

experiments with it were at first apparently successful as a weighting and solidifying tan, some constituent appeared to accumulate in the liquors which led ultimately to the production of brittle or tender leather. Whether this was due to mismanagement, the writers cannot at the moment say, but so far as they are aware, but little of the extract has been sold to tanners under its own name. It is, however, obviously a tempting material for the extract manufacturer, as considerable quantities can be added to tanning extracts without altering their appearance, and it shows a good percentage of tanning strength by the ordinary method of analysis. It is therefore important in the interests of the tanner that means should be discovered for the detection, and if possible, the estimation of pinewood extract in mixture, and a good deal of time has been devoted by the writers to the attempt to discover a satisfactory qualitative colour reaction, and it has been found that the following modification of the ordinary test for lignine with aniline and hydrochloric acid is very delicate and quite satisfactory.

To 5 c.c. of the extract solution, which should be of about the ordinary strength employed for analysis, 0.5 c.c. of aniline is added, and the whole is well shaken, and 2 c.c. of concentrated hydrochloric acid is then added to the mixture. With all ordinary extracts this has the effect of immediately clearing the turbidity caused by the aniline, and a perfectly transparent solution results, but where pinewood extract is present, even in comparatively small quantity, a precipitate is rapidly produced which gradually rises to the top of the liquid. Heating is not necessary, and on the whole not desirable, though it sometimes increases the rapidity of the separation of precipitate. The reaction, however, is immediate, and any slight turbidity which arises after considerable standing should be disregarded, as it sometimes occurs in the case of unmixed extracts, possibly from minute traces of ligneous matter. It is possible that this method may be developed into a quantitative form, but this has not yet been attempted by the authors.

It was also found that the "tanning substance" of the pinewood, while it was estimated as tannin by the ordinary hide-powder process, was only to a very small extent capable of reducing permanganate in the Löwenthal method, and therefore gave almost negative results in tannin, a pinewood extract showing about 25 per cent. of matters absorbed by hide being only equivalent by the Löwenthal method to about 4 per cent. of gallotannic acid. This property of low oxidisability is not shared to nearly an equivalent extent by any ordinary tanning material, and therefore pinewood extract can be detected, and even estimated approximately if present in considerable quantity, by comparison of the gravimetric and Löwenthal results.

The following table gives the values as compared to gallic acid of the tanning matters absorbed by hide-powder from 3 samples of sulphite cellulose extract, and average values for those of oakwood and chestnut extracts, with which it is most likely to be mixed.

Extract.	Galleic acid value of 1 gm. tannin.
"Fichtenholz" I.	0.120
" " II.	0.090
" " III.	0.137
" " average	0.110
Chestnut "	0.604
Oakwood "	0.527

It was hoped by the authors to develop on this basis an approximate quantitative method; and arithmetically, if a be the gallic acid value of the genuine extract, b the (lower) value for "pinewood," and c that experimentally found for an unknown mixture, $\frac{a-c}{a-b}$ should be the fraction of the total "tannin" found by ordinary gravimetric analysis which is due to "pinewood." Not only, however, are the required constants usually unknown, and subject to considerable variation in

different extracts made from the same material, but even when the method is applied to known mixtures, the results are only approximate, and usually indicate less than the actual amount of "pinewood" really present, suggesting that the absorption of one of these matters by the hide is affected by the presence of the other. This point is still under investigation, and may lead to interesting results.

DISCUSSION.

Mr. H. G. BENNETT said that the facts just given showed that pinewood extract contained none of those bodies ordinarily known as "tannins." It contained, however, some substance absorbed by hide-powder. It had been suggested as profitable for weighting sole leather in drum or vat. The Löwenthal method showed the absence of true tannins.

Mr. C. E. PARKER asked how quickly the matter absorbed from pinewood extracts would wash out from leather.

Mr. H. G. BENNETT replied that it would probably wash out at the same rate as the ordinary weighting extracts, but possibly less readily.

Prof. A. SMITHIELLS remarked that if the substance dissolved out of the pinewood by bisulphite was of an aldehydic nature, it might be expected to have some degree of tanning power.

Prof. H. R. PROCTER said he had tested for furfural and other aldehydes with negative results, but proved the presence of lignin by the aniline test.

Mr. J. E. BEDFORD suggested that a stipulation should be introduced into contracts made by tanners prohibiting the addition of pinewood extracts to tanning extracts.

Mr. C. E. PARKER welcomed the suggestion and said he would bring it before the United Board of the Tanners' Federations. Some such clause should be introduced, since the I.A.L.T.C. method of analysis did not detect the presence of pinewood extract.

THE USE OF THE LOEWENTHAL METHOD IN THE CONTROL OF TANNERY LIQUORS.

BY PROF. H. R. PROCTER AND S. HIRST.

For the purposes of a recent paper on "The Detection of Sulphite Cellulose Liquors" (see page 293), factors were determined for the calculation of Löwenthal results to equivalent values of "tanning matters" as estimated gravimetrically, for a considerable variety of extracts and other tanning materials. The Löwenthal method is fully described in Procter's "Leather Industries Laboratory Book," and details need not be repeated, but as a large number of titrations had to be made, some mechanical improvements were adopted which greatly facilitated the operation. Self-filling burettes of the simple form shown in the figure were used both for permanganate and indigo, and the titration was carried out in a beaker of about 1 litre capacity fitted with a spindle carrying two small screw propellers, made either of stiff celluloid or of brass coated with celluloid varnish, and driven by a small turbine or electric motor. For comparison, a similar beaker filled with an already titrated liquid was placed in a similar light and beside that in use. Under these conditions titrations were very rapidly made and with almost absolute concordance, and the systematic use of the method for control of the tanning strength of liquors naturally suggested itself. Of course there is nothing new in such an idea, but no carefully thought-out and systematic mode of work has hitherto been published. For practical purposes the method requires to be as simple and rapid as is compatible with concordant results, and as tanning materials are now almost universally bought by the I.A.L.T.C. method of analysis, it is important that the figures should be comparable with this method, and on this account determination by chromed hide-powder was

preferred to that by gelatine, although the latter is theoretically more exact, being less affected by astringent non-tanning matters, such as gallic acid.

Since the actual amount of permanganate used varies somewhat with the operator and the details of titration, the usual method of calculating the results of a Löwenthal analysis is by direct comparison with a supposed pure solution of gallo-tannic acid, but as actually pure gallo-tannic acid cannot be obtained, allowances have to be made for an assumed but unascertained amount of impurity; commercial gallo-tannic acid of the best quality usually reducing more permanganate than the theoretically pure substance. Gallic acid, being crystallisable, is readily obtained in a pure form, and is oxidised by permanganate in a similar way to gallo-tannic acid, 1 gm. of crystallised gallic acid reducing approximately the same amount of permanganate as 1.34 grms. of the portion of the purest obtainable gallo-tannic acid absorbed by chromed hide-powder. There is, however, little advantage in calculating in this way, since few, if any, of the tanning materials in use contain solely gallo-tannic acid, and the different tannins are well known to reduce permanganate in somewhat varied proportions. It is therefore more practical and convenient to state the results of experiment in terms of gallic acid, and it is easy to obtain a factor by which the latter can be approximately calculated to any tannin as determined by the hide-powder method.

The following solutions are employed:—(1) Pure air-dried gallic acid, 0.1 gm. per 100 c.c. freshly made. (2) Purest indigo-carmin, 5 grms. per litre, with 50 grms. of concentrated sulphuric acid, 25 c.c. being used for each determination. A solution of 1 gm. "indigo pure B.A.S.F." in 25 c.c. concentrated sulphuric acid diluted to 1 litre with 25 c.c. added sulphuric acid, may also be employed. These solutions both keep well. 25 c.c. of either must require 25—30 c.c. of permanganate for oxidation, or a larger measured volume must be used. (3) Permanganate of potash solution, 0.5 gm. per litre, made by the dilution of a 5 gm. per litre solution at frequent intervals, as very weak solutions do not keep satisfactorily.

The liquor to be tested must be so diluted that 5 c.c. will not consume more than two-thirds of the permanganate required by the 25 c.c. of indigo always used, and thus the complete titration can always be made with the contents of a 50 c.c. burette. Sufficiently accurate readings can be made from the upper edges of the liquids without the use of a float. It is important that the stirring turbine should run with fair uniformity (if hand-stirring is relied on, it must be constant and efficient), and the dropping should be at a regular rate. Generally this may be as fast as separate drops can be counted, until the original blue colour has become yellow-green, after which permanganate is added drop by drop to complete discharge of the blue. It is well occasionally to time the titration so as to ensure constant work. The titration is even more easy by good artificial light diffused by ground glass or tissue paper than by daylight, the removal of the last trace of blue being shown by a very marked brightening of colour; but as the end-points are not quite identical, all the titrations for any single analysis must be done in the same light.

The tanning matter is of course indicated by the difference of titration of the original and detannised liquor, but as neither dissolved salts or traces of hide-substance have any appreciable effect on the titration, the detannisation may be much simpler than that required for actual gravimetric analysis. Washing of hide-powder after chroming is quite needless, the powder being merely chromed, pressed, weighed, and the requisite water added; and 6 c.c. of the detannised liquor counted as five; but a still greater simplification may be effected by the use of Prof. Paessler's dry "lightly chromed" powder, or by the use of freshly air-dried chrome leather machine shavings as suggested by Kopecky. About 7 grms. of the dry powder and a little kaolin should be added to 100 c.c. of the diluted liquor, well mixed by hand shaking, and shaken for 10—15 minutes in the machine. The moisture of such quantity of a powder only amounts at most to 1 gm. even if the whole of it acts as water of dilution, which is very doubtful, and can at most cause an error of 1/100th of

the total tannin in the diluted liquor; and as the analysis is only for comparative purposes, and the error, such as it is, is a constant one, it may well be neglected. The detannised liquor is filtered till clear through paper, and 5 c.c. is with 25 c.c. of indigo twice titrated. If the work is systematic, the amount of dilution required for each class of liquor will be known sufficiently nearly; if not, a simple titration of the undetannised liquor will be a sufficient guide, and for this purpose it is better to dilute too much than too little. The final result is of course divided by the number of c.c. of original liquor taken per litre and multiplied by 1000. It is best to use distilled water for this dilution, but any good tap water will do for titration. Whether the liquor should be filtered clear before or after dilution, or not at all, is a matter for consideration; but if not, any suspended redds, such as those of quebracho, or the catechin of gambier, will largely dissolve on dilution, and be estimated as tannin, which is not necessarily an error, since to some extent the same thing happens as liquors become exhausted in the tannery. It is not necessary to filter the liquor for detannisation, and a good compromise would be to filter only the portion of diluted liquor required for titration, through any good quantitative paper. The systematic method of work would then be that the liquors to be tested would be brought to the laboratory first thing in the morning, and there diluted as required. 100 c.c. of each of the diluted liquors would be placed in shaking bottles with the requisite dry chromed hide-powder and kaolin and shaken by hand till well mixed; and a portion of each of the diluted liquors filtered, the first turbid portions being rejected. The operator would then shake the bottles in the machine, and set their contents to filter while he proceeded with the titrations of the diluted liquors.

The first step is to make fresh the weak permanganate by diluting 100 c.c. of 5 gm. per litre strength to 1 litre, as the strong solution keeps well while the weak soon alters, and to shake this very thoroughly in the stock-bottle to ensure complete mixture. 25 c.c. of the indigo is then twice titrated alone, and the titration repeated with 5 c.c. of the freshly-made gallic acid solution, 0.1 gm. in 100 c.c. The sum of the differences between these will give the permanganate value of 0.01 gm. of gallic acid, which will be practically constant from day to day with careful work and a single operator, and perhaps need not be every day repeated.

The titration of 5 c.c. of the diluted liquors is now similarly performed, and then that of 5 c.c. of the corresponding detannised portions, the titrations always being done in duplicate to check possible errors, and the sum of the two results taken. If now the result of the detannised liquor be deducted from that of the original diluted liquor the quantities of permanganate consumed by indigo will cancel each other, and the result will be the permanganate value of the tannin of 10 c.c. of (diluted) liquor; and

Permanganate consumed by gallic acid	permanganate consumed by liquor	::	1 gm. per litre gallic acid	:	gram. per litre of tannin in liquor expressed as gallic acid.
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If for 1 gm. per litre, the weight of the actual tannin corresponding to 1 gm. of gallic acid be substituted, the strength of the diluted liquor will be obtained directly in gm. per litre in "tanning matter"; and from this by simple multiplication by the dilution, that of the original liquor. 1.34 in place of 1 will give the strength in terms of gallo-tannic acid; 1.76 is the average of about 30 analyses of all the common tanning materials, and Table I. gives factors averaged from several analyses of each of the more important.

If, however, it be desired to obtain an actual experimental figure for the liquors of the particular tannery, or for any particular tanning material, this is easily done by combining the Löwenthal with an ordinary gravimetric analysis of an average liquor by the shake method; the actual "total soluble" and "non-tannin" solutions being used for the titration. Then the result in gm. per litre found gravimetrically, divided by the "gallic acid value" by Löwenthal, will give the factor required, *viz.*, the weight of the tannin corresponding to 1 gm. of gallic acid.

TABLE I.

Material.	Tannin value of 1 gm. gallic acid.	Gallic acid value of 1 gm. tannin.	Gallic acid value of 1 gm. non-tans.
Chestnut extract.....	1.52	0.055	0.005
" "	1.07	0.596	0.085
" "	1.04	0.607	0.050
" "	1.77	0.565	0.100
" "	1.70	0.590	0.200
Solid "	1.06	0.600	0.245
Chestnut wood	1.61	0.618	0.313
Average	1.65	0.504	
Oakwood extract	1.70	0.557	0.115
" "	1.03	0.516	0.047
" "	1.08	0.504	0.068
Oakwood	1.88	0.531	0.116
Average	1.80	0.527	
Myrobalans extract ..	1.70	0.586	0.157
" "	1.82	0.549	0.185
Myrobalans	1.67	0.597	0.126
Average	1.73	0.577	
Mimosa D extract ...	1.74	0.574	0.053
" "	1.66	0.602	0.184
" "	1.71	0.584	0.094
Liquid quebracho extract	1.63	0.612	0.222
Quebracho wood	1.70	0.588	0.220
Average	1.69	0.592	
Larch bark	1.06	0.509	0.056
Hemlock bark	1.07	0.501	0.083
Hemlock extract.....	2.28	0.437	0.035
Spruce bark.....	2.53	0.395	0.104
Average	2.18	0.460	
Valonia extract	1.80	0.553	0.000
Valonia	1.58	0.632	0.086
Sumach	1.53	0.650	0.073
"	1.47	0.680	0.084
Oakbark	1.71	0.583	0.112
Mimosa bark	1.88	0.529	0.031
Mangrove bark	1.46	0.682	0.004
Gambler cube	1.78	0.559	0.325
Average of all above materials.....	1.76	0.573	
Gallotannic acid	1.34	0.742	—
Fichtenholz I.	7.75	0.129	0.006
("Pinewood extract") ..			
Fichtenholz II.	11.11	0.090	0.043
" III.	7.3	0.137	0.031
Average	8.72	0.110	

The Löwenthal method as applied to liquors not only has the advantage over the gravimetric method of much greater rapidity, but is probably of greater relative accuracy with weak liquors, as no concentration is required; the following figures obtained independently for a set of liquors by two different students illustrating the sort of concordance to be expected. The factor used was $\frac{1}{2}$ or 1.66, which was the average of several determinations of the materials used.

TABLE II.

Liquor.	Tanning matter per cent.	
	A.	B.
1st Suspender	0.17	0.17
2nd "	0.30	0.30
1st Handler	0.85	0.82
2nd "	1.20	1.20
3rd "	1.48	1.50
4th "	2.13	2.12
5th "	3.33	3.27
6th "	4.23	4.21

The method is one which can easily be mastered by any intelligent youth without much chemical knowledge, and if it were combined at the same time with lime-water determinations of acidity, would give information as to variations in the working of a yard which could hardly fail to be valuable commercially. It is, however, only to be recommended for continuous and systematic work, and its use for occasional analyses is more troublesome than the ordinary gravimetric method.

The method is equally adapted to the control of spent tans, since very weak liquors can be as accurately determined as strong ones, 10 c.c., or more, if necessary, being used for each titration instead of 5, so that a sufficient quantity of water can be used for complete exhaustion. The material can be dried, ground fine, and extracted in the Procter extractor in the usual way; but for comparative tests it would often be sufficient to boil up 5 lb. of the wet material as it comes from the leaches with a gallon of water for half an hour, allow to stand overnight, and draw off the liquor, making up to one gallon, if necessary, by the addition of enough water to the material to supply the loss by evaporation, and Löwenthal the liquor. Though this would give no precise information as to the exact amount of tannin left in the material, it would at once detect any variations in the completeness of the leaching, and if compared to an occasional more complete analysis, would probably give all necessary information.

As regards the theoretical significance of the Löwenthal results, it is interesting to note that the table of factors given, partially bears out the statement formerly made that catechol tannins reduce materially less permanganate than gallotannic acid or pyrogallol tans. 1 gm. of the purest gallotannic acid is only equal in reducing power to 0.742 gm. of gallic acid, and in all cases the reducing power of the "tanning matters" absorbed by hide-powder is still lower, the highest being that of sumach, of which in one sample 1 gm. had equal reducing power to 0.680 gm. gallic acid; while the lowest are the tannins of coniferous barks, ranging from about 0.4 for spruce bark to 0.5 for larch and hemlock. Chestnut extracts average about 0.6. Oakwoods and myrobalans range from 0.5 to 0.6, while mangrove bark, a pronounced catechol tan, reached 0.68. These differences are not so large as was *a priori* to be expected, a fact which greatly facilitates the use of the method for liquor testing, but which proves that the permanganate required is dependent rather on the differences of constitution of the individual tannins than on the catechol or pyrogallol nucleus. It is also evidence that even in those tannins most allied to gallotannic acid, the substance estimated by hide-powder is not simply gallotannic acid, but either includes other less oxidisable matters or compound tannins of a more complex character, and very possibly in many cases, glucosides.

The gallic acid values of the different tannins are characteristics which may be used, like the saponification values and iodine values of fats, as a means of identification. Thus an "oakwood" extract with a gallic acid value over 0.6 may be justly suspected of being a chestnut. Even in genuine extracts the differences in value which are found, no doubt point to real differences in the character of the tannin due to manufacture, mode of growth, or age, which deserve closer investigation.

In this connection it may be interesting to quote some results of detanninisation by gelatine (described in Procter's "Leather Industries Laboratory Book" *), as compared with various hide-powders. It has been shown that by this modification of the method, the separation of gallotannic acid from gallic acid is very approximately accurate, although perhaps by a compensation of errors, traces of gallic acid being precipitated and traces of the tannogelatin dissolved in the acid liquor. Addition of more salt diminishes the latter error, but increases the former.

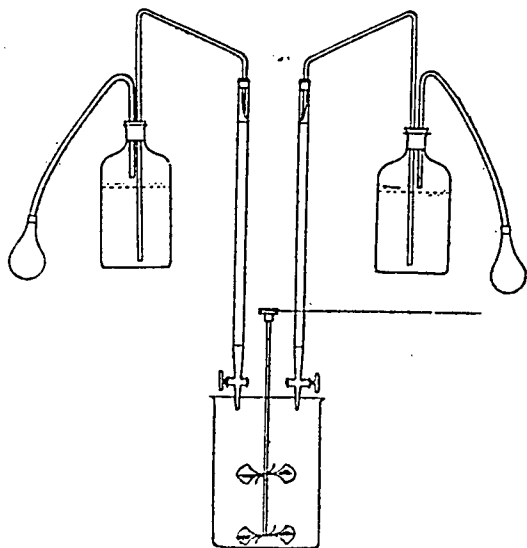
* To 50 c.c. of liquor add 25 c.c. of fresh 2 per cent. gelatine solution, 25 c.c. of a saturated solution of salt containing 50 c.c. of sulphuric acid per litre, and a teaspoonful of kaolin, shake for 15 minutes and filter and titrate 10 c.c. instead of 5 c.c.

TABLE III.
Gallic acid equivalent to non-tannins.

Extract.	Gelatine salt and acid.	Freiberg unchromed powder.	Vienna unchromed powder.	Pacssler's chromed powder.	American chromed I.A.L.T.C.
Oakwood, (reputed)	0-255	0-221	0-163	0-149	0-149
Oakwood, Gondolo	0-160	0-144	0-132	0-115	0-115
Chestnut, solid	0-331	0-354	0-320	0-242	0-245
Chestnut, liquid	0-207	0-300	0-297	0-209	0-199

It will be observed that in most cases the non-tannins are highest in the case of gelatine precipitation, though in some cases they are approached or even exceeded by the unchromed hide-powders used by shaking, while those of the chromed powders are invariably much lower. It appears therefore that as regards the oxidisable matters estimated by permanganate, the unchromed powders give results nearer the scientific truth, but the much closer concordance of the chromed powders fully justifies their use for commercial purposes, and further it must be remembered that in gravimetric analysis these oxidisable and generally astringent non-tannins form only a small portion of the whole. The close agreement of Prof. Pacssler's lightly chromed powder with that officially chromed, establishes the suitability of the former as a detannising agent for the Löwenthal process, and encourages the hope that a dry chromed powder may ultimately be produced, which will avoid not only the chroming, but the much more troublesome washing immediately before use which is now required.

If the gelatine method is preferred to hide-powder for liquor control it is quite as rapid, and probably less affected by large amounts of non-tannins, but the results are not directly comparable with gravimetric analysis, and some samples of gelatine exercise a slight reducing effect on permanganate, not amounting in blank experiments to more than about 0.2 c.c. per 10 c.c. of the non-tannin filtrate, and probably due to traces of sulphites. This, if desired, is easily determined and allowed for.



DISCUSSION.

Prof. W. M. GARDNER suggested the investigation of the effect of reducing instead of oxidising substances on tannins. The action of the latter was the basis of the methods of estimation at present used. If a definite substance such as benzoic acid could be obtained as a result of reduction, much more definite results might be obtained. Under certain conditions tannic acid and many other phenolic bodies gave benzoic acid on reduction.

Mr. F. W. BRANSON asked if absolutely pure chemicals were necessary when a correction factor could be used.

Mr. H. G. BENNETT said that difficulties were always experienced with certain tannins where the methods of estimation broke down. He emphasised the value of a volumetric method such as the Löwenthal method, which combined speed and accuracy, since the hide-powder process involved difficulties such as the possible presence of difficultly volatile substances like lactic acid, the impossibility of drying the exhausted extract to a constant weight, &c.

Note by Prof. H. R. PROCTER: I have not tested the recently-suggested reduction methods for the investigation of tannins, which are of great scientific interest, but do not seem as yet likely to supersede those in use for practical estimation. In reply to Mr. Branson's question, there is no doubt that in many cases absolutely pure chemicals are of the greatest importance. In the Löwenthal process the purity of the gallic acid is of the highest importance, and the indigo must be free from indigo red and other products which obscure the end-point.

NOTE ON THE DIFFUSION OF CHROMIUM, IRON AND ALUMINIUM SALTS THROUGH GELATINE JELLY.

BY PROF. H. R. PROCTER AND DOUGLAS J. LAW.

The experiments described in the following note were prepared in the first instance as a lecture demonstration, but though the results throughout must merely be regarded as qualitative they appear to present some points of interest which make them worthy of a permanent record.

If a solution of a coloured crystalline salt, such as copper sulphate, is poured on the top of solidified gelatine jelly, it diffuses into it somewhat rapidly, its progress being easily traced by the change of colour in the transparent jelly. It has been shown by Fick that in many cases diffusion in jellies is practically as rapid as in still water. In the case of coloured substances of a less definitely crystalline character the diffusion is slower, and the ultimate penetration less, while solutions of a distinctly colloidal nature either do not penetrate at all or do so to a comparatively small extent. If a mixture of two coloured substances is employed of different degrees of diffusibility two zones of diffusion are formed, of which the deeper consists only of the more diffusible substance. When operating with colourless salts, bases, or acids, it is frequently easy to determine their progress by the addition of a suitable indicator, thus that of strong bases is shown by the addition of phenolphthalein, or that of acids, by the same reagent coloured with a trace of caustic alkali.

As salts of chromium and other metals of the same group are very prone to hydrolysis and the formation of basic salts, it was of interest to determine not merely the progress of the chromo salt but that of the hydrolysed acid, and for this purpose a 5 per cent. jelly was used coloured pink with slightly alkaline phenolphthalein. This was allowed to set in Nessler cylinders, or for the purpose of lantern demonstration, in parallel-sided cells, and the solution to be tested was poured upon the top of the jelly. That gravitation had little influence on the rapidity of the diffusion was proved by repeating a similar experiment with an inverted tube. As the chromo salts diffused into the jelly, their progress was clearly noted by their colour, which, whatever the colour of the solution, is generally in the jelly of a dull bluish green, somewhat