assay is the better for telluride ores, and that the loss of gold in the assay is very great if the charge is not properly made up as regards the amount of litharge present. He does not locate the loss or make corrected assays.

In the discussion of Mr. Smith's paper, Mr. Wm. P. Jenney states that he believes an oxidizing charge with a small quantity of ore would be beneficial. The excess of litharge, of course, has an oxidizing action, but to try this point further the assays in Table IV were made by the following charge :

Ore, one-fifth assay ton.
Litharge, four assay ton.
Soda, one and a half assay tons.
Silica, one assay ton.
Six loops of wire.
Twenty grams of niter.

The wire acted as the reducing agent with the sulphur. The buttons were good and malleable, but on cupellation gave no better results than charges with litharge alone.

ON THE LINDO-GLADDING METHOD OF DETERMINING POTASH.

By A. L. Winton[1] and H. J. Wheeler.[2]

Received June 15. 1898.

In view of certain criticisms of the Lindo-Gladding method of potash determination which have appeared of late, notably those by Vogel and Haefcke,[3] we were appointed a committee by the Association of Official Agricultural Chemists of the United States to prepare an article setting forth certain work bearing upon the points involved.

At the regular meeting of the Association in Washington in 1890, Frear and Sweetser[4] called attention to certain comparative determinations made by them, which indicated that the use of sodium chloride was unnecessary. The mean difference in

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[1] Chemist Conn. Agricultural Experiment Station and Reporter on methods of potash determination for the Association of Official Agricultural Chemists for the years 1896 and 1897.

[2] Chemist R. I. Agricultural Experiment Station and Reporter on methods of potash determination for the Association of Official Agricultural Chemists for the years 1894 and 1895.

[3] Die landw. Versuch-Stationen 47 (1896), pp. 112-117.

[4] U. S. Dept. of Agr., Div. of Chem., Bull. 28 (1890), p. 73.

the results with and without sodium chloride amounted to but 0.04 per cent., and in but two cases out of fifty was the difference over 0.10 per cent. In 1891, Winton[1] investigated the matter thoroughly and in tests conducted with commercial potash salts and twenty-four mixed fertilizers, showed that the results with and without the addition of sodium chloride were practically identical.[2] The same line of study was further pursued in 1892 by Payne,[3] in cooperation with twenty-two chemists in seventeen different laboratories, working with a variety of substances. As a result of these investigations by the Association the use of sodium chloride was discontinued.[4] This was done not because inaccurate results were obtained by its use, but in order to abbreviate the method by striking out a cumbersome and useless detail.

Notwithstanding the fact that it had already been abundantly shown that there was practically no difference in the results obtained with and without the use of sodium chloride, Breyer and Schweitzer[5] asserted that its use was a source of error Their claim that it was unnecessary was merely a reiteration of what had already been shown by the work of the Association.

Aside from the undesirability of employing sodium chloride the only unfavorable criticism of the Lindo-Gladding method worthy of note, which has appeared, is based upon the assumption that a considerable error is introduced through double decomposition resulting from contact of the ammonium chloride wash solution with potassium platinichloride. Breyer and Schweitzer[6] and N. Robinson[7] mention errors thus arising and the two former chemists claim that the amount of the same is considerable. Their conclusions in this respect are based chiefly upon the amount of potassium chloride said to have been recovered from the ammonium chloride wash solution which had already been employed in washing precipitates of potassium platinichloride. It does not appear, however, that blank determinations were made for the purpose of ascertaining the amount

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[1] U. S. Dept. of Agr., Div. of Chem., Bull. 31 (1891), pp. 148–150.

[2] Compare Fresenius' *Ztschr. anal. chem.*, 16, 63.

[3] U. S. Dept. of Agr., Div. of Chem., Bull. 35 (1892), pp. 58–61.

[4] U. S. Dept. of Agr., Div. of Chem., Bull. 35 (1892), pp. 197, 198.

[5] *J. Anal. Appl. Chem.*, 6, (*1892*), 477.

[6] *J. Anal. Appl. Chem.*, 6, (*1892*), 474–477.

[7] This Journal, 16, (*1894*), pp. 366, 367.

of potash, if any, contained in the ammonium carbonate, ammonium oxalate, and in the seven grams of barium hydroxide and other reagents employed in the recovery of the potash. In view of the fact that considerable amounts of potash are frequently present in certain so-called chemically pure reagents employed in potash determinations,[1] it would appear that a large part of the potash, said by Breyer and Schweitzer to have been recovered from the wash solution, may have been derived from their reagents. It is obvious, therefore, that their results instead of serving as a proper basis for the criticism of a method, are themselves open to serious criticism.

The ammonium chloride wash solution experimented with by Breyer and Schweitzer was the same as that employed by the Association, the preparation of which is described in a succeeding foot-note. That a great amount of double decomposition may result with this solution, under exaggerated conditions, has been shown by the work of the Association[2] during 1894 and 1895. This fact alone furnishes no suitable basis for the condemnation of the method, provided the amount of error arising in the ordinary course of analysis is practically insignificant.

During the years 1894[3] and 1895[4] one of us (H. J. W.) conducted comparative determinations to learn whether washing with ammonium chloride solution, according to the Lindo-Gladding method, introduced an appreciable error. The analytical work was carried out with the cooperation of analysts of the Association of Official Agricultural Chemists of the United States, nine taking part during the first year and ten during the second year, no two of them working in the same laboratory or with the same reagents.

In 1894 portions of four grams each of pure potassium chloride were made up to one liter with water and twenty-five cc. of this solution, representing one-tenth gram of the salt, were taken for each determination. As the salt contained a small amount of water, which, in the portions sent to the different analysts, varied from 0.06 to 0.16 per cent., the results have in

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[1] U. S. Dept. of Agr., Div. of Chem., Bull, 43 (1894), pp. 21, 22; also Bull. 47 (1895), pp. 16, 17; and Bull. 49 (1896), pp. 30-32.

[2] U. S. Dept. of Agr., Div. of Chem., Bull. 43 (1894), pp. 23, 24; and Bull. 47 (1895), p. 22.

[3] U. S. Dept. of Agr., Div. of Chem., Bull. 43, pp. 17-25.

[4] U. S. Dept. of Agr., Div. of Chem., Bull. 47, pp. 14-23.

each case been calculated to correspond with one-tenth gram of the dry material (see Table I).

TABLE I.

COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD OF WASHING WITH ALCOHOL ONLY (1894). ONE-TENTH OF A GRAM OF POTASSIUM CHLORIDE TAKEN IN EACH DETERMINATION.

Analyst.	Potassium platinichloride washed with alcohol only. Potassium chloride found. Gram.	Potassium platinichloride washed with alcohol and ammonium chloride solution, (Lindo-Gladding method). Potassium chloride found. Gram.	Results by washing with ammonium chloride are more (+) or less (—) than those without. Gram.
W. A. Powers, Illinois Station	0.10053	0.10134	
	0.10114	0.10159	
Average	0.10084	0.10147	+0.00063
F. P. Veitch, Maryland College	0.09867	0.09864	—0,00003
J. B. Lindsey, Massachusetts Station.	0,10112	0.10082	
	0.10066	0.10097	
	0,10066	0.10060	
		0.10005	
Average	0.10082	0.10061	—0,00021
W. L. Rossman, Michigan Station	0.09957	0.09974	
	0.09951	0.09956	
	0.09957	0.09971	
	0.09933	0.09965	
Average	0.09950	0.09967	+0.00017
J. P. Street, New Jersey Station	0.09838	0.09807	
	0.09868	0.09838	
	0.09871		
Average	0.09859	0.09823	—0.00036
B. L. Hartwell, Rhode Island Station	0.09960	0.09898	
	0.09954	0.09913	
		0.09934	
Average	0.09957	0.09915	—0.00042
K. P. McElroy, U. S. Dept. of Agr	0.10000	0.10015	
	0.10012	0.10040	
Average	0.10006	0.10028	+0.00022
R. de Roode, West Virginia Station	0.09996	0.09993	—0.00003

The determinations carried out in 1895 were made on solutions of fifty cc. each, containing from three-tenths to one gram of pure potassium chloride, thus exposing to the action of the ammonium chloride solution three to ten times as much potassium platinichloride as in the preceding year.

The salt used was from a new lot containing uniformly 0.45 per cent. of moisture; the weights of potassium chloride taken, as given in Table II, represent, however, the dry salt.

In the determinations of both years, each solution of the pure salt was evaporated to a paste with an excess of platinum solution. The residue, after cooling, was stirred for twenty minutes with thirty cc. of eighty per cent. alcohol (sp. gr. 0.8645) and the liquid decanted on a weighed Gooch crucible. The washing was further continued by decantation, using ten cc. portions of alcohol and stirring for from two to three minutes after each addition.

In some cases the salt, without further washing, was dried at 100° C. and weighed; in others it was first washed with six portions of ammonium chloride solution[1] of ten cc. each and finally with eighty per cent. alcohol, according to the Lindo-Gladding method.

Blank determinations were made by both methods on the reagents. From the analytical data secured in these determinations, which were given in full in *loc. cit.*, Tables I and II have been prepared.

In calculating the results the total weight of potassium platinichloride obtained in each determination was first corrected by deducting the average weight obtained by the same analyst from the reagents.

For the conversion of potassium platinichloride to potassium chloride the factor 0.3069[2] was employed for reasons stated later.

A careful study of the results given in the tables will make it evident that the potassium platinichloride was very slightly, if at all, acted upon by the ammonium chloride solution. Finkener[3] found that a saturated solution of ammonium chloride at 22° C., when in contact with finely divided potassium platini-

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[1] A solution of 100 grams of ammonium chloride in 500 cc. of water, which had been shaken for from six to eight hours with five to ten grams of pulverized potassium platinichloride, allowed to settle over night, and filtered.

[2] Platinum 195.0, potassium 39.11, chlorine 35.45.

[3] Pogg. *Ann.*, 129, 627.

TABLE II.

COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD OF WASHING WITH ALCOHOL ONLY (1895).

Analyst.	Potassium platinichloride washed with alcohol only.			Potassium platinichloride washed with alcohol and ammonium chloride solution (Lindo-Gladding method).		
	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
W. A. Powers, Illinois Station				0.3976	0.3954	—0.0022
				0.3872	0.3871	—0.0001
B. L. Hartwell, Rhode Island Station[1]	0.4776	0.4780	+0.0004	0.4534	0.4532	—0.0002
	0.4458	0.4463	+0.0005	0.4799	0.4797	—0.0002
	0.4665	0.4668	+0.0003			
	0.5437	0.5442	+0.0005			
G. Wm. Gray, West Virginia Station	0.5114	0.5110	—0.0004	0.5028	0.5002	—0.0026
				0.5080	0.5049	—0.0031
F. P. Veitch, Maryland College	0.5004	0.5002	—0.0002	0.5043	0.5058	+0.0015
	0.5666	0.5685	+0.0019	0.5149	0.5163	+0.0014
	0.5005	0.5027	+0.0022			
W. H. Allen, North Carolina Station				0.2987	0.2989	+0.0002
				0.2987	0.2988	+0.0001
				0.2987	0.2985	—0.0002

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[1] These results have been corrected for an error in the original table.

TABLE II.—(*Continued*).

COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD OF WASHING WITH ALCOHOL ONLY (1895).

Analyst.	Potassium platinichloride washed with alcohol only.			Potassium platinichloride washed with alcohol and ammonium chloride solution (Lindo-Gladding method).		
	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
J. B. Lindsey, Massachusetts Station...	0.4978	0.4987	+0.0009	0.4978	0.4985	+0.0007
	0.4978	0.4986	+0.0008	0.4978	0.4979	+0.0001
W. G. Brown, U. S. Dept. of Agr.......	0.6479	0.6506	+0.0027	0.5550	0.5559	+0.0009
	0.5731	0.5749	+0.0018	0.5557	0.5560	+0.0003
	0.4796	0.4798	+0.0002			
J. P. Street, New Jersey Station	0.4978	0.4981	+0.0003	0.4978	0.4996	+0.0018
	0.4978	0.4977	—0.0001	0.4978	0.4993	+0.0015
				0.4978	0.4985	+0.0007
E. P. Stone, New Hampshire Station ..	0.5022	0.5043	+0.0021	0.5022	0.5043	+0.0021
	0.5883	0.5902	+0.0019	0.5883	0.5902	+0.0019
A. L. Winton, Connecticut Station.....	0.4500	0.4508	+0.0008	0.5011	0.5010	—0.0001
	0.5004	0.5013	+0.0009			
	0.5331	0.5338	+0.0007			
	0.5310	0.5313	+0.0003			

chloride for one hour, decomposed but 0.27 per cent. of the latter. Since the Lindo-Gladding method, at least as applied to the potash salts, secures the double salt in a granular condition, which according to Finkener is not so rapidly acted on, and since operating with a Gooch crucible the ammonium chloride solution is not in contact with the double salt longer than two or three minutes, errors from this source would not be expected to be and, as numerous results show, are not appreciable. There are few if any analytical methods where the precipitate is absolutely insoluble in the wash liquid and it is absurd to discriminate against the Lindo-Gladding method for theoretical reasons which have no practical significance.

Breyer and Schweitzer state that it is very "doubtful whether the method of Lindo-Gladding is a simplification of Fresenius' method." At all events, it should be stated that the members of the Association after having given both methods an extended trial find the latter decidedly shorter.

Breyer and Schweitzer state that potassium platinichloride obtained by them by the Lindo-Gladding method contained impurities, notably magnesium and calcium sulphates, but as they give no figures it is to be assumed that the amounts present were not determinable.

If the potash exists as chloride, and chlorides of sodium, magnesium and calcium are the only soluble impurities, evaporation with platinum solution and washing with alcohol should yield pure potassium platinichloride, the salts of chloroplatinic acid with the other bases being readily soluble in alcohol. Were this not true neither the Lindo-Gladding nor the Stassfurt method would be practicable.

If, however, the bases mentioned are combined wholly or in part with sulphuric acid, the potassium platinichloride, obtained by the Lindo-Gladding method, is usually, after the first washing with alcohol, contaminated with magnesium and calcium sulphates, subsequent washing with ammonium chloride solution being depended upon to remove these impurities.

Magnesium sulphate is readily soluble in the ammonium chloride solution. Even when a very considerable amount is present, the first addition of the reagent removes almost instantly the greater part of it. Calcium sulphate does not dissolve so readily but it is contained only in small amount in the potash manure salts on sale in the United States and the treatment with ammonium chloride solution effectually removes both this salt and the magnesium sulphate.

That this is true is shown by the figures obtained by one of us (A. L. W.) which are given in Table III. The results calculated from the weights of potassium platinichloride (together with many others equally accurate obtained by seven American chemists) were reported to the Association of Official Agricultural Chemists in 1896,[1] but those calculated from the weights of metallic platinum are here given for the first time.

The materials used were chemically pure potassium sulphate, which had been ignited until all water was removed, and three mixtures representing the water-soluble impurities contained in "sulphate of potash (ninety per cent.)," "sulphate of potash and magnesia," and "kainit." The solutions for analysis, representing half gram portions of the commercial potash salts named, were prepared by mixing weighed portions of the pure salt with the corresponding amounts of the mixtures of impurities, dissolved in each case in twenty-five cc. of water. The determinations of potash in these solutions presented the same analytical difficulties as would have been encountered in the analysis of the real commercial salts, but the exact amount of potash present was in each case known and the results obtained could be compared with theory.[2]

The Lindo-Gladding method of the Association[3] was strictly followed except in the case of kainit solution, which was evaporated directly with platinum solution, without previous separation of lime, as was originally directed by Gladding.[4] The potassium platinichloride was weighed on Gooch crucibles, reduced in hydrogen, washed with hot water, ignited, and finally

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[1] U. S. Dept. of Agr., Div. of Chem., Bull. 49, pp. 27-38.

[2] At the present time only four Stassfurt products are used in any considerable amount for agricultural purposes in the United States; viz., "ninety per cent. sulphate of potash," or "high grade sulphate of potash," "sulphate of potash and magnesia," or "low grade sulphate of potash," "kainit," and "eighty per cent. muriate of potash." Each of these is reasonably uniform in composition, containing, in addition to the potash salts, a certain proportion of chlorides and sulphates of soda, magnesia, and lime. In making the mixtures above described, the average composition of the commercial salts, as published by the German Kali Works, was followed.

[3] U. S. Dept. of Agr., Div. of Chem., Bull. 46, p. 23.

[4] U. S. Dept. of Agr., Div. of Chem., Bull. 7, p. 41.

weighed as metallic platinum, all of which was accomplished without transfer.

The small amounts of potash in the "impurities" were determined by careful analysis and calculated as potassium sulphate.

The conversion factors employed were: K_2PtCl_6 to K_2SO_4, 0.3587; and Pt to K_2SO_4, 0.8937. These were derived from the following atomic weights: Pt = 195.0, K = 39.11, Cl = 35.45, S = 32.06, O = 16.0.

The factors which have been commonly used in potash determinations (0.3056 for converting K_2PtCl_6 to KCl, 0.3570 to K_2SO_4 and 0.19308 to K_2O) are those based on an atomic weight of platinum long since abandoned. Fresenius[1] found in some determinations made on pure potassium chloride, shortly after the now accepted atomic weight of platinum was determined by Seubert[2] that the factor 0.3056 gave results nearer theory than the factor derived from the later atomic weights. But it has been shown by one of us (A. L. W.)[3] that when platinum solution is added to a concentrated solution of the potash salt, as was done by Fresenius, much of the potassium platinichloride separates out at once as a finely divided precipitate, which, examined under the microscope, may be seen to consist of radiating crystals, enclosing numerous globular cavities containing liquid. Part of the enclosed liquid is slowly driven off at 100°, more at 130°, and more still at 160° C. As Fresenius dried at 130°, the water was presumably only partially removed and for this reason the lower factor gave the best results.

Winton has further shown, however, that when the solution of the potash salt is so dilute that the addition of the platinum solution either forms no immediate precipitate or one that dissolves on heating, the potassium platinichloride deposits slowly, on evaporation, in the form of coarsely granular crystals which appear under the microscope to be almost entirely free from enclosed liquid and which dry as completely on heating three hours at 100°, as when heated for many hours at 130° and 160° C. When the salt is obtained by this latter method, as was the case in all the determinations of Tables I, II, and III, the factors

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[1] *Ztschr. anal. Chem.*, **21**, 238.

[2] *Ann. Chem.* (Liebig), **207**, 1.

[3] This Journal, **17**, 453.

based on the latest atomic weights give satisfactory results. The fact that the results (given in Table III) obtained by the Lindo-Gladding method and calculated by the revised factor, agree closely with those calculated from the weight of the platinum and with theory, is of itself a strong indication of the purity of the potassium platinichloride and the perfection of the process. It is only in the case of methods which yield an impure double salt that it is necessary to resort to the unscientific procedure of retaining incorrect factors in order to compensate for errors of the method.

Vogel and Haefcke,[1] as their first point against the Lindo-Gladding method, claim that the addition of sodium chloride is unnecessary and is liable to prove a source of error. This intended criticism was made in 1896, five years after the matter was first considered by the Association and three years after the Association had ceased to employ it, a fact which they might have ascertained had they consulted the published records of the proceedings of the Association.

Again, Vogel and Haefcke, after calling attention to the well-known fact of the double decomposition which results when potassium platinichloride is acted upon by ammonium chloride, further add that proof is lacking to show that the ammonium chloride, even after having been brought in contact with potassium platinichloride, is not capable of effecting still further double decomposition. Assuming that such further action results to a degree which practically interferes with the accuracy of the method, they find therein another point against it. In fact two years before this theoretical criticism was published, the Association had shown that the wash solution was capable, under greatly exaggerated conditions of treatment, of further effecting a considerable amount of double decomposition; but at the same time, as has already been shown, it was proved that in actual analytical work the amount of error thus introduced was practically so small as to furnish no valid objection to the method. Vogel and Haefcke could have learned these facts also before their criticisms appeared, had they consulted the published records of the association whose official methods they were discussing. It must be conceded that upon theoretical

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[1] Die landw. Versuchs-Stationen, 47, (1896), pp. 115-116.

TABLE III.

RESULTS BY THE LINDO-GLADDING METHOD ON MIXTURES REPRESENTING "SULPHATE OF POTASH NINETY PER CENT.," "SULPHATE OF POTASH AND MAGNESIA," AND "KAINIT."

Taken impurities corresponding to 0.5 gram of	Potassium sulphate, pure salt, taken.	Potassium sulphate, in impurities, taken.	Potassium sulphate, total taken.	Potassium platinichloride found.	Platinum found.	Results calculated from weight potassium platinichloride.		Results calculated from weight platinum.	
						Potassium sulphate found.	Potassium sulphate, error.	Potassium sulphate found.	Potassium sulphate, error.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
"Sulphate of potash 90 per cent."	0.4042	0.0002	0.4044	1.1248	0.4523	0.4035	—0.0009	0.4042	—0.0002
	0.4121	0.0002	0.4123	1.1483	0.4615	0.4119	—0.0004	0.4124	+0.0001
	0.4110	0.0002	0.4112	1.1448	0.4591	0.4106	—0.0006	0.4103	—0.0009
"Sulphate of potash and magnesia"	0.3040	0.0003	0.3043	0.8470	0.3408	0.3038	—0.0005	0.3046	+0.0003
	0.2686	0.0003	0.2689	0.7490	0.3017	0.2687	—0.0002	0.2696	+0.0007
	0.2566	0.0003	0.2569	0.7136	0.2866	0.2560	—0.0009	0.2561	—0.0008
"Kainit"	0.1387	0.0005	0.1392	0.3860	0.1547	0.1385	—0.0007	0.1383	—0.0009
	0.1727	0.0005	0.1732	0.4807	0.1922	0.1724	—0.0008	0.1718	—0.0014

grounds only, many valuable and reliable methods of analysis would have to be discarded if the solvent action of the wash liquids, regardless of the degree of solubility, were the sole basis for such a procedure.

The variation in the time employed in washing the potassium platinichloride due to unequal rapidity of filtration and the size of the crystals to be washed, are also urged by Vogel and Haefcke as logical objections to the method. However, by the use of the Gooch crucible and by precipitating the potassium platinichloride from dilute solutions by which large crystals are obtained, it must be obvious and in fact it has been shown by abundant analytical data, that these objections hold only from a theoretical, and not from a practical, standpoint.

Vogel and Haefcke still further assert, based upon assumption or upon the previously mentioned statements of Breyer and Schweitzer, that the potassium platinichloride obtained by the Lindo-Gladding method contains many impurities and therefore that it is not advisable to weigh the double salt as such. However, as has been shown by the results in Table III, the potassium platinichloride obtained by the Lindo-Gladding method even in the presence of such impurities as are in commercial ninety per cent. sulphate of potash and sulphate of potash and magnesia, as well as in kainit, is practically pure and the results accord as closely as could be desired with those obtained by reduction and weighing the metallic platinum.

From what has been said above it will be seen that Vogel and Haefcke were not well informed as to the work of the Association nor in relation to the status of the method in vogue when their unfavorable criticisms were made ; furthermore, they present no analytical data of their own in support of their assumptions and in the main the points which they sought to make were but a reiteration of the previous unfavorable criticisms of Breyer and Schweitzer, which have been shown by abundant data to have been, so far as practical considerations go, utterly unfounded.