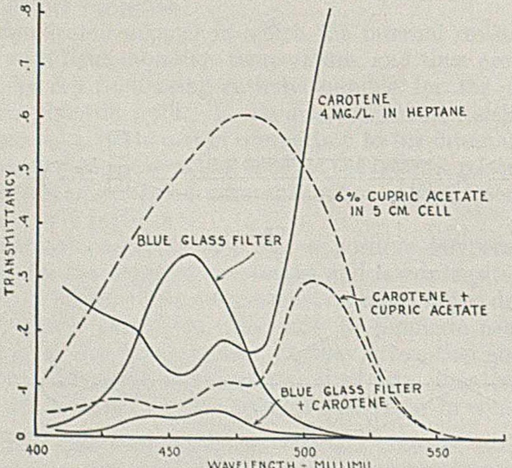

Figure 5. Transmission Curves for Carotene and Various Filter Combinations

Assuming that sufficient radiant energy is available, the use of narrow band pass filters very greatly increases the sensitivity of a colorimeter. This increase in some cases may be as great as a hundred fold. The logarithmic calibration curves shown in Figure 4 are for carotene in heptane and graphically show the effect of various degrees of filtering. Carotene has absorption maxima only in the blue (Figure 5), so that unless filters are used, little effect on the total response of a cesium oxide photocell would be expected for large changes in carotene concentration. This is due to the masking effect of other radiation not selectively absorbed. When no filter is used, the curve has a very small slope and changes in the highest concentrations are barely detectable. With a 6 per cent cupric acetate filter (Figure 5) which has a relatively wide transmission band, the slope is greater than with no filter but not so great as in the case of a Jena glass filter combination of BG12 and GG5 (blue glass filter), the transmission band of which centers on the carotene absorption band. The steepest slope is obtained with a visual spectrophotometer in which the spectrometer functions as an optical filter transmitting a waveband of only a few millimu.

The filtering effect of an absorbing medium contained in the absorption cell may seriously alter the linear relationship of a logarithmic calibration curve, even though the absorbing medium itself obeys Beer's law. A comparison of the calibration curves for carotene obtained with two different filters used in a colorimeter employing a pair of cesium oxide cells shows this relationship (Figure 4). With the use of a 5-cm. cell of 6 per cent cupric acetate which has a wide transmission band, the calibration curve is not a straight line but falls off at the higher concentrations. At high concentrations, carotene has an appreciable filtering effect of its own and does not absorb equally over the transmission band of the filter. The resultant filtering effect of the carotene (4 mg. per liter) and the cupric acetate is shown in Figure 5. A decided maximum occurs in the longer wave lengths of the band. The presence of this off-peak maximum accounts for the deviation of the calibration curve from a linear relationship.

The case is different with the blue Jena glass filter in combination with the 1 per cent cupric sulfate solution. Here the filter band is so narrow that it is rather completely covered by the carotene absorption band. The transmission band resulting from a combination of the blue glass and carotene is reasonably symmetrical and has no off-peak maximum. The calibration curve is practically linear, as is also true in the case of the spectrophotometer.

Stable band pass light filters add greatly to the accuracy with which a double photoelectric cell colorimeter operating into a bridge circuit is compensated for variations in intensity of the light source due to line voltage fluctuations. Since slight voltage fluctuations are greatly magnified in terms of variations in light intensity, very complete compensation is necessary when a colorimeter is to be used on the average power supply. The only alternative to compensation in the instrument itself is voltage control by such devices as storage batteries and constant power transformers, which are bulky, expensive, and generally less satisfactory.

In the case of either of the bridge circuits shown in Figures 2 and 8, the same proportionate change in response of both cells will not affect the balance of the galvanometer if the potentiometer has been previously adjusted for zero deflection. If, however, the responses do not change in the same proportionate degree, the galvanometer will cease to be on zero deflection. As the temperature of the filament changes because of voltage fluctuations, the radiation emitted by the lamp will change, not only in intensity but in quality also.

The change in quality is due to the shift in spectral energy distribution of the filament with temperature. Therefore, the unfiltered radiation will produce equally proportionate changes in cell response only if the cells are identical in relative spectral sensitivity. This condition is very difficult to obtain even with present-day photoelectric cells. If the radiation from the lamp is filtered by a pair of identical narrow band pass filters, only a small but equal portion of the spectral sensitivity curve of each photocell is excited and difference in relative sensitivity on either side of the narrow spectral range transmitted by the filter is of no consequence. Under these conditions of filtering, it has been found that it is not necessary to have closely matched photoelectric cells for satisfactory line voltage compensation.

There are several types of light filters available for colorimetric work. The glass filters, such as the Corning (*3*) and Jena (*6*), are the most satisfactory from the standpoint of stability but they are often lacking in sharpness of transmission band. The cemented dyed gelatin filters, such as those made by Eastman (*5*), are more satisfactory as filters but in most cases lack the great stability of the glass types just mentioned. In general, it is best to select glass filters when possible and to use the less permanent dyed gelatin type only when sufficiently narrow transmission bands are not obtainable in the glass type.

Details of Colorimeter

The photoelectric colorimeter shown in Figure 9 and presented diagrammatically in Figures 7 and 8 was designed around a pair of Cetron (Continental Electric Company) cesium oxide vacuum photoelectric cells of the emission type (P_1 and P_2). The various parts of the instrument are mounted rigidly on a solid base of oak. Rigidity is a prime requisite for a satisfactory colorimeter of this type, since the slightest distortion of the base will deflect the light beam enough to cause annoying drifting of the galvanometer. An iron casting is excellent as a base.

The housing, *H*, is of 19-gage cadmium-plated black iron, and is divided into seven compartments by sheet-iron partitions. Adequate ventilation is provided in the lamp compartment by openings in the side and a short chimney on the top. A pair of readily removable aluminum lids exposes the two compartments at either end, which house the photocells and absorption cells. These are shown in the photograph.

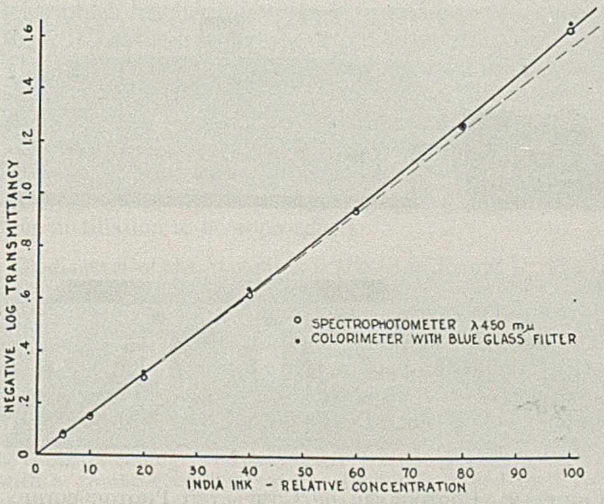

FIGURE 6. INDIA INK CALIBRATION CURVES

Obtained with a Bausch and Lomb spectrophotometer and the photoelectric colorimeter

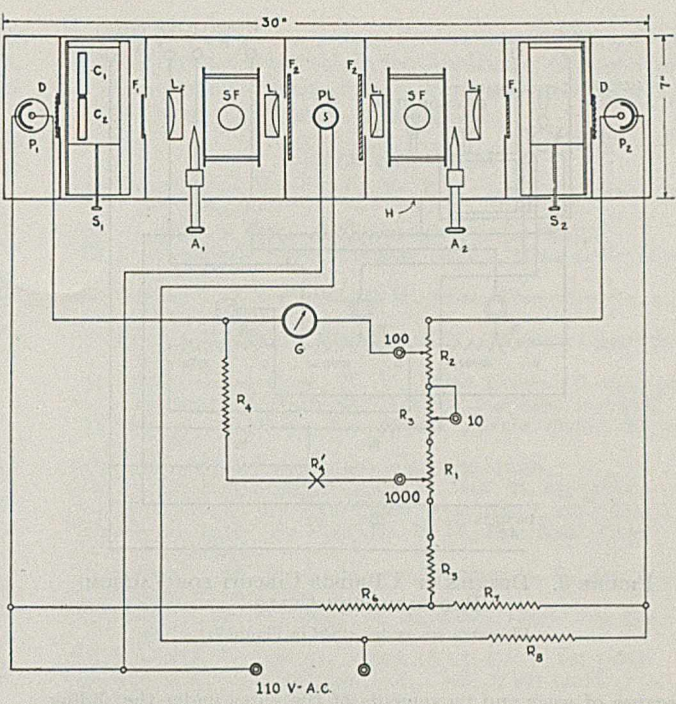

FIGURE 7. DIAGRAMMATIC VIEW OF COLORIMETER AND BRIDGE CIRCUIT EMPLOYED

PL.	100-watt projection lamp, 2.1875-inch light center
F_2.	1/8-inch Aklo plate glass
L_1.	Condensing lens, 5.625-cm. (2.25-inch) focus (Leitz 2.5× hand lens)
SF.	Solution filter cell, 5 cm. (Zeiss water cell)
F_1.	Narrow band pass filter
C_1, C_2.	Absorption cells
D.	Diffusex glass
P_1.	Cesium oxide vacuum photoelectric cell (Continental Electric Co. "Cetron")
S_1, S_2.	Absorption cell slide handle
A_1, A_2.	Adjustment for balancing light flux
H.	Iron housing
G.	Galvanometer, short period type, sensitivity 0.0005 mm. 1 μa.
R_1.	Dial decade, 10 × 1000 ohms
R_2.	Dial decade, 10 × 100 ohms
R_3.	Dial decade, 10 × 10 ohms
R_4.	10,000-ohm wire-wound fixed resistor
R_4'.	1000-ohm slide wire rheostat for balancing (optional)
R_5, R_6, R_7.	10,000-ohm wire-wound fixed resistor
R_8.	1000-ohm wire-wound fixed resistor

The lamp source, *PL*, is a 100-watt T-10 projection lamp in a medium prefocus base. The lamp has a light center of 5.47 cm. (2.1875 inches). The selection of lamps with this light center distance makes it possible to use 100-, 200-, and 500-watt lamps interchangeably in the same socket and still have the filament at the same focal point.

The lenses are Leitz hand magnifiers. L_1 is 50 mm. in diameter, 4 magnification, and L_2 is 54 mm. in diameter, 2.5 magnification. The lamp filament is at the focus of L_1.

The filter system consists of a pair of panes of 0.3-cm. (0.125-inch) Aklo plate glass, F_2; a pair of Zeiss 5-cm. deep absorption cells, *SF*, for solution filters or water; and provision for inserting a pair of 5-cm. (2-inch) square glass or cemented gelatin filters, F_1. The diffusing screen, *D*, is Diffusex glass.

The solutions of unknown density are placed in the absorption cell, C_1, and the solvent is placed in cell C_2. The two cells ride on a sliding carriage which moves by the handle, S_1, between movable stops. In some types of determinations it is desirable to place absorption cells in both light paths and therefore a second carriage was incorporated at S_2.

The tapered screws, A_1 and A_2, are for finely balancing the radiant energy of the two beams. Since the radiation is essentially parallel between the two lenses, L_1 and L_2, the addition of an opaque object does not result in seriously uneven flux distribution on the photoelectric cells.

The bridge circuit shown diagrammatically in Figure 7 and in detail in Figure 8 was made up as shown.

The dial decade resistances are accurate to 0.1 per cent. The fixed resistances, R_4, R_5, R_6, R_7, and R_8 are wire-wound units having a tolerance of 1 per cent.

Attempts to use a slide wire rheostat type of potentiometer in place of the dial decade units have not proved very satisfactory. Such high-resistance potentiometers do not hold their calibration,

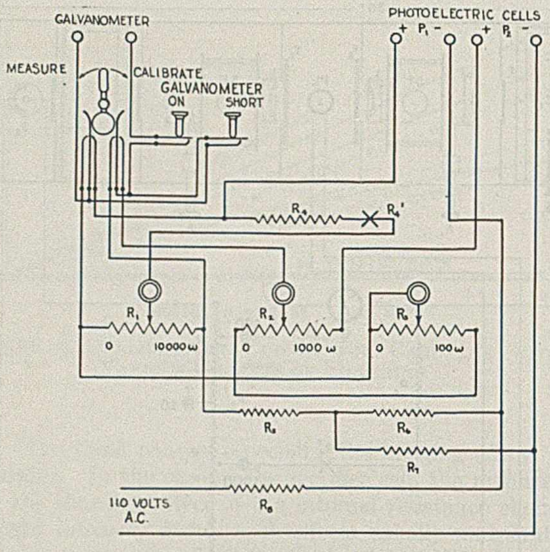

FIGURE 8. DETAILS OF A BRIDGE CIRCUIT FOR VACUUM PHOTOEMISSION CELLS

Elements are as described in Figure 7.

because of wear and movements of the wires under the sliding contact. Furthermore, most potentiometers of this type are not wound to an accuracy of better than 5 or 10 per cent.

The decade resistances are arranged on the instrument panel in the order shown in Figure 8, with the high unit on the left. The readings are made in terms of per cent in units of 0.1.

The double-pole, double-throw key switch is for quickly setting the bridge for calibration, with the decade units set for a total resistance of 10,000 ohms, regardless of the position of the decade switch arms. With this setting of the switch, the light intensity is balanced by means of the screws, A_1 and A_2, with the blank absorption cell, C_2, in place. The balancing can be made just as readily by means of a rheostat of 1000 or 2000 ohms at R_4' when vacuum emission cells are used.

After the instrument is balanced, the switch is thrown to "measure" and the absorption cell, C_1, which contains the solution to be measured, is slid into place. A new balance is now made, using the three dials, and the transmittancy is read directly.

Several methods were used to determine whether the instrument and the photocells were strictly linear. The Cetron photoelectric cells were found to be as closely linear in response to intensity with the bridge circuit used as the methods employed could detect. The most conclusive test made was the determination of the transmittancy of a series of India ink solutions of arbitary concentrations, the determinations being made by means of the colorimeter and a Bausch and Lomb polarizing spectrophotometer. The data are plotted in Figure 6. Both sets of data present curves which fall very closely to the same line. The deviation from a straight line is probably due to the ink itself, since both sets of data show the same deviation.

The ability of the colorimeter to retain its calibration accurately over a period of 6 months is exemplified in Table I. These figures are the results secured with different lamp bulbs and different photocells.

A dilute India ink solution and a 5-cm. (2-inch) square of Corning glass No. 555 were used as absorbing media. The filter consisted of the Jena blue combination BG12 and GG5. Only a few tenths difference in reading is occasioned by the use of two different pairs of photoelectric cells. These cells are obviously not matched, since they were purchased from the manufacturer almost a year apart. The deviation is only 0.5 per cent when projection lamps of two different voltages are employed. When the transmittancy of the glass was determined over a period of 6 months, the reading likewise varied only a matter of 0.1 per cent. In order to attain these accuracies, it is necessary to allow the lamp to heat up for 20 or 30 minutes before taking any readings. For ordinary accuracies of the order of 1 per cent, no appreciable time needs to be allowed. If the instrument had been more rigidly mounted on a cast-iron base, these heating effects would probably not have been so pronounced.

TABLE I. RESULTS WITH DIFFERENT LAMP BULBS AND PHOTOCELLS

Date	Lamp	No. of Photocell in Socket P_1	P_2	Absorbing Medium	T
	Watts				%
6-30-35	100	1	2	India ink	47.8
6-30-35	100	2	1	India ink	47.8
6-30-35	100	3	1	India ink	47.8
6-30-35	100	4	1	India ink	47.9
6-30-35	100	3	4	India ink	47.8
6-30-35	100	1	2	Corning No. 555	61.7
6-30-35	100	2	1	Corning No. 555	61.7
6-30-35	100	1	3	Corning No. 555	61.8
6-30-35	100	1	4	Corning No. 555	61.8
6-30-35	100	3	4	Corning No. 555	61.6
6-31-35	100	1	2	Corning No. 555	61.7
6-31-35	200	1	2	Corning No. 555	62.1
4-14-35	100	1	2	Corning No. 555	60.3
4-18-35	100	1	2	Corning No. 555	60.3
4-20-35	100	1	2	Corning No. 555	60.3
4-21-35	100	1	2	Corning No. 555	60.3
4-23-35	100	1	2	Corning No. 555	60.3
5-27-35	100	1	2	Corning No. 555	60.3
6-15-35	100	1	2	Corning No. 555	60.3
6-25-35	100	1	2	Corning No. 555	60.2
7-31-35	100	1	2	Corning No. 555	60.2
8- 3-35	100	1	2	Corning No. 555	60.3
9-20-35	100	1	2	Corning No. 555	60.3
10- 3-35	100	1	2	Corning No. 555	60.4
10-14-35	100	1	2	Corning No. 555	60.3
10-24-35	100	1	2	Corning No. 555	60.3

TABLE II. CALIBRATION DATA OF POTASSIUM DICHROMATE SOLUTIONS WITH PHOTOELECTRIC COLORIMETER

Concentration	T_1	T_2	T_3	T_4
G./100 cc.	%	%	%	%
0.002	96.6	96.5	96.55	96.5
0.010	84.9	84.9	84.85	84.7
0.020	72.6	72.8	72.8	72.5
0.030	62.5	62.8	62.8	62.5
0.050	47.7	48.3	48.35	47.9
0.070	37.7	37.9	38.3	38.0
0.100	27.8	28.4	28.4	28.2

Table II presents a set of readings taken with potassium dichromate solutions by three different individuals over a period of 8 hours. With the exception of one concentration, the readings do not have a maximum variation of more

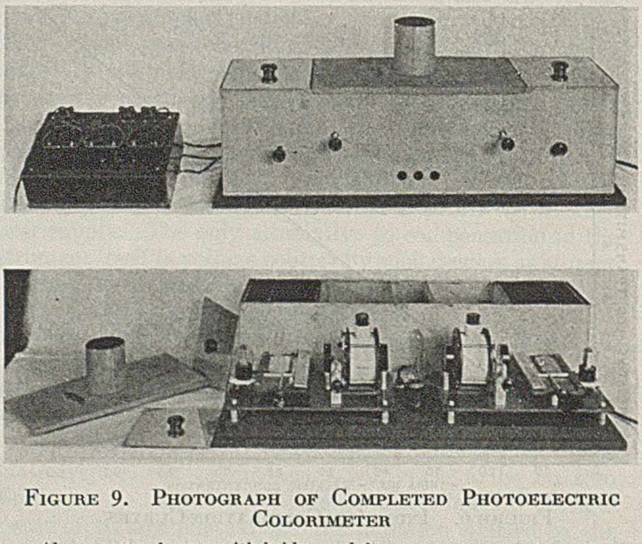

FIGURE 9. PHOTOGRAPH OF COMPLETED PHOTOELECTRIC COLORIMETER

Above, setup for use with bridge on left.
Below, colorimeter with housing removed to show placing of parts.

than 0.5 per cent. Some of this variation is undoubtedly due to foreign matter on the face of the absorption cells. It is very difficult to keep the cells absolutely clean when constantly refilling with solutions such as dichromate.

The degree to which the instrument is compensated for fluctuating line voltage was tested by inserting a variable resistance in series with the lamp source. The voltage was varied from 116 to 90 volts, which resulted in more than a 50 per cent decrease in light intensity. Under these conditions, the galvanometer balance did not shift sufficiently to necessitate a 0.1 per cent change in dial setting. This complete compensation is lost if the optical system is not filtered with absolute symmetry. For this reason, it is always advisable to purchase filters as matched pairs.

Summary

The principles of design of precision photoelectric colorimeters are discussed. An instrument based upon these principles is described which has the following characteristics:

The complete colorimeter consists of three units: colorimeter unit, dial decade bridge, and galvanometer, either wall or portable type depending upon the sensitivity required.

In measuring transmittancy, the instrument has an absolute accuracy of the order of 1 per cent and a reproducible accuracy of 0.1 per cent.

The accuracy of the instrument inherently depends only upon the retention of the linear response of the photoelectric cells and it is independent of other gradual changes in characteristics.

The calibration is not appreciably affected by changes in lamp source or in line voltage fluctuations. Fluctuations of ±5 volts are not detectable in the operation of the instrument.

The colorimeter reads directly in percentage transmission.

The instrument exhibits no lag effects.

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A Microdistillation Apparatus

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SUCCESSFUL chemical investigation of small amounts of material is largely dependent upon special manipulation designed to supply the same treatment as do the customary macroprocedures. Obviously microdistillation and fractionation require special technic because of the very small volume of the liquid. In the investigation of the ergot alkaloids which has been in progress in this laboratory for some time, it has been necessary to do many microdistillations. The apparatus described below was designed for this purpose and has proved invaluable to the work. Microsublimation followed by condensation on a small area has long been known. This apparatus, however, is an adaptation of the Siwoloboff (*1*) micromethod for taking boiling points, combined with an adaptation of the principle of microsublimation and allows a true distillation to be approached.

A diagram of the apparatus is shown in Figure 1. The main part of the apparatus is made from glass tubing approximately 17 mm. in diameter. The lower part is drawn out into a capillary which is about 30 mm. long and has an inside diameter slightly larger than 1 mm. On the lower end of the capillary is sealed a small, thin-walled bulb, *A*, of 0.25-cc. capacity. Projecting through and almost filling the capillary and extending to the bottom of the bulb is an ebullition stick, *B*, made of a solid glass rod, with the exception of the lower end on which is sealed 1 mm. of capillary tubing. The condenser, *C*, is fitted into the apparatus with a ground-glass joint at *F*. Its top is closed by a rubber stopper through which a glass tube, *D*, extends to the lower end of the condenser. The condenser is cooled by a stream of cold water entering through the glass tube, *D*, filling the condenser, and emerging at *G*. During the distillation, liquid condenses on the outside of the tip of *C* and is held there by surface attraction. In order that more liquid may adhere to the tip of the condenser, it is strongly indented. By making the proper inverted cup on the tip, 0.2 cc. of a mobile organic liquid will easily adhere. Following distillation, the distillate can be removed from the condenser by means of a capillary pipet and the tip of the condenser then placed in a small, short test tube and the last traces of distillate removed with the appropriate solvent.

The apparatus is immersed in an oil bath to a point above the tip of the condenser as shown. The oil bath is fitted with a mechanical stirrer and a thermometer for recording the temperature. The temperature of the oil bath is slowly raised until the liquid visibly boils or until a steady stream of

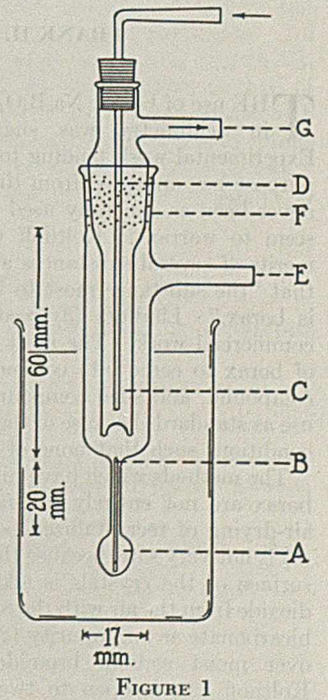

Figure 1

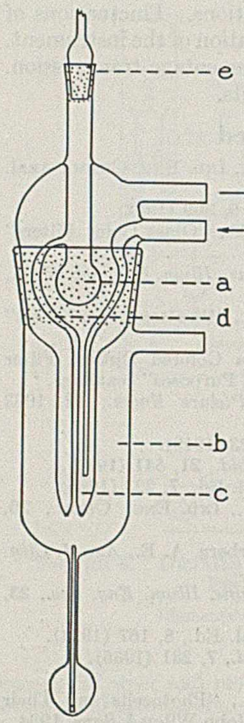

Figure 2

bubbles comes from the tip of the ebullition stick, *B*. In order to determine the boiling point, experience has shown that a correction of a few degrees must be subtracted from the temperature of the oil bath at this point. The boiling point is of the same order of accuracy as the boiling point taken by the Siwoloboff micromethod (*1*) for taking boiling points. An indication of the boiling point can be obtained only when the liquid is a pure compound, since the temperature recorded gives the boiling point of the liquid and not that of the distillate. When fractionation is necessary, each fraction is redistilled and the true boiling point thus approached.

The liquid to be distilled is placed in the bulb, *A*, by means of a capillary pipet and the ebullition stick, *B*, is then replaced. *B* fits the capillary of the apparatus rather snugly and allows passage of the vapors of the liquid to the condenser, *C*, essentially only at the boiling point of the liquid. Herein lies the advantage of the apparatus described, since, without the capillary, vapors would pass from the liquid to the condenser at a temperature considerably below the boiling point because of evaporation and rapid diffusion to the condenser through the larger opening. The conditions presented by distillation from the customary flasks used for macrodistillation are thus more nearly reached by use of the capillary constriction which is nearly filled by the ebullition stick, *B*.

As many fractions as desired can be taken during each distillation. Each fraction, however, corresponds to only a flash distillation, as there is no fractionation from reflux. A complete distillation can be done very quickly and is practically quantitative, as only the condenser is below the temperature of the boiling point of the liquid and there is no loss due to a large condenser surface. Accordingly, the process may be repeated several times and thus arrive at a fractionation in the truest sense of the word. Distillations under reduced pressure can be made equally well by evacuating the flask at the opening, *E*, although one of the usual means of avoiding fluctuations of the pressure is necessary since the distillation must take place without bumping. Thus, the apparatus is adaptable for distillation of a wide range of substances at temperatures and pressures at which any distillation can be accomplished on the customary macroscale.

When the volume of the distillate is more than 0.2 cc., an apparatus of the type shown in Figure 2 has been found to be useful. This operates in principle like the previous apparatus, with the exception that provision has been made for the collection of the larger volume of distillate by modification of the condenser.

A capillary tube is fitted to the top of the condenser at *e* with a small ground-glass joint and leads to a mercury leveling bulb, the purpose of which is to change the pressure in the collection chamber, *a*, so that it can be made less than that in *b*. By proper adjustment, the droplet of distillate as it collects at *c* will be forced up through the capillary, *d*, and into *a*, where it can be obtained with a capillary pipet after the distillation is finished.

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Borax as an Acidimetric Standard

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The use of borax, $Na_2B_4O_7 \cdot 10H_2O$, as a primary standard in acidimetry was suggested many years ago (*8*). Experimental work tending to confirm its suitability for this purpose has appeared from time to time (*1*, *4*, *6*), but it has never been as generally used as its many advantages would seem to warrant. Kolthoff (*1*), in comparing the relative merits of several substances as acidimetric standards, states that "the substance most to be recommended as a standard is borax." Lindfors (*3*) recommends it highly for routine commercial work. The most probable reason for the failure of borax to come into common use is that it is a hydrated compound, and such compounds are not usually suitable for use as standards because of the difficulty of drying them under conditions such that none of the water of hydration is lost.

The methods which have hitherto been proposed for drying borax are not entirely satisfactory. The process of simple air-drying of recrystallized borax recommended by Lindfors (*3*) is not very safe, because the solution which remains on the surface of the crystals is alkaline enough to absorb carbon dioxide from the air with the formation of sodium carbonate or bicarbonate as an impurity (*2*). The technic of drying borax over moist sodium bromide, which is recommended by Kolthoff (*2*), is open to two practical objections—namely, that sodium bromide is relatively expensive, and that the drying process requires considerable time. Moreover, the suitability of this desiccant has recently been questioned by Menzel (*5*) on theoretical grounds. Menzel proposes in place of sodium bromide a solution saturated with respect to both sugar and salt (sucrose and sodium chloride), since this solution was found to have the proper vapor pressure for maintaining borax in the decahydrated state over a wide range of temperature. This last desiccant, while it is apparently free from all theoretical criticism, is nevertheless objectionable because of its slow action. Unless an easy, rapid, and exact method for drying borax is available, its usefulness as a standard substance is obviously limited. In the present paper a very easy method of drying with alcohol and ether is described, and the purity of borax dried in this way is tested by comparison with borax dried by Menzel's method and also with pure sodium carbonate.

Purification and Drying of Borax

Pure borax was prepared by the recrystallization of the c. p. material, using quantities of borax and water (50 ml. of water to every 15 grams of borax) such that no crystallization could occur above 55° C., thus eliminating the possibility of the formation of the pentahydrate of sodium tetraborate (transition temperature, decahydrate ⇄ pentahydrate, 61° C.). The borax crystals were freed from mother liquor by suction, then washed twice with water.

The first method of drying consisted in washing the damp crystals with two portions of 95 per cent ethyl alcohol, followed by two portions of ethyl ether, each washing being followed by suction to remove the wash liquid. The portions of alcohol and ether used were about 5 ml. for 10 grams of the borax crystals. This drying treatment has been applied with success in analytical work to magnesium ammonium phosphate hexahydrate. Following the treatment with alcohol and ether, the borax was spread out in a thin layer on a watch glass and allowed to stand at room temperature to permit the evaporation of the ether.

The second method of drying consisted in spreading the damp crystals on a watch glass and placing it in a desiccator over a solution saturated with respect to both sugar and salt, the desiccant recommended by Menzel.

Stability of Borax

Before proceeding to analytical tests of the purity of borax prepared and dried by the methods described, it was desired to gain some information about the stability of the substance in air at room temperature, and in the presence of saturated sugar and salt solution. One of the principal advantages in the use of borax is that it may be weighed directly in air, since it is not hygroscopic. It has long been known, however, that borax loses its water of crystallization very slowly when kept in air at room temperature. In order to determine the rate at which this loss occurs, a 3-gram sample of borax, dried with alcohol and ether and allowed to stand overnight to permit the evaporation of the ether, was placed in a crucible and allowed to remain for a long period of time in contact with air at room temperature (24° to 33° C.). From time to time the crucible was weighed and the loss in weight noted. The loss of weight at the end of several periods of exposure was as follows: 5 days, 0.027 per cent; 17 days, 0.050 per cent; 25 days, 0.076 per cent; 52 days, 1.04 per cent. During the first 25 days the loss in weight was regularly about 0.1 mg. per day. Between the fifty-second and fifty-third days the loss amounted to 1.6 mg. It appears, therefore, that the rate of loss of water, though very small at first, increases with time. It seems probable from these results that leaving borax for as long as a week or 10 days would be safe in ordinary work, except under very unusual conditions of temperature and humidity.

The stability of borax in the presence of saturated salt and sugar solution was also tested. Menzel (*5*) found that the maximum variation in weight of a sample of borax kept for 12 months in a vacuum desiccator over this solution amounted to only −0.02 per cent. To test the efficacy of this solution in the drying of borax, 3.5 grams of damp borax crystals were spread out on a watch glass and placed in a desiccator over this solution. After 3 days the crystals appeared to be quite dry. The loss in weight on the fourth day amounted to only 0.1 mg., and after 52 days to 0.9 mg. (0.026 per cent). Another 3.5-gram sample of borax which had been dried with alcohol and ether also showed a loss of 0.026 per cent in weight on standing over sugar-salt solution for 55 days. It appears from these measurements that the desiccant proposed by Menzel is satisfactory, and that borax may be safely stored over sugar-salt solution for an indefinite length of time.

A further study of the stability of borax is now in progress.

Purity of Borax Dried with Alcohol and Ether

To ascertain whether the alcohol-ether method of drying yields pure decahydrated borax, samples purified and dried by this method were compared with another sample dried by Menzel's method and also with pure sodium carbonate, by means of hydrochloric acid. The borax dried with alcohol and ether was allowed to stand overnight before it was used. That dried over saturated sugar and salt was allowed to remain in the desiccator for a week. The pure sodium carbonate used for the comparison was prepared from c. p. sodium bicarbonate by the method of Reinitzer (*7*), and was dried to constant weight by heating at 270° to 300° C.

Standard solutions (0.05 *M*) of the borax samples and of sodium carbonate were prepared and 25-ml. portions of the solutions titrated with approximately 0.1 *M* hydrochloric acid. All the instruments used in the preparation of the standard solutions and in the titrations were calibrated to give an accuracy of 0.1 per cent or better.

In the borax titrations methyl red was used as the indicator, and the end point was matched with a color standard prepared by adding 5 drops of methyl red to 70 ml. of a solution containing 1.0 gram of sodium chloride and 2.2 grams of boric acid in 500 ml. of water. This solution represents approximately the stoichiometrical point of the titration of 25 ml. of 0.05 *M* borax with 0.1 *M* hydrochloric acid, assuming 20 ml. of wash water to be used in the titration. This color standard must be boiled to remove carbon dioxide which may be dissolved in the water. If properly prepared it has a straw color, different from the pure yellow of methyl red in alkaline solution, but not yet pink. By the use of the color standard the borax titration may be performed without titration error (*2*), for the stoichiometrical point of the titration comes within the range of color change of methyl red. However, the use of a color standard in routine work with borax is practically superfluous, since the color change of methyl red occurs so rapidly and is so distinct that the first change from pure yellow may be taken as the end point without making any serious error.

The sodium carbonate titrations were performed at the boiling point, using methyl red. Under these conditions the titration error amounts to less than 0.01 ml. of 0.1 *M* acid, which is beyond the limit of error of the buret readings. Methyl red was chosen in preference to methyl orange for the carbonate titration because the indistinctness of the methyl orange end point renders the measurements uncertain.

The molarity of the 0.1 *M* hydrochloric acid was calculated from titrations against three samples of borax, two of which were dried with alcohol and ether and one over sugar-salt solution, and from one sample of sodium carbonate. All four titrations gave the same molarity for the acid (0.1024 *M*). This concordance indicates that the alcohol-ether method of drying borax is entirely satisfactory. In view of the ease with which the method may be carried out, the only disadvantage which has hitherto prevented the extensive use of borax—namely, the difficulty of obtaining the dry salt—appears to be now obviated.

Acknowledgment

The writer wishes to thank Arthur F. Scott for his interest and coöperation in this work.

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Loss of Pyrethrins during Analysis of Mineral Oil–Pyrethrum Extracts by the Seil Method

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MINERAL oil-pyrethrum sprays for household use are ordinarily perfumed to cover the objectionable mineral oil odor. The perfumes used usually contain esters or other compounds which interfere with the determination of the active principles, pyrethrin I and pyrethrin II, by methods based on the titration of their mono- and dicarboxylic acids. Seil (*2*) and Ripert (*1*) suggest steam distillation of such products to remove the perfume before proceeding with the analysis. Preliminary tests having indicated that there was a loss of pyrethrins in the analysis of these commercial extracts following Seil's procedure, a more complete study of the method was made.

Three preparations of the mineral oil-soluble portions of pyrethrum were prepared by extracting 750-gram portions of powdered pyrethrum in a large extractor with petroleum ether (boiling range 35° to 40° C.); the petroleum ether was evaporated by immersing the flask in a water bath, the temperature of which was maintained between 50° and 55° C., and the residue was then treated successively with 200-cc. portions of the oil solvent, filtered, and made to 6 liters with mineral oil. In the preparation of sample A a commercial purified white mineral oil of the type used as a base for commercial household fly sprays was used as a vehicle, and for samples B and C kerosene highly purified in the laboratory was used. (The purified kerosene used had a distillation range from 165° to 300° C. with 84 per cent distilling between 175° and 250°, while the fly spray oil base had a distillation range from 200° to 250° C.) No perfume or other interfering substances were added. These prepared samples were stored in brown glass bottles in a dark cupboard from which they were removed only during the actual time of sampling.

These preparations were analyzed by the Seil method, subjecting them to steam distillation just as though perfume were present. Since the volume of distillate necessary to remove all the perfume from commercial samples varies within rather wide limits, four 100-cc. aliquots of each sample were distilled and distillates of 250, 500, 1000, and 1500 cc., respectively, were collected, in order to simulate conditions met in the analysis of commercial samples. Pyrethrins were determined in the distillate as well as in the residue remaining in the distillation flask. As a means of comparison pyrethrins were also determined in the original samples without steam distillation.

In making the analyses the procedure outlined by Seil was followed as closely as possible. However, because of the formation of emulsions during the steam distillation and also during the boiling off of the alcohol after the saponification, it was necessary to introduce slight modifications. The emulsion formed in the flask during the steam distillation was broken by adding a small quantity of saturated sodium sulfate solution and 25 to 50 cc. of petroleum ether. The emulsion formed during the boiling of the alkaline solution after saponification was more difficult to break, but separation usually was possible after adding a little petroleum ether and a few cubic centimeters of a 20 per cent sodium hydroxide solution.

After titrating for pyrethrin I in the portions of the distilled oil, the qualitative color test described by Seil (*2*) was also applied. In each case the test was positive, showing that the chrysanthemum monocarboxylic acid was definitely present.

The analytical results are given in Tables I and II. The results in Table I show that there is a progressive loss in the pyrethrin content of the sample during the steam distillation.

TABLE II. PYRETHRINS DETERMINED IN PYRETHRUM EXTRACTS WITHOUT STEAM DISTILLATION

Sample	Pyrethrin I	Pyrethrin II	Total
	Mg./100 cc.	*Mg./100 cc.*	*Mg./100 cc.*
A	31.7	45.2	76.9
B	36.4	47.5	83.9
C	24.6	52.0	76.6

In two cases the method of distillation was modified with the idea of holding a larger proportion of oil in the distillation flask. In the first case 100 cc. of the fly spray oil base were added to the aliquot to be distilled and in the second case 50 cc. of a highly purified mineral oil having a distillation range of from 300° to 400° C. were added before distillation. In each case there was a slight increase in the pyrethrins recovered but the loss was still considerable. This loss is only partially due to volatilization of the pyrethrins with the steam. A large part is due to decomposition or other chemical change, as is shown by the fact that the sum of the pyrethrins determined in the distillate and in the residue is considerably below the value obtained by direct saponification of the sample.

TABLE I. PYRETHRINS DETERMINED IN PYRETHRUM EXTRACTS AFTER STEAM DISTILLATION

Sample	Volume of Distillate		Pyrethrins in Distillate			Pyrethrins in Residue			Total Pyrethrins
	Water	Oil	Pyrethrin I	Pyrethrin II	Total	Pyrethrin I	Pyrethrin II	Total	
	Cc.	*Cc.*	*Mg./ 100 cc.*	*Mg./ 100 cc.*	*Mg./ 100 cc.*	*Mg./ 100 cc.*	*Mg./ 100 cc.*	*Mg./ 100 cc.*	*Mg./ 100 cc.*
A	250	...	4.1	3.4	7.5	24.0	34.6	58.6	66.1
	500	90	6.4	3.6	10.0	24.0	31.3	55.3	65.3
	1000	90	5.0	4.9	9.9	22.4	33.1	55.5	65.4
	1500	95	6.4	3.3	9.7	19.5	29.4	48.9	58.6
	500[a]	105	Not determined			25.6	33.3	58.9	..
B	250	50	3.5	2.4	5.9	27.6	37.9	65.5	71.4
	500	75	4.3	3.2	7.5	26.7	35.4	62.1	69.6
	1000	80	4.3	2.2	6.5	25.4	31.5	56.9	63.4
	1500	90	4.3	2.6	6.9	23.7	32.2	55.9	62.8
	1000[b]	70	3.3	2.0	5.3	26.9	34.0	60.9	66.2
C	250	50	5.6	2.0	7.6	12.6	34.0	46.6	54.2
	500	70	5.8	2.2	8.0	10.5	35.7	46.2	54.2
	1000	90	7.3	3.1	10.4	10.9	33.0	43.9	54.3
	1500	95	6.6	2.9	9.5	9.9	30.8	40.7	50.2

[a] Distillation made after addition of 100 cc. of a commercial fly spray oil base.
[b] Distillation made after addition of 50 cc. of purified high boiling mineral oil.

Summary

A study of the Seil method for the determination of pyrethrins in mineral oil extracts of pyrethrum shows that there is a loss of pyrethrins during the steam distillation for the removal of perfume. The loss is due to volatilization with steam and to decomposition or other chemical change. In the case of the materials here reported the loss approximated 25 per cent of the pyrethrins.

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A One-Piece Glass Micro-Kjeldahl Distillation Apparatus

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DESPITE the popularity and increasing use of the micro-Kjeldahl method for nitrogen determination, there have been few fundamental improvements of the distillation apparatus originated by Parnas and Wagner (*3*). Their design has a number of inherent drawbacks which are generally recognized. Schulek and Vastagh (*4*) criticize the use of rubber connections. In some cases these have been replaced by glass joints, but this increased the fragility of the apparatus and rendered it difficult to assemble. Neither did it improve the design with regard to the number of pieces to be mounted and table space occupied. Hoppe-Seyler (*1*) has eliminated a portion of the clumsiness of the apparatus, but has also increased fragility without a large gain in compactness.

Since it has been found in this laboratory and elsewhere (*2*) that condensers of Pyrex brand glass gave results identical to those of silver, a completely new Kjeldahl distillation apparatus was designed. (It was constructed through the coöperation of C. M. Flanders, Box 232, Berkeley, Calif., who can now supply this apparatus in quantity.)

Tests of this apparatus showed it to have a number of points of superiority over the usual type of equipment. All rubber connections were eliminated from the distillation train; danger of breakage was reduced by the strong, compact construction; multiple outfits were easily built up, because of the upright shape and small size; considerably less attention during the course of distillation was necessary; only one burner was used to operate the apparatus and one clamp to hold it in place; very little condensation of steam occurred in the flask; and no diminution in volume took place during distillation.

With a single distillation outfit, the time required for an analysis was not shortened; but, owing to the very slight attention required during distillation, one operator could conveniently operate a small battery and save time in this way. Only one precaution was found necessary, i. e., prevention of sucking back of the sample. This was readily accomplished by the procedure described below.

Experimental

The apparatus, shown in Figure 1, consists of a distillation flask, the bulb of which contains 25 to 35 ml., inclosed in a glass jacket which serves as a steam generator. A tube sealed inside the flask and opening into the generator leads steam through the solution being distilled. The arm of a Y in this tube is sealed through the wall above the generator to the filling funnel. Above the flask is a trap and head leading to a small glass internal condenser which drains through a vertical delivery tube into the receiver. An overflow and by-pass carry the condenser water either to the drain or to the steam generator, which is equipped with an auxiliary drain tube. The total height of the apparatus is 35 cm. (14 inches). The steam generator jacket is 42 mm. in diameter and 16 cm. in height, the bulb being 60 mm. in diameter. The internal effective portion of the condenser is 18 mm. in diameter and 55 mm. in length.

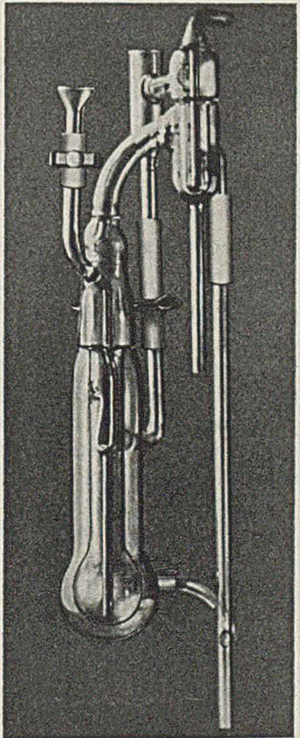

FIGURE 1

TABLE I. ANALYSIS OF NITROGEN-CONTAINING SOLUTIONS

Sample		Nitrogen Found	Error
Substance	Nitrogen		
	Mg.	*Mg.*	%
$(NH_4)_2SO_4$	0.210	0.2096	−0.2
		0.2082	−0.8
		0.2082	−0.8
		0.2096	−0.2
$(NH_4)_2SO_4$	0.418	0.420	+0.5
		0.417	−0.2
		0.420	+0.5
		0.420	+0.5
Urea	0.792	0.783	−1.1
		0.787	−0.6
		0.786	−0.7
		0.785	−0.8
p-Amino benzoic acid	0.388	0.387	−0.3
		0.388	0000
		0.387	−0.3
		0.388	0000
p-Amino benzoic acid	0.762	0.758	−0.5
		0.761	−0.1
		0.762	0000

Around the steam generator may be wrapped an insulating asbestos jacket (not shown) to prevent sudden cooling from draughts. A few boiling chips of porcelain or silicon carbide are used in the generator to prevent irregular boiling. Silicon carbide chips are superior to those of porcelain. It was found desirable to use a moderate flame for the initial heating and a strong flame as soon as boiling started. Only at this point was there any tendency to suck back. As soon as distillation started, no further attention was necessary.

The apparatus was used in a fashion similar to the usual micro-Kjeldahl distillation. The digested sample was rinsed in through the filling funnel, followed by the caustic, with formation of two layers in the flask. With the by-pass and generator drains closed with pinchcocks, the water in the generator was heated to boiling and the steam distillation continued for 5 minutes, after which the receiver was lowered and rinsed internally by heating 1 or 2 minutes longer. The outside of the delivery tube was rinsed into the receiver. On removing the flame, the condensation of steam served to suck the contents of the flask into the generator. This usually required about a minute, and could be accomplished instantaneously by opening the by-pass pinchcock momentarily, thus admitting a trickle of cold water. The flask was rinsed with distilled water which promptly sucked into the generator. The generator drain was opened, followed by the by-pass, thus allowing the condenser water to flush out the generator, an operation requiring only a short time. The apparatus was then ready for the next sample, which could be introduced while the generator was still being flushed.

Some typical analyses are shown in Table I. Excellent checks were readily obtained, though the absolute accuracy of the method is not notably different from the usual micro-Kjeldahl, since no fundamental operations are altered. Modifications tending to eliminate inherent errors may be made as easily as with the older forms of equipment.

This work was aided by a grant from the Research Board of the University of California.

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Laboratory Bubble-Cap Columns of Glass

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This paper contains a description of two all-glass bubble-cap columns of a greatly improved design. These columns are exceedingly easy to operate and may be used for vapor velocities up to 31.3 and 65.5 cm. (1.0 and 2.2 feet) per second, respectively. Since the height of the equivalent theoretical plate of one of these columns is about 2 cm., it is now feasible to build columns with separating powers equivalent to between 100 and 150 theoretical plates in a laboratory of average height.

IN PREVIOUS papers (*2*, *3*) various all-glass bubble-cap columns for laboratory use have been described. These columns have been used extensively for many years by a variety of different laboratories and have been found exceptionally valuable, particularly for distillations of mixtures containing organic compounds that tend to undergo decomposition or chemical changes under the catalytic influence of metal packings.

Since the time of the last publication it has become apparent to the writer that important improvements in the efficiency of these columns could be made if the height of the individual plate sections could be reduced without a corresponding sacrifice in vapor velocity.

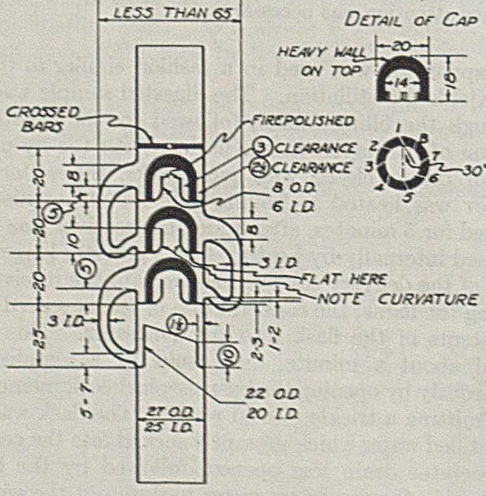

Figure 1. Redesigned Bubble-Cap Column, 2-Cm. Sections

Slots in bubble cap, as shown, about 0.5 to 1 mm. wide and 3 mm. deep, at an angle of 30° with radius, fire-polished. Material, Pyrex laboratory glass. All dimensions are in millimeters. Exact dimensions are circled.

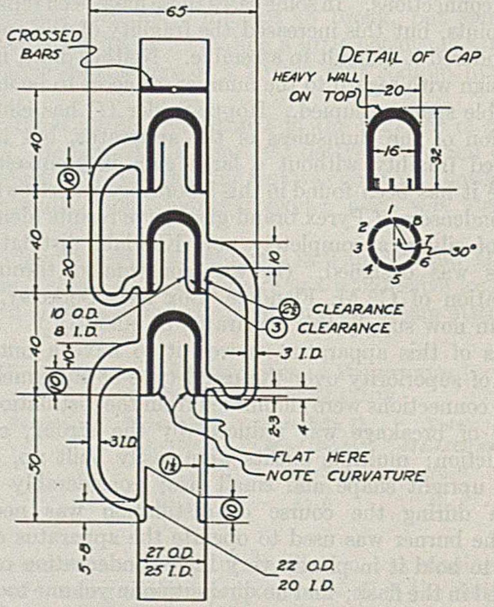

Figure 2. Redesigned Bubble-Cap Column, 4-Cm. Sections

Slots in bubble cap, as shown, about 0.5 to 1 mm. wide and 5 mm. deep, at an angle of 30° with radius, fire-polished. Material, Pyrex laboratory glass. All dimensions are in millimeters. Exact dimensions are circled.

Reconstruction of the Bubble-Cap Column

A series of short (2-plate) experimental columns having the same internal diameter, but of different designs and dimensions, was made up successively, and tested with respect to vapor velocity, holdup, plate efficiency, ease of operation, etc. The data obtained during the operation of these experimental columns have led to a complete redesign of the glass bubble-cap column, with the result that the degree of separation (number of theoretical plates per meter) now obtainable by columns of the new design is up to 400 per cent as high as that obtained with the old column of the same height and diameter.

Detail drawings of the redesigned bubble-cap columns are given in Figures 1 and 2. While these figures represent columns containing only three plates each in addition to the liquid seal customarily used between the still pot and the column, any desired number of plates may be added to the columns. Readers who are not familiar with the working principles of these columns are referred to the earlier paper (*3*).

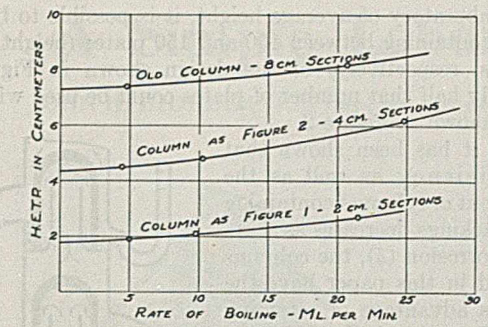

FIGURE 3. VARIATIONS OF THE HEIGHT OF THE EQUIVALENT THEORETICAL PLATE WITH RATE OF BOILING

Carbon tetrachloride–benzene mixture

By comparing the columns shown in Figures 1 and 2 with that of the same internal diameter described in the earlier publication (*3*), it may be noted that the following major improvements have been made:

1. The "holdup" of liquid per section has been reduced to a mere fraction of its former value. Thus the columns shown in Figures 1 and 2 have holdups of 0.7 and 1.4 ml., respectively, per plate, which represent only about 16 and 32 per cent, respectively, of the former holdup (4.4 ml.). These values apply to the columns while in normal operation, during which about 50 to 60 per cent of the liquid on the plate is displaced by vapor.
2. The vertical slots in the bubble caps have been ground at an angle of about 30° with the radii, in such a manner that the vapor bubbles will be forced to describe a circular motion around the bubble caps. This will naturally lead, not only to a more intimate contact and prolonged rectification between the ascending vapor and the descending reflux liquid, but also to a decided improvement in the circulation of the liquid on the plates. It is also believed that the new type of slots will have a tendency to reduce entrainment at higher rates of distillation.
3. Perhaps the most important improvement is the elimination of the excessive vapor friction exhibited by the earlier bubble-cap columns through an unproportionally high liquid head in the side arms. This vapor friction constituted a serious drawback, inasmuch as the individual plate sections had to be made unnecessarily high (8 cm.) if the columns were to be used for ordinary rates of distillation. The cause of the friction was found to be inadequate clearance between the "vapor riser" and the bubble cap. By providing a clearance of 2.5 to 3 mm. at this point, the author has found that, at ordinary rates of boiling, the liquid level in the side arms rarely rises above the value corresponding to the hydrostatic head of the plate above (Figure 5).
4. The hydrostatic pressure difference between two successive plates—that is, the height of the liquid on each plate—has been reduced from 30 mm. in the older column to 5 mm. in the column described in Figure 1 and to 10 mm. in the column shown in Figure 2. Because of the more intimate contact provided between the vapor and liquid by the above-mentioned angular slots, this reduction has been accomplished without an appreciable sacrifice in plate efficiency.

As shown in Figures 1 and 2, the height of each plate section, formerly 80 mm., has been decreased to 20 and 40 mm., respectively. This accomplishment obviously reduces the height of a column containing a certain desired number of actual plates to one-fourth and one-half, respectively, of its former value.

TABLE I. EFFICIENCY RUNS USING MIXTURES OF CARBON TETRACHLORIDE AND BENZENE (TOTAL REFLUX)

Column (25-Mm. Inside Diameter)	Height of Column	Rate of Boiling	Mole per cent of CCl_4 Still pot	Mole per cent of CCl_4 Top of column	Number of Theoretical Plates −1	H.E.-T.P.
	Cm.	*Ml./min.*				*Cm.*
5-Plate column in 2-cm. sections (Figure 1)	10	5.1	26.6	44.6	5.4	1.9
		9.8	26.6	42.9	4.8	2.1
		21.5	26.6	39.7	3.7	2.7
5-Plate column in 4-cm. sections (Figure 2)	20	4.5	27.1	42.4	4.4	4.5
		10.3	27.1	41.6	4.2	4.8
		24.6	26.9	39.7	3.7	5.4
5-Plate column in 8-cm. sections, old column (*3*)	40	4.8	26.6	45.6	5.7	7.1
		20.7	26.6	43.1	4.9	8.2

TABLE II. EFFICIENCY TEST RUNS USING MIXTURES OF *n*-HEPTANE AND TOLUENE (TOTAL REFLUX)

Column (25-Mm. Inside Diameter)	Height of Column	Rate of Boiling	Mole per cent of C_7H_{16} Still pot	Mole per cent of C_7H_{16} Top of column	Number of Theoretical Plates −1	H.E.-T.P.
	Cm.	*Ml./min.*				*Cm.*
5-Plate column in 2-cm. sections (Figure 1)	10	2.5	9.9	57	4.9	2.0
		5.1	9.9	55.2	4.7	2.1
		10	9.9	52.5	4.3	2.3
		20	9.9	48.7	3.8	2.6
5-Plate column in 4-cm. sections (Figure 2)	20	3.6	9.9	58	5.1	3.9
		7.5	9.9	55	4.7	4.3
		11.7	9.9	53.2	4.4	4.5
		20.7	9.9	51.0	4.2	4.8
		31.2	9.9	49.8	4.0	5.0
5-Plate column in 8-cm. sections, old column (*3*)	40	7.3	9.9	57.5	5.0	8.0
		22.0	9.9	57.5	5.0	8.0
		29.3	9.9	54.5	4.6	8.7

Efficiency Data on the New Column

In order to obtain strictly comparable data on the relative efficiencies of the reconstructed and the older type bubble-cap columns, a 5-plate column was made of each of the three types and tested under identical and carefully controlled conditions. Each column was surrounded by means of an electrically heated transite jacket, provided with glass windows and thermometers, so that the columns could be operated without heat loss during the test runs. For each efficiency run a charge of 1500 ml. of the test mixture was used, and the column was allowed to operate under total reflux until equilibrium had been obtained. The rate of boiling at the top of the column was calculated by the usual method (*4*) from the amount of heat absorbed by the condenser water. A sample was taken from the top of the column as well as from the still pot, and from the analysis (by means of refractive index) of these fractions and from the vapor-liquid composition diagrams, the theoretical number of plates required to effect the accomplished separation was calculated by the method of McCabe and Thiele (*5*). By dividing the actual height of the column used by the number of theoretical plates corresponding to the degree of separation effected, the height of the equivalent theoretical plate (H. E. T. P.) was derived. Account was taken of the separation accomplished in the still pot by subtracting one plate from the theoretical number deduced from the McCabe-Thiele diagram. The results of the efficiency runs are tabulated in Tables I and II.

Each of the three columns was carefully tested at various rates of boiling and by means of two different kinds of test

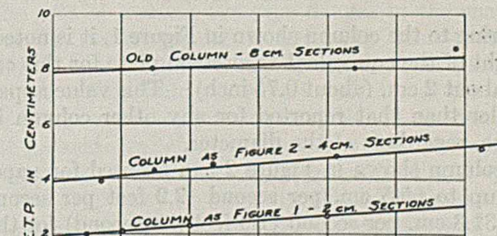

FIGURE 4. VARIATIONS OF THE HEIGHT OF THE EQUIVALENT THEORETICAL PLATE WITH RATE OF BOILING

n-Heptane–toluene mixture

mixtures, notably, carbon tetrachloride–benzene (difference in boiling points = 4.1° C.) and *n*-heptane–toluene (difference in boiling points = 12° C.).

The vapor-liquid composition diagram as well as the refractive index curve for the carbon tetrachloride–benzene system was calculated from the data published by Rosanoff and Easley (*6*), while the corresponding data for the system heptane–toluene were taken from the experimental values (based upon density measurements) of Bromiley and Quiggle (*1*).

In Tables I and II, it is noted that while the heights of the three columns used are widely different and vary from 10 up to 40 cm., the effected separations of the test mixtures are very much the same. As a result of the reconstruction of the bubble-cap column the height of the equivalent theoretical plate has been reduced from about 8 cm., in the case of the older column, to about 2 cm. for the column shown in Figure 1.

For the lower rates of boiling, some of the plate efficiencies obtained were above 100 per cent. It is believed that this inconsistency was contributed largely by errors in data used for the construction of the vapor-liquid composition curve, since a comparatively small error in this diagram will have a large effect upon the calculated plate efficiency.

In Figures 3 and 4, the heights of the equivalent theoretical plates for the various columns have been plotted against the rate of boiling. The effect of the rate of boiling is small in comparison with the difference in height of the equivalent theoretical plate between the various columns tested. Thus the column shown in Figure 1, for instance, even if operated at a rate of 21.5 ml. per minute, or near its maximum or most inefficient rate, would still have an "H. E. T. P." which would only be about 38 per cent of that of the old column operated at its minimum or optimum rate (see Figure 3).

TABLE III. MAXIMUM VAPOR VELOCITIES AND RATES OF BOILING

Column	Rate of Boiling at Top of Column, Ml./Min. of Benzene	Vapor Velocity at Top of Column	
		Cm./sec.	*Ft./sec.*
As shown in Figure 1, 20-mm. sections	30	31.3	1.0
As shown in Figure 2, 40-mm. sections	64	65.5	2.2
Old design (*3*), 80-mm. sections	41	42.4	1.4

Table III shows the maximum vapor velocities and rates of boiling at which the columns, in the absence of bumping, may be operated without flooding. Since these tests were carried out with benzene, it is evident that a higher rate of boiling in milliliters per minute should be expected if liquids of higher molecular weights were used.

Conclusions

Referring to the column shown in Figure 1, it is noted that the height of the equivalent theoretical plate for this column is only about 2 cm. (about 0.75 inch). This value appears to be smaller than that reported for any other column in the literature, regardless of the diameter.

The column shown in Figure 2 can be used for vapor velocities up to 65.5 cm. per second (2.2 feet per second) as against 31.3 cm. per second (1.0 feet per second) for the column shown in Figure 1, and is therefore recommended for use in laboratories where speed of distillation is essential. For most purposes, however, the column shown in Figure 1 is to be preferred, since the degree of separation in this column is 200 per cent as great as that obtained in the column shown in Figure 2 and about 400 per cent as great as the older type of bubble-cap columns.

In a laboratory of average height, it is possible to build a column containing between 100 and 150 plates (height 2 and 3 meters, respectively) of the design shown in Figure 1, while only half that number of plates could be used with the column shown in Figure 2.

While it has been shown that the efficiency as well as the throughput of columns containing metal packings decreases as a result of corrosion (*4*), the columns described in this paper have the obvious advantage of retaining their efficiencies indefinitely. Thus, strictly reproducible results can be obtained over indefinite periods of time.

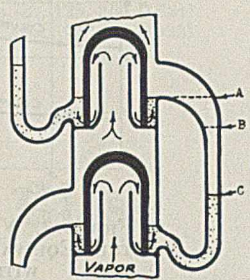

FIGURE 5. OPERATING RATE OF COLUMN AS A FUNCTION OF LIQUID LEVEL IN SIDE ARMS

A. Flooding point
B. Maximum operating rate
C. Normal operating rate

As the older type of all-glass bubble-cap columns has been shipped by the manufacturer to distant places, and as they have been used extensively by many laboratories without a single reported breakage, it is believed that the new columns, properly mounted (*3*), should be at least as sturdy and long-lasting.

The new columns are exceedingly easy to operate. For a given liquid the jacket temperatures may be varied within wide limits without causing any disturbances or flooding, and the columns require, practically speaking, no attention except that of charging as well as removal of the distillate fractions. Another unique feature of the new columns is the fact that it is possible for the operator, by a glance at the liquid levels in the side arms, to get a rough indication of the rate of boiling. As shown in Figure 5, the liquid level is considerably higher up in the arm when the column is operating near its flooding point. With this in mind, the column may be adjusted to a safe operating rate and then left, more or less, to take care of itself.

Manufacturing of Columns

The columns described in this paper have been made by the Otto R. Greiner Company, 55 Plane St., Newark, N. J. In order to avoid any misunderstanding, it should be noted that both of the columns described in this paper (Figures 1 and 2) are entirely different and much superior to an unpublished column (40-mm. sections) which has been designed by the author and made by the same manufacturer during the past two years.

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A Simple Laboratory Shaking Machine

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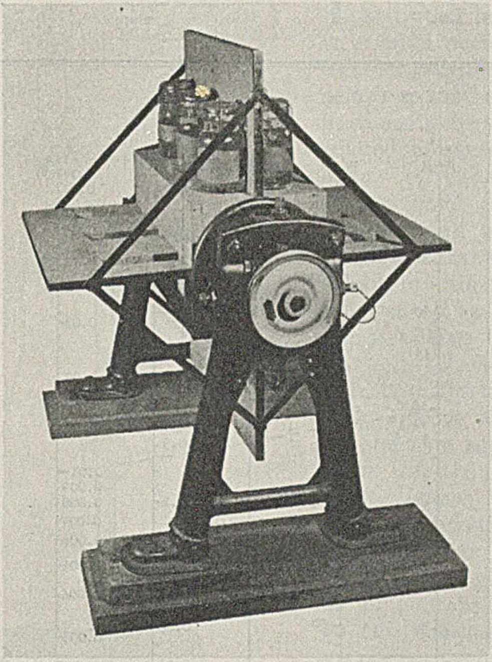


FIGURE 1. LARGE MODEL

MOST of the laboratory shaking machines on the market suffer from the faults of overcomplication and lack of adaptability. Inasmuch as agitation is a frequent and important operation in this laboratory, both in analytical and experimental work, considerable thought was devoted to the design of a machine which would present the utmost in simplicity and versatility. It was particularly desired to keep as simple as possible the method of holding in place the containers to be agitated, and at the same time permit the simultaneous use of different sizes of vessels on the machine. The principle adopted to these ends, and incorporated in the two machines shown in Figures 1 and 2, has been in satisfactory use in this laboratory for the past 3 years.

The larger of the two machines, shown in Figure 1, will accommodate 24 bottles of any size up to about 2 liters. The body consists of a rectangular box 30.5 × 30.5 × 61 cm. (12 × 12 × 24 inches), from each side of which projects a 30.5 × 61 cm. (12 × 24 inch) board, mounted on its long edge along the center line of the box. The boards, which are of 1.91-cm. (0.75-inch) stock, are fastened to the box with screws, and held rigidly in place by means of 1.91-cm. (0.75-inch) strap iron supports. Three slots, 5.1 × 17.8 cm. (2 × 7 inches), are cut in the lower side of each board, next to the face of the box. The whole is mounted, by means of two short lengths of 3.014-cm. (1.187-inch) steel shaft secured to the ends of the box by means of metal face plates, between two inverted pressed-steel shaft hangers, which serve as supports. Ring oiling bearings are used in the hangers, which are of 58.4-cm. (23-inch) drop, mounted on wooden blocks so that the shaft center is 67.3 cm. (26.5 inches) above the floor. The machine is rotated by a belt drive through a speed reducer of 50 to 1 ratio, driven by a 0.25 h. p. motor. Speeds of 30 to 60 r. p. m. are satisfactory for most purposes, and may easily be altered to suit the particular work by means of multiple pulleys.

The essential idea of the machine is the method of holding the containers in place. For this purpose use is made of large circular elastics cut from discarded rubber inner tubes. For most sizes of bottles or jars these are most satisfactorily cut in 6.4- to 7.6-cm. (2.5- to 3-inch) widths. Such an elastic is slipped around the container, which is then set on the box next to one of the slots. The elastic is then pulled through the slot from the other side of the board, and stretched to permit the insertion of a second container on that side. The containers are thus securely held in pairs, one on each side of the board, and their attaching or removal is merely a matter of slipping the elastic on or off. For the larger sizes of containers the elastics should be cut from one of the large-size inner tubes used in truck tires. These are easily obtainable at most garages.

For use with smaller sizes of containers the modification shown in Figure 2 was suggested by W. P. Doelger of this department. The same method of fastening the bottles on the machine is used, but as the weight is not so great in this case, no base is necessary for them to rest on, and they are supported only by the elastics passed through the slots as before.

The apparatus consists essentially of a 2.54-cm. (1-inch) oak board, 91.4 cm. (36 inches) long, which rotates about its long axis. Five 5.1 × 20.3 cm. (2 × 8 inch) slots make it possible to accommodate 10 containers. The board is suspended between two shaft hangers by means of two 20.3-cm. (8-inch) lengths of 2.54-cm. (1-inch) steel shaft, each of which is welded to a pipe flange bolted to one of the end pieces of the board. The shaft hangers are of 20.3-cm. (8-inch) drop and are mounted by means of wooden blocks so that the shaft center is 24.1 cm. (9.5 inches) above the table top. The machine is driven by a 0.125 h. p. motor operating through a speed reducer of 50 to 1 ratio.

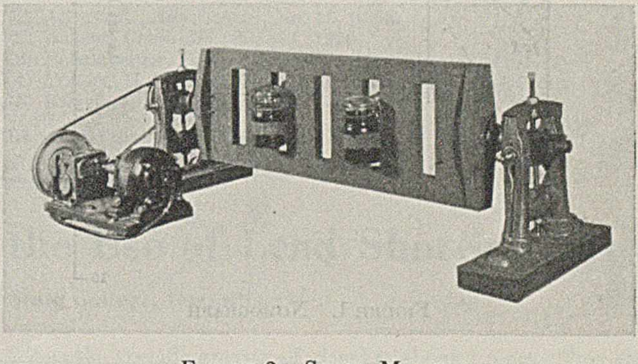


FIGURE 2. SMALL MODEL

The relative cheapness of such a machine is realized from the fact that the cost of the smaller model was approximately fifty dollars. This includes the motor and speed reducer, and the cost of welding the pipe flanges to the shaft. The cost of the larger model is naturally somewhat higher, principally because of the use of larger shaft hangers and motor. A saving could probably be effected in the construction of these machines by the substitution of wooden supports for the pressed-steel shaft hangers, but the convenience and neat appearance of the latter, together with the ease with which the shaft may be properly aligned by means of their adjusting screws, makes their added expense well justified.

Acknowledgment

The writer is indebted to E. K. Moore of this department for much help in the design and construction of these machines.

RECEIVED March 12, 1936.

Nomographs for Determining Molecular Weights by the Freezing Point and Boiling Point Methods

W. S. GILFOIL, Omega, La.

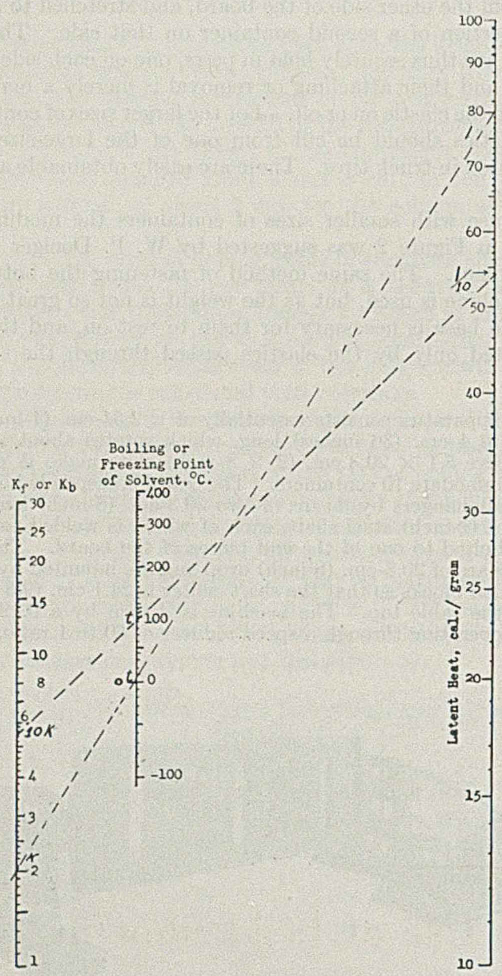


FIGURE 1. NOMOGRAPH

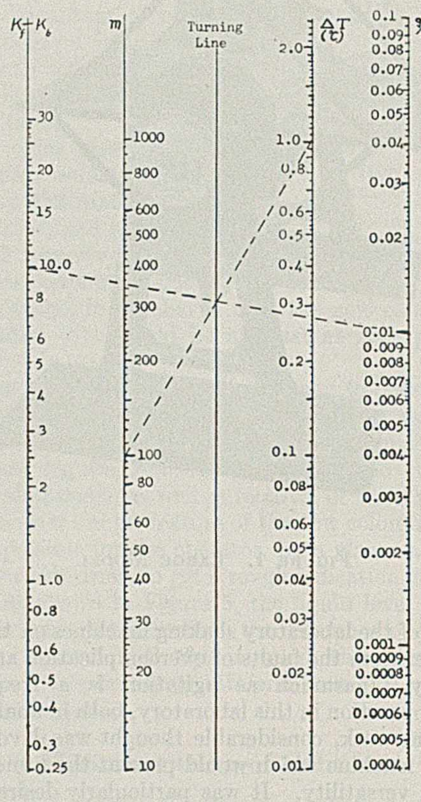


FIGURE 2. MOLECULAR WEIGHT NOMOGRAPH

$$m = 1000 \frac{K \times g/G}{\Delta T}$$

THE determination of molecular weights is a common step after the ultimate organic analysis of a compound. As a rule the data obtained are less accurate than the nomographs, which are satisfactory for all practical purposes. The method makes use of two sets of analogous equations. The boiling point equations are the same as those given here for the freezing point method, and the same charts are used for both.

$$K_f = T_0^2 / 503\, l_f \qquad (1)$$

$$m = 1000K_f \times g / G \times \Delta T_f \qquad (2)$$

where K_f represents the molal depression of the freezing point
T_0, the freezing point of the solvent in degrees Kelvin
l_f, the latent heat of fusion in calories per gram
G, the weight of solvent
g, the weight of solute, expressed in the same units
m, the molecular weight of the solute
ΔT_f, the observed freezing point depression

The correction of temperature to the Kelvin scale is taken care of in the charts, so that Centigrade temperature is used.

In case a value falls off the chart, as in the case of l_v for water, divide by 10 (for simplicity's sake); running the line from 53.9 through 100° C., we obtain a value on the K_f line which, when divided by the same number, 10, gives the proper value of K_f (Figure 1).

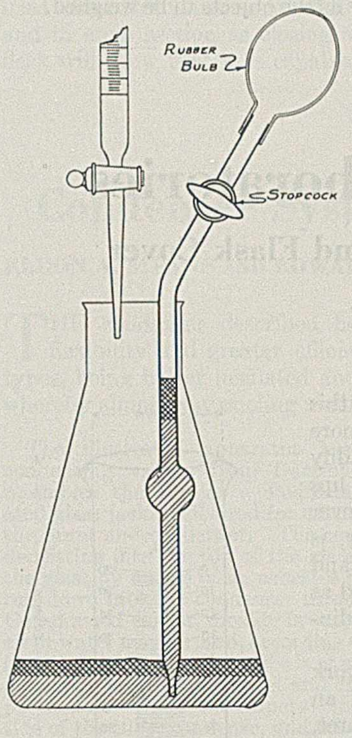
In the formation of the second nomograph (Figure 2), as there are four variables, a turning line is necessary. Its use may be illustrated by the following example:

Experimental data give a ratio g/G of 0.010, the difference in temperature between the freezing point of solvent and solution was 1.000° C., and K_f was 10.0. Draw a straight line from 10 on the K line to 0.01 on the g/G line. From the point where this line intersects the turning line, draw a straight line through the m line and the point 1.000 on the ΔT line. The value of m is then read as 100, the proper value.

RECEIVED June 19, 1935.

Pipet for Titrating Dark-Colored Liquids in Two Phases

MILDRED M. HICKS-BRUUN AND LAWRENCE W. CLAFFEY, Sun Oil Company Research Laboratory, Norwood, Pa.



IN THE petroleum and other industries it is often necessary to determine the free acidity as well as saponification numbers of dark-colored substances. As many of these substances have comparatively high melting points and are very little soluble in alcohol, in recent years it has become the practice to use a benzene-alcohol solution, both for titrations with aqueous alkali (*1*, *4*), and as a saponification medium with caustic potash and subsequent titration with aqueous acid (*5*). In either case the addition of an aqueous solution to the benzene-alcohol mixture precipitates a second layer; the dark-colored substance remains in the upper phase (the benzene-alcohol layer), while the acidic constituents and excess alkali remain in the aqueous alcoholic layer. Coburn (*4*) has pointed out that sodium chloride may be added to render the two-phase separation sharper.

Methods in which the benzene-alcohol solution is used are often helpful in the determination of the end point, and moreover a top benzene layer serves to protect caustic alkali solutions from atmospheric carbon dioxide during titration. However, the top layer is often dense and black and refuses to remain intact during the necessary swirling of the flask in titration. Furthermore, after the two layers are broken it not only requires several minutes for them to separate again, but also it is difficult to determine the exact end point of a yellowish or reddish solution beneath a heavy black layer.

To meet this need a pipet was devised in this laboratory which materially aided the operator's ability to determine the end point. The pipet was made a convenient length to remain in the titration flask throughout the titration, and may be of clear glass or with a white background. From time to time, the stopcock was opened and a convenient depth of the liquid was sucked into its stem by means of the rubber bulb, after which the stopcock was closed. If a portion of the benzene layer entered the pipet, it rose to the top of the liquid. The color of the indicator could then be closely observed and the liquid returned to the flask by opening the stopcock and applying pressure to the bulb. In this manner the progress of the titration could be noted until a satisfactory end point had been reached.

Although there are several titration flasks with forms of sealed-in tubes, such as those of Bezzenberger (*3*) and Baader (*2*), the pipet here described was found not only to be simpler and more effective, but also better adapted for the technic of saponification numbers. Many uncertainties in the end points of dark-colored solutions have been avoided by its use.

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RECEIVED February 12, 1936.

Errors in Microweighing Due to the Use of Lead Shot in Tares

ROGER J. WILLIAMS, Oregon State College, Corvallis, Ore.

THE Kuhlman microbalance which is most highly recommended by Pregl and his followers is provided by the manufacturer, in accordance with Pregl's recommendations, with a numbered series of small tare bottles of various sizes, and about 50 grams of fine lead shot with which to prepare tares for the different vessels in which material may be weighed.

The writer had occasion to weigh small samples of material in relatively large glass weighing bottles (weighing about 6 grams) and, although the balance seemed to be working perfectly and the temperature fluctuations were not excessive, constant values could not be obtained. In one case a weighing differed from that of the previous day by nearly 50γ.

The cause of the excessive variations was traced to the use of the lead shot which had been provided. As soon as the lead was discarded and broken glass substituted for it in the tares, the difficulty promptly disppeared and weighings became constant.

Calculations show that if 5 grams (0.37 cc.) of lead are used to balance a glass vessel (this quantity is not excessive since the balances have a capacity of 20 grams), the difference in the volumes of air displaced by the lead and the glass (taking 2.7 as the specific gravity of glass) is about 1.5 cc. This air, if dry at standard pressure and 25° C., would weigh 1.78 mg. Under actual conditions, however, the weight of this excess air displaced by the glass vessel will vary 6γ per degree of temperature variation, 23γ per cm. of barometric variation, and about 21γ for the difference between dry and saturated air.

Users of microbalances have always attempted to work at as constant a temperature as possible. It is evident, however, that the errors due to temperature variation are greatly magnified by the use of lead shot. More serious is the barometric variation because changes of a centimeter or more in the barometric reading, which readily occur, may introduce a serious error if lead shot is used. The error due to humidity variation may easily be considerable under some conditions.

If one insists on using lead shot, he can record temperatures, barometric readings, and humidities and make suitable corrections, but it is vastly simpler to render all these corrections entirely unnecessary by discarding the lead shot and using tares made of the same material as the vessel to be weighed.

It is clear to the writer that manufacturers should supply somewhat larger tare bottles and glass beads (or possibly aluminum shot) to use in them. In case heavier objects are being weighed, care should be taken to have the vessel and the tare made of the same material, since the difference even between quartz and glass is sufficient to introduce appreciable errors in case the vessels are relatively heavy. Though the writer has had no experience in this connection, it appears that the weighing of the absorption tubes used in carbon and hydrogen determinations must be subject to especially large variations when lead shot are used in the tares, because of the relatively heavy objects weighed. The use of weights instead of tares leads to the same needless errors unless the weights have the same density as the objects to be weighed.

RECEIVED April 3, 1936.

New Apparatus for Analytical Laboratories

Crucible Support for Desiccators, Graduated Cylinder, and Flask Cover

F. E. TUTTLE
University of Kentucky, Lexington, Ky.

AS A RULE desiccators are supplied without plate or other device for support of crucibles and, on account of the inflexibility and expense of porcelain plate supports, the time and ingenuity of the user are often consumed in the fabrication of makeshift substitutes of glass, pipestem, etc.

The crucible support, Figure 1, described in this article is designed for use in the regular 15-cm. (6-inch) Scheibler desiccator and will hold six No. 0 or 00 porcelain crucibles with covers or the same number of platinum crucibles of corresponding sizes.

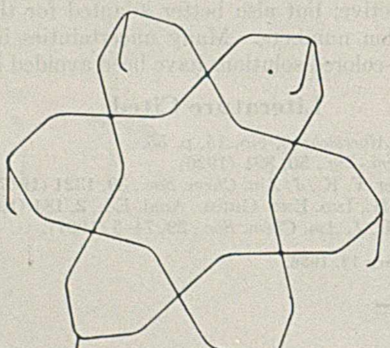


FIGURE 1

The support is made of pure nickel wire with all intersections securely brazed. Long and continuous use of the support justifies the following claims: By adjusting the legs it is readily adapted to variations in the shapes of desiccators, is held firmly in position during any legitimate use of the apparatus, holds the crucibles securely, may be deformed slightly to accommodate crucibles of different sizes, allows unrestricted circulation of air, and is kept bright with a minimum expenditure of time and the use of a little fine steel wool.

GRADUATED CYLINDER. In those chemical operations where one has occasion to measure rapidly volumes of liquid reagents, solvents, etc., there is great need of a handy measuring cylinder of moderate capacity, one that is sufficiently accurate, not easily upset, sturdy in construction, and not readily broken.

The cylinder illustrated in Figure 2 has all these characteristics and has been used in the different laboratories with great satisfaction, particularly in quantitative analytical work. Whereas the tall, narrow, 100-ml. cylinder in regular use at present is characterized by great instability, generally resulting in breakage when tipped over unless protected by some sort of shock absorber, this short, wide cylinder stands more firmly on the table, is more readily filled and emptied, has two lips for convenient pouring, has never broken when tipped over, is graduated both up and down, and allows volumes to be measured as accurately as in any other cylinder of the same diameter.

It is not recommended for work that should be done only by an accurately calibrated pipet, buret, or certified tall narrow cylinder, but when made according to the dimensions given it stands supreme as a general-purpose measuring cylinder of 100-ml. capacity.

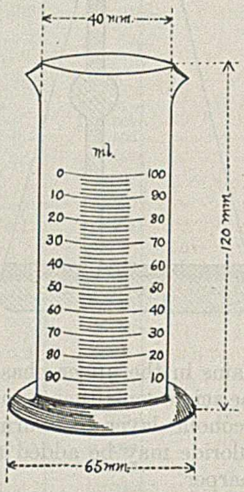


FIGURE 2

FLASK COVER. Many times, particularly when corrosive liquids are being boiled in flasks, it is desirable to resort to some device for control of spattering, evaporation, prevention of free access of air, dust, etc. In the past small funnels, inverted porcelain crucible covers, and glass bulbs have been employed for this purpose and generally with unpleasant results, because the center of gravity of the miscellaneous covers is above the rim of the vessel being covered.

The cover as illustrated (Figure 3) is designed upon a new

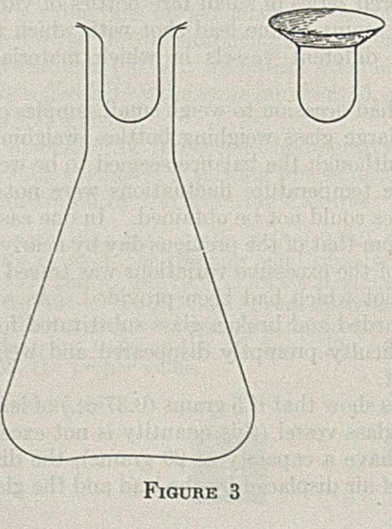


FIGURE 3

principle which places nearly its entire weight inside and below the rim of the vessel, so that it will remain securely in position even while the flask is being shaken.

Thus far three sizes of this cover have been successfully used and a careful inspection of the cut of the No. 3 size singly and in cross section as closing a 300-ml. Pyrex Erlenmeyer flask will show that it is capable of being used upon a wide range of flask sizes—e. g., No. 1 may be used to close orifices from 11 to 19 mm. diameter, No. 2 those from 16 to 29 mm., and No. 3 those from 21 to 39 mm. Other sizes may be made if desirable.

The apparatus described in this article may be secured from Eimer & Amend, New York, N. Y.

Received March 19, 1936.

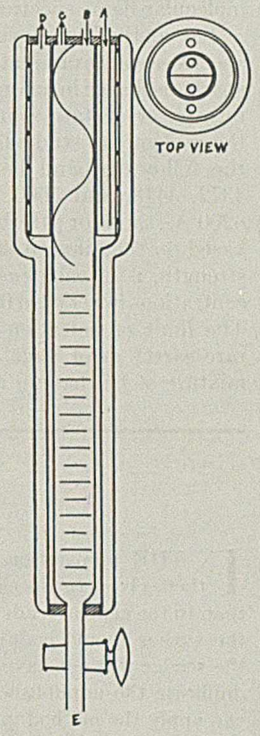
Condenser System for Fractional Distillation

ELDON A. MEANS and EDWARD L. NEWMAN, The Eldon A. Means Co., Wichita, Kans.

THE condenser described here has the advantages of flexibility and greater efficiency over the conventional types, being better insulated and providing an arrangement whereby almost any cooling medium may be used.

The illustrated apparatus has given great satisfaction in condensing vapors from fractional distillations. It greatly resembles the top of a Podbielniak column (*2*). An evacuated glass jacket, silvered for efficient heat insulation, surrounds the buret and condenser. The condenser itself is a metal cylinder fitting into the top of the glass jacket and is insulated from the glass by means of an asbestos cord. The cooling medium is run down into the condenser through tube *A* and escapes at *D*. Compressed carbon dioxide is very satisfactory, although liquid air or water may be used, according to the condensing range. The inner tube or condensing tube is of metal and contains a spiral strip extending down to the buret and dividing the tube into two compartments. Thus the vapors coming in at *B* pass down one side of the tube, condense, and fall into the buret. Displaced air must pass up the other side of the dividing strip and emerge at *C*, losing condensable vapors in transit. The metal condenser tube is connected to the glass buret by soldering to the platinized glass (*1*). This provides an air-tight seal between the metal and glass.

This apparatus is particularly useful in the distillation of gasoline. Lighter fractions and gases can be condensed by use of a low-temperature cooling medium such as carbon dioxide or liquid air. The condenser is well adapted to vacuum distillation, the vacuum connection being made at *C* and liquid extracted at *E* by any of the conventional methods for extraction of liquids during vacuum distillation.



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Received March 9, 1936.

Dithizone as a Reagent for Dissolving and Determining Spray Residue Lead

WAYNE E. WHITE, Western Reserve University, Cleveland, Ohio

THE readiness with which dithizone (diphenylthiocarbazone) reacts with minute amounts of lead even when the lead is in such insoluble compounds as the sulfate and arsenate leads to the thought that this reagent might be made to assume a dual role in the analysis of spray residues for lead. The reagent might serve as the solvent for the removal of the lead from the analyzed fruits as well as in its ordinary capacity as colorimetric reagent. Were this possibility borne out by experimental investigation, and were there no other complicating factors, we should have an analytical method superior to any of those in present use in respect to speed and simplicity (*1*, *2*).

After considerable investigation of this problem the writer desires to announce the following results and conclusions:

1. Lead is dissolved from the surface of fruits by a solution of dithizone in chloroform in the presence of an aqueous solution of potassium cyanide, ammonia, and citric acid. In order to effect a rapid and complete removal, a number of washings (two to six, depending on the amount of lead and the tenacity with which it is held) are necessary.

2. The dithizone color change due to the presence of lead occurs just as in the ordinary procedures. The contact with the organic matter of the fruit skins does not seem to affect the reagent. As in other dithizone methods of spray residue analysis, there are no probable contaminants which will interfere in the lead determination. An occasional turbidity due to undissolved, suspended matter does not appear to be particularly detrimental to a close comparison of colors.

3. The multiple washings prevent the expected economy of time and materials and may decrease the accuracy and precision of a determination. Further work may reveal a way of increasing the solvent power of the dithizone solution and thereby the most serious obstacle to the success of this direct method of spray residue analysis will be removed.

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Received December 2, 1935. A more detailed discussion of the application of this method was presented under the title "A Field Method for the Estimation of Lead as Spray Residue" before the Division of Food and Agricultural Chemistry at the 90th Meeting of the American Chemical Society, San Francisco, Calif., August 19 to 23, 1935.

Detection of Lanthanum, Yttrium, and Ytterbium from Spark in Flame Spectra

O. S. PLANTINGA AND C. J. RODDEN, Washington Square College, New York University, New York, N. Y.

THE simplified spark in flame spectra method of Hultgren (*1*), previously reported by the authors (*4*), has been applied to the detection of lanthanum, yttrium, and ytterbium in rare earth salts. Lundegårdh (*2*) detected neodymium down to $0.01\,M$ by a flame spectrum method, and Piccardi and Sberna (*3*) found limits of 0.01 per cent for lanthanum oxide and 0.001 per cent for yttrium oxide, using molecular flame spectra.

The method employed by the authors involves the visual spectroscopic examination, with a hand spectroscope, of a spark discharge in an ordinary gas flame in which the chloride, nitrate, or acetate solution of a sample is volatilized. The three elements studied were detected by the appearance of the following band heads in the spectra: for lanthanum, 4372, 4418, and 5600 Å.; for yttrium, the group 5892 to 6200 Å.; and for ytterbium, 5700 Å. The limit of detection, based on the dilution of a solution of each element of known strength, is in each case about $0.0001\,M$, although for concentrations lower than $0.001\,M$, the spectra flashed unsteadily. The limit of detection is affected by the presence of other rare earths or of large amounts of sodium. For example, a mixture of lanthanum and praseodymium chloride solutions, in which the concentration of praseodymium was $1.5\,M$, showed a limit of detection of lanthanum only one-tenth of the value of pure lanthanum. A rough estimate of the amounts of the three elements may be made by examining the spectra of successive known dilutions of the sample until the bands disappear.

The method of detection outlined is economical and rapid, about 0.1 cc. of solution being used in a test requiring about a minute. The value of the method as applied to laboratory samples of the rare earths is illustrated by the examination of a sample of c. p. erbium which was found to contain 40 per cent of yttrium. The method has been successfully applied, in a few cases, in following the fractionation of rare earths.

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RECEIVED December 17, 1935.

Note to Authors

IN THE preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental
    - Outline of proposed method
    - Description of apparatus and reagents
    - Procedure
    - Data
        - Interfering substances or conditions
        - Concentration range through which the method is applicable
        - Accuracy of the method
        - Precision of the method
3. Discussion and summary

The author should state at the outset what the original features of the paper are. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater detail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

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(Comments of a visitor to the Merck Control Laboratory)

TAKING me by the arm, my guide pointed to the door of the Merck Control Laboratory Building. "Come let us go in here," he said.

We entered the office of the Director, who greeted us cordially but who remarked with professional modesty that there really wasn't much to interest a visitor in his particular branch of the business.

"We cannot put on much of a show here," he explained, "because our work is very largely routine—and necessarily so."

"That may be true," I replied; "but won't you tell me what your routine work consists of? Certainly those hundreds of bottles and jars, glass tubes and burners, charts and other equipment suggest some interesting possibilities for scientific experimentation. And how about those chemists; what kind of work are they doing?"

"Routine work," he replied; "routine work made necessary by the standards which have been established for our products. You see, this Control Laboratory is really the policeman or guard of our organization. It is our duty to see to it that no material of any kind gets into our factory or out of it and into use unless it meets the Merck standards of purity and uniformity.

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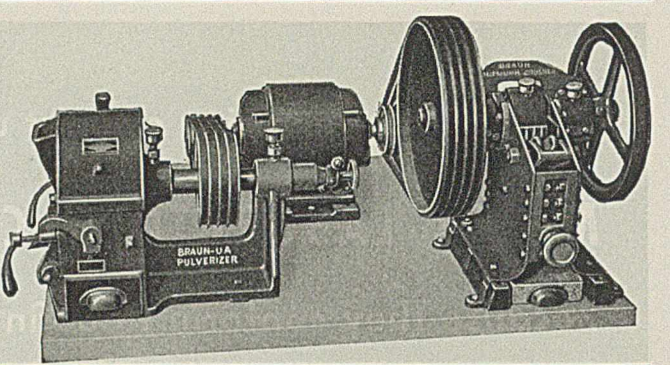
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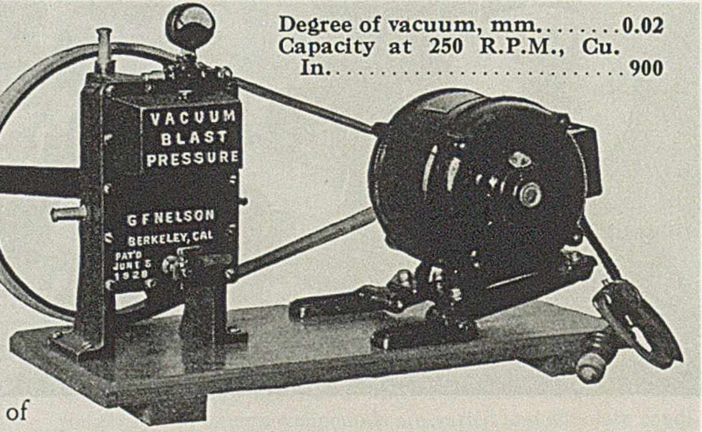
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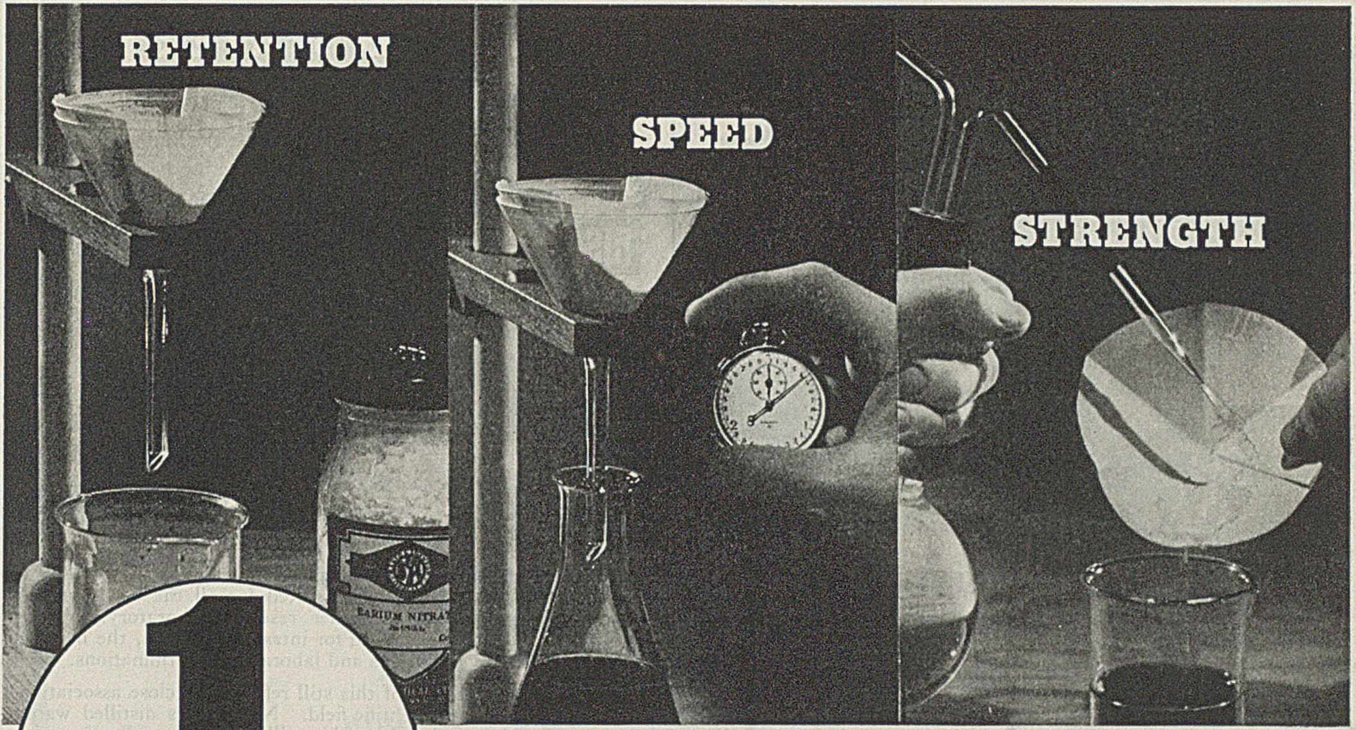
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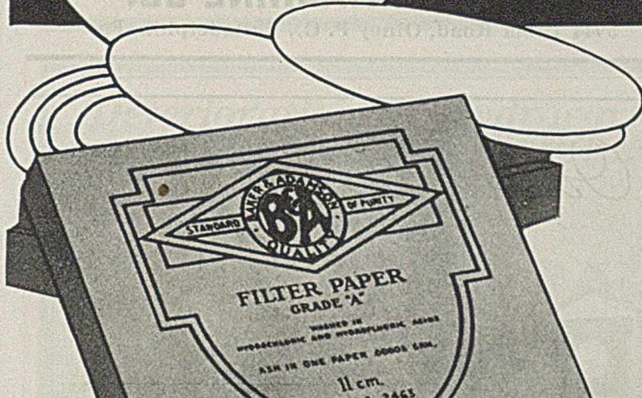
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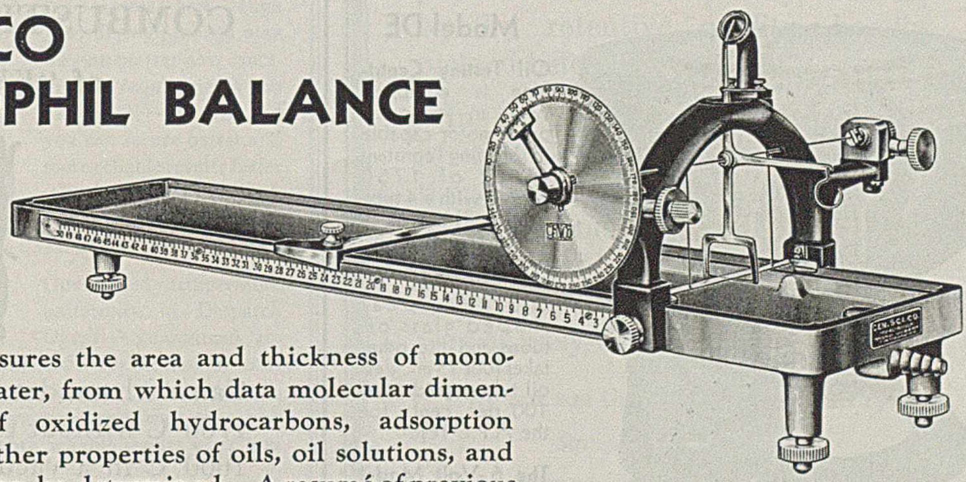
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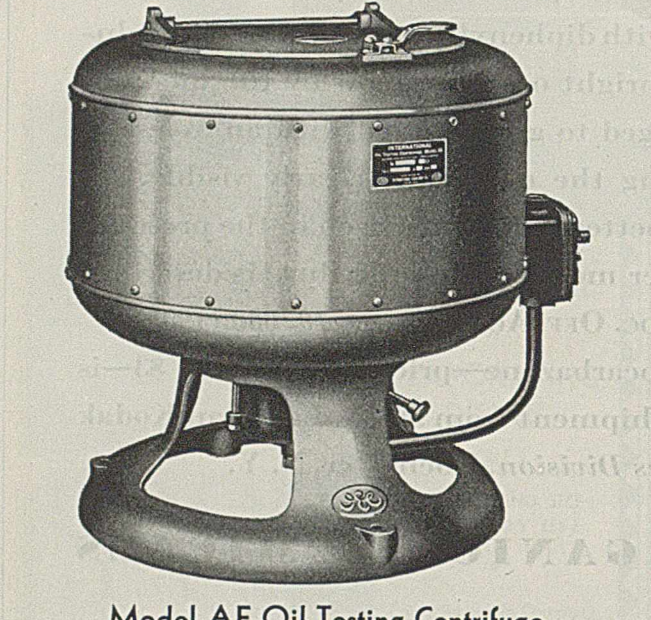

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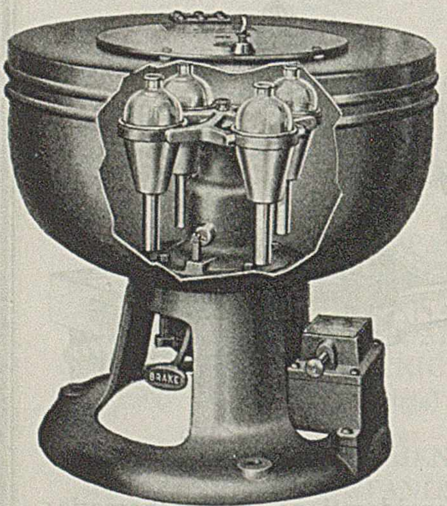

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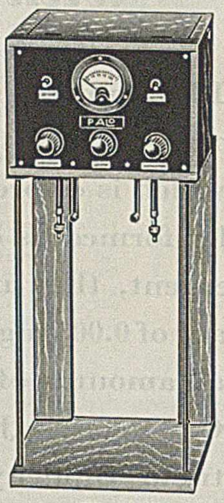

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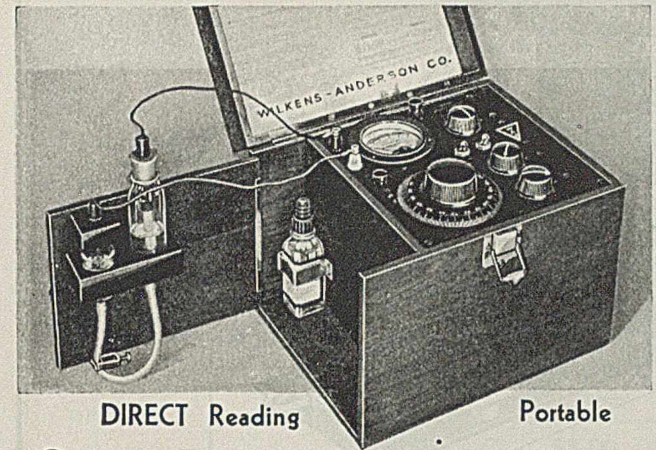

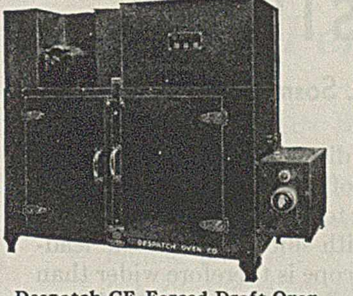


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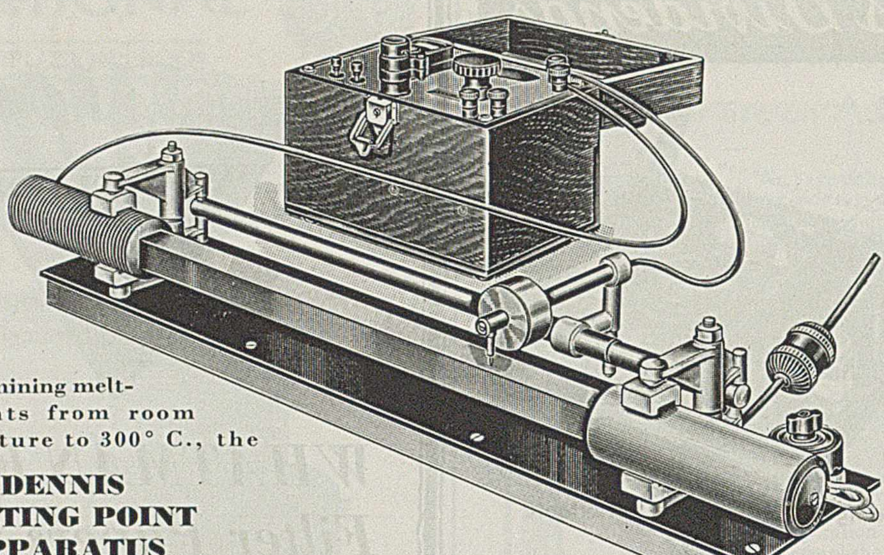

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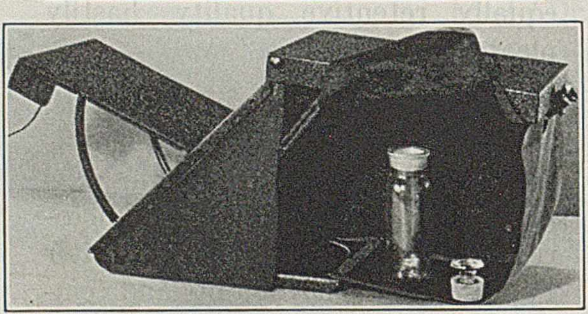

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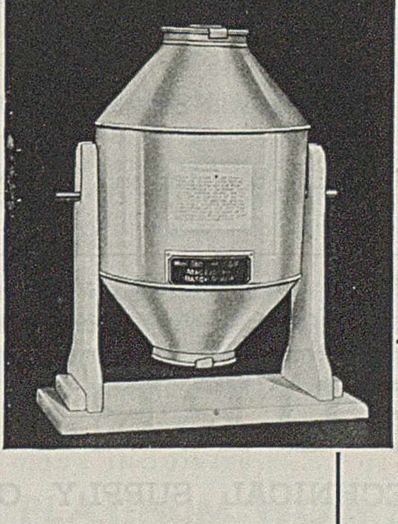

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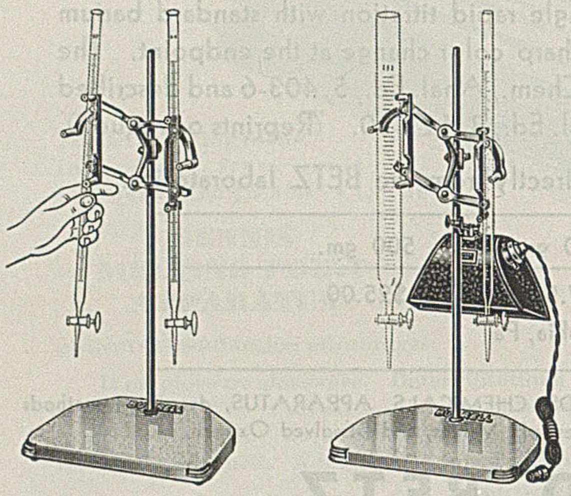

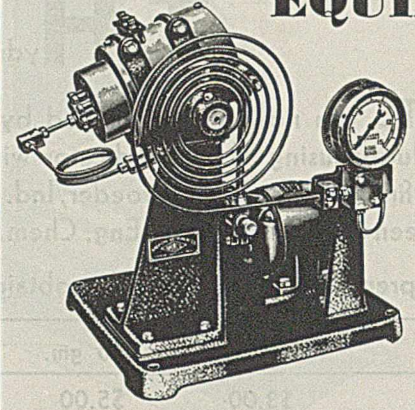

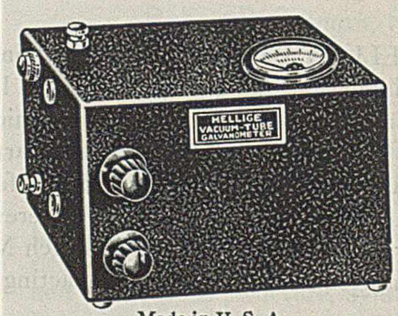
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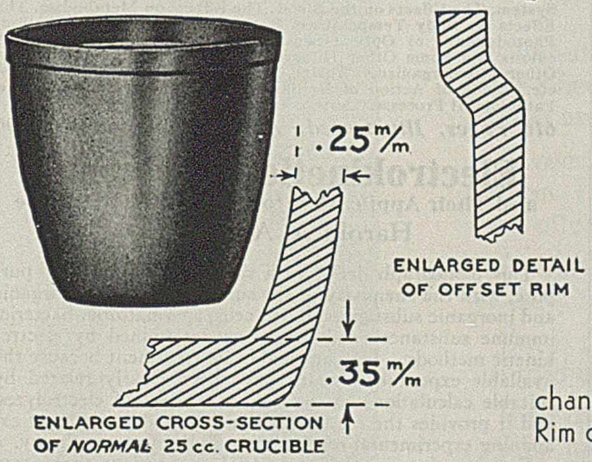

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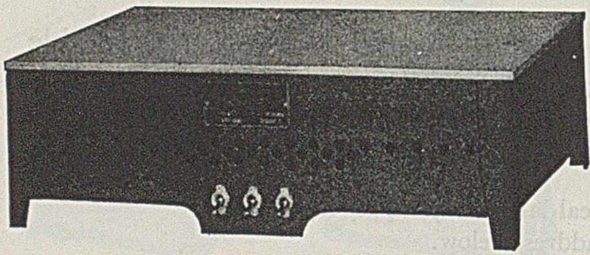

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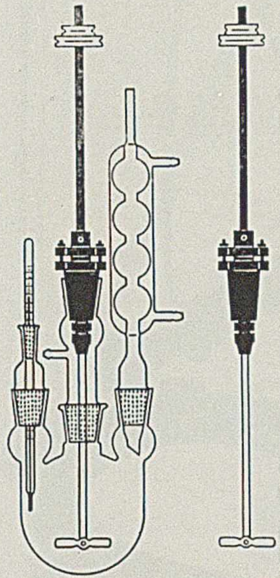

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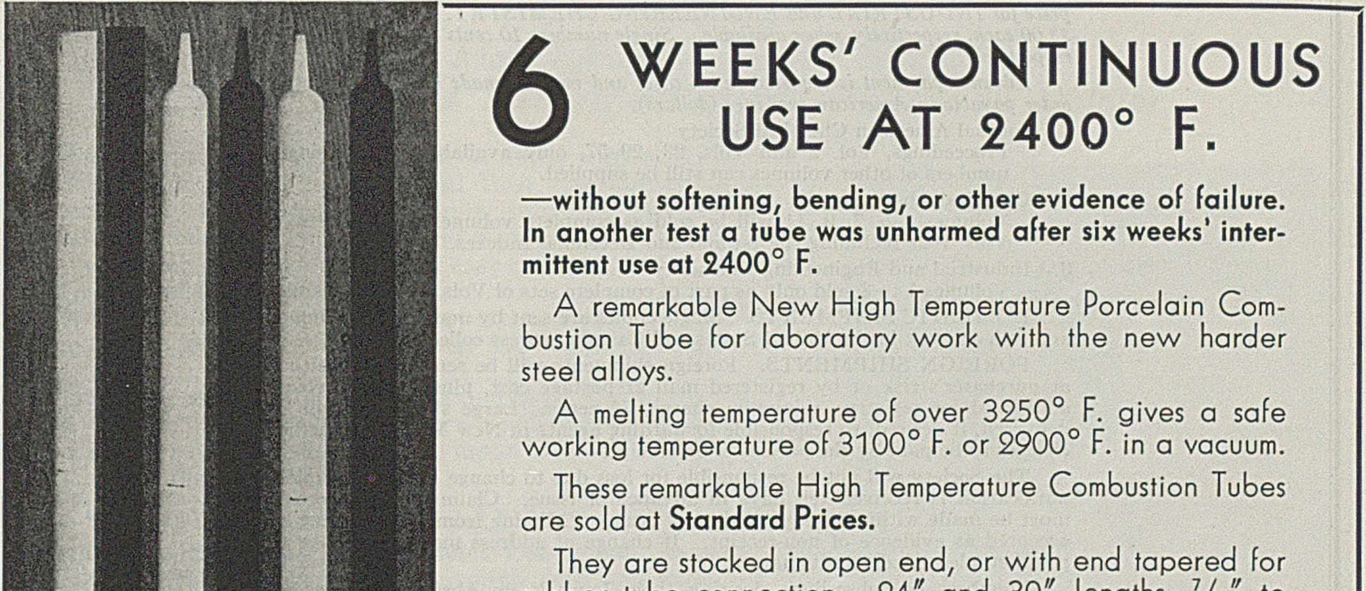

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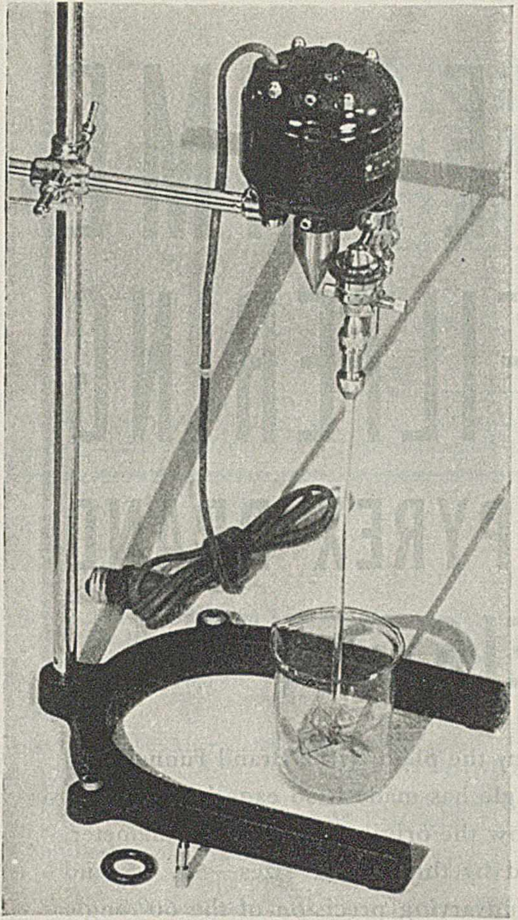

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Cone drive permits continuous adjustment of speed throughout a range of 75 to 1300 r.p.m. with the full transmission of motor power at all speeds.

Its freedom from vibration and its useful, steady and uniform range of low speeds make it particularly useful for such applications as the rotation of electrodes, calorimeter paddles, etc., where the most desirable operating speeds are below 200 r.p.m. The motor is equipped with binding posts for electrolytic analysis and with a special connecting post for the cathode which prevents scratching of the cathode wire.

The cone is of stainless steel, highly resistant to corrosion, the motor is finished in baked black enamel, and all other parts are heavily chromium plated.

9571 Cone Drive Stirring Motor, Sargent

Complete with cross support rod, one extra friction ring, chuck with two collets, connecting cord and plug.

For 110 v. 60 cycle	$30.00
For 110 v. D.C.	32.00
For 220 v. 60 cycle	31.00

Please specify voltage when ordering.

30% More Efficiency without Splash
Sargent Model LC Stirring Motor with Centrifugal Agitator

The Sargent Centrifugal Agitator supplied with model LC stirring motor is 30% more efficient than propeller types as measured by rate of solution of copper sulphate. The entire agitator is made of Monel metal, and its head is separable and only 3/4 inch in diameter, permitting easy cleaning and insertion into vessels of small neck diameter.

Distance of the motor from the support stand may be exactly adjusted by sliding the motor along the horizontal support arm.

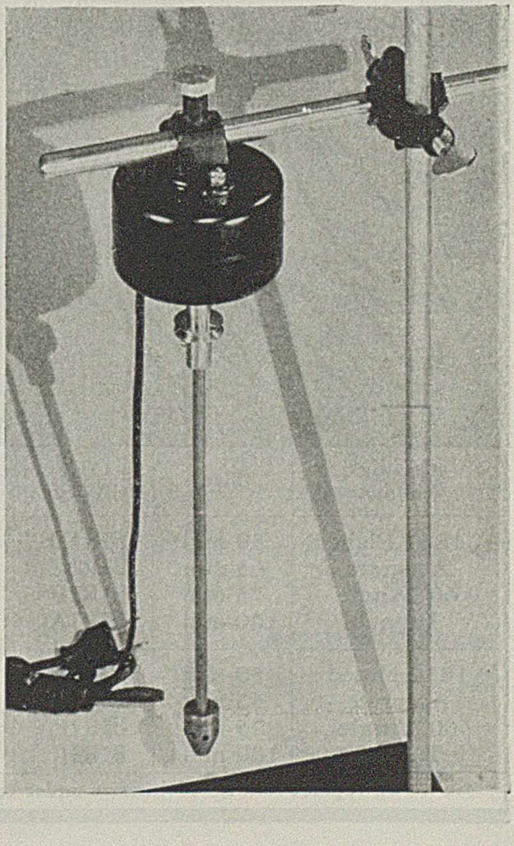
The motor is a 3000 r.p.m. induction type and so may be used with absolute safety in the presence of inflammable vapors. On and off switch is enclosed in the motor case and a pulley is attached to the motor shaft.

9581 Stirring Motor, Sargent Model LC.

Complete with Sargent Monel metal Centrifugal Agitator, switch, support arm and rubber covered cord and plug for connection to standard outlets. For 110 volt A.C., 60 cycle. **Each**..$7.50

9587A Sargent Centrifugal Agitator, Only, Monel Metal

Shaft diameter 1/4 inch. **Each**........................$2.25

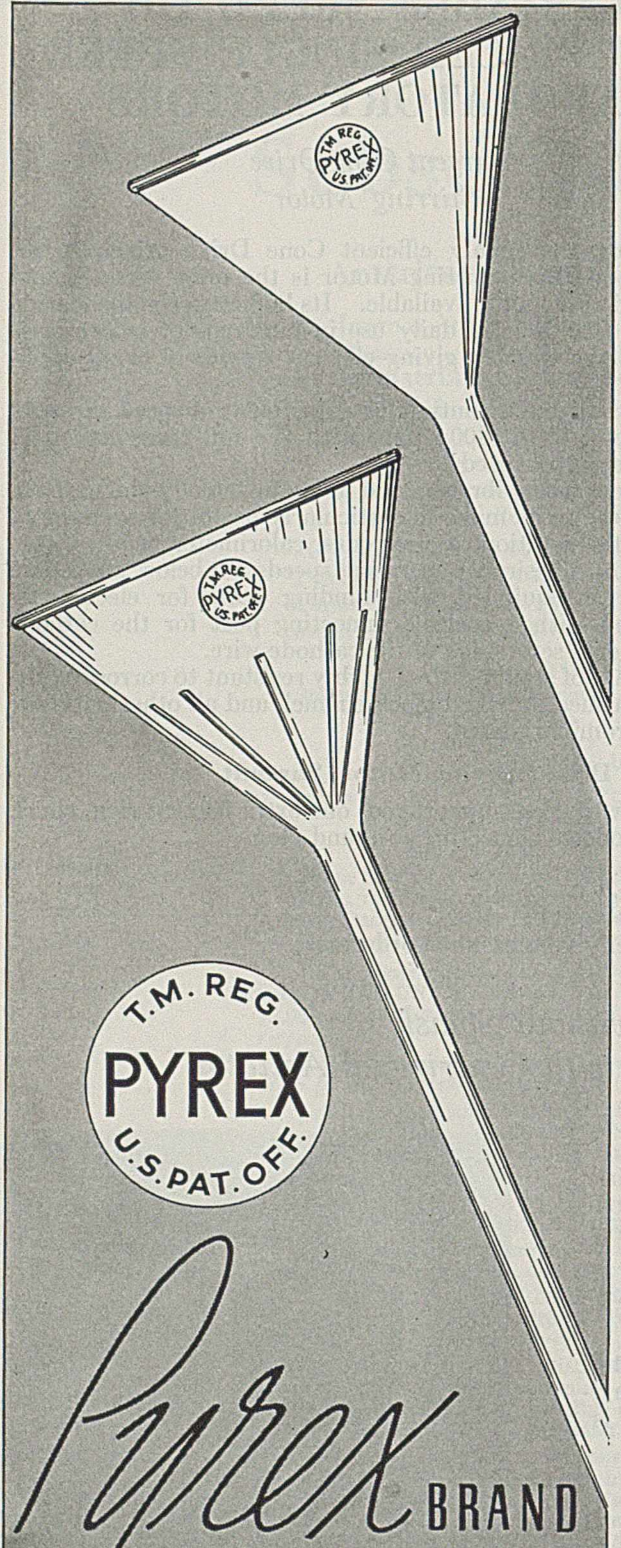


SARGENT

E.H. SARGENT & CO. CHICAGO

LABORATORY SUPPLIES

155-165 E. Superior St. Chicago, Ill.



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WITH PYREX BRAND FUNNELS . . .

TIME SAVED by the plain Pyrex Brand Funnel with accurate 60° angle has made it so eagerly sought by chemists that now the original size, 65 mm diameter, is supplemented by three other sizes—50, 75 and 100 mm. The unvarying precision of the 60° angle gives more accurate fitting of the filter paper, and reduces filtering time, as compared with an ordinary Bunsen funnel by about *one half.*

And now a further improvement! The accurate 60° angle funnel *fluted.* These flutings greatly increase the effective filtering area, (almost double), and reduce filtering time still further.

Pyrex Brand accurate 60° angle funnels may be had from your regular dealer—plain, in all four sizes; fluted, in the 65 mm size, only. The other three sizes of *fluted* funnels will be available after May 15th.

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LABORATORY WARE

Catalog Number	Size	Code Word	Quantity Per Pkg.	Net Price Each	Net Price per original pkg. in lots of 1 Pkg.	25 Pkgs.	50 Pkgs.	100 Pkgs.
1851 Plain Accurate 60° Angle Funnel	50 mm*	BIRID	72	$.32	$20.74	$19.70	$18.67	$17.63
	65 mm	BIRIC	72	.35	22.68	21.55	20.41	19.28
	75 mm*	BIRIB	60	.38	20.52	19.49	18.47	17.44
	100 mm*	BIRIA	48	.48	20.74	19.70	18.67	17.63
1852 Fluted Accurate 60° Angle Funnel	50 mm†	BIRHD	72	.35	22.68	21.55	20.41	19.28
	65 mm	BIRHA	72	.38	24.62	23.39	22.16	20.93
	75 mm†	BIRIF	60	.42	22.68	21.55	20.41	19.28
	100 mm†	BIRII	48	.53	22.90	21.76	20.61	19.47

*To replace funnels of this size under catalog No. 1850. †Available after May 15th.