

PRACTICAL LEATHER CHEMISTRY

A HANDBOOK OF LABORATORY NOTES
AND METHODS FOR THE USE OF
STUDENTS AND WORKS' CHEMISTS

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PREFACE

ALTHOUGH this laboratory manual has been designed in the first instance for the student of chemistry specialising in the leather industry, it will, it is hoped, also be of use to the works chemist. During the last few years there have been published in such journals as the *Collegium*, *Journal of the Society of Leather Trades' Chemists* and the *Journal of the American Leather Chemists Association* a large number of important papers dealing with methods of chemical analysis as applied to the leather trade. As a consequence, existing text books on this subject are becoming somewhat out of date. With this point in mind, the author has made full use of the above publications, and referred to the more important papers contained therein in the present work. In this connection it is hoped that the list of references given at the end of each chapter will be of use to the student wishing to go further into any particular point.

The writer would here take the opportunity of impressing upon the mind of the student the necessity of constant reference to such journals as those mentioned above, as it is only by so doing can he expect to keep himself in touch with such progress as is continually being made. For the use of the reader in making notes relevant to such, a few blank sheets have been left at the end of each chapter.

In conclusion, the author wishes to express his best thanks to Mr. A. B. Bradley for his assistance during the writing of this book, while thanks are also due to Messrs. A. Hilger, Ltd., for the loan of the block for Fig. 7.

A. H.

LONDON, S.W.

TWO IMPORTANT BOOKS FOR THE LEATHER TRADE.

PRACTICAL TANNING.

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LEATHER MANUFACTURE.

A Practical Handbook of Tanning, Currying, and Chrome Leather Dressing. By A. WATT. Fifth Edition, Revised and Enlarged. 8vo, cloth. 14s. net.

CROSBY LOCKWOOD AND SON

ABBREVIATIONS USED IN THIS VOLUME

COLL.	Collegium.
COLL. (LOND. EDIT.)	Collegium. London Edition.
J.C.S.	Journal Chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. IND. ENG. CHEM.	Journal of Industrial and Engineering Chemistry.
J. SOC. DYERS COLS.	Journal Society of Dyers and Colourists.
JOUR. SOC. LEATHER TRADES CHEM.	Journal of the Society of Leather Trades' Chemists.
JOUR. AMER. LEATHER CHEM. ASSOC.	Journal of the American Leather Chemists Association.
CHEM. ZEIT.	Chemiker Zeitung.
ZEIT. ANGEW. CHEM.	Zeitschrift für angewandte Chemie.
ANN. CHIM. ANALYT.	Annales de Chimie Analytique.
ANN. DI CHIM. APPL.	Annali di Chimica Applicata.

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PRACTICAL LEATHER CHEMISTRY

CHAPTER I

WATER ANALYSIS

THE following determinations are usually carried out when examining a water for its suitability either for tanning or leather dyeing purposes. In order to detect the presence of putrefactive organisms, which are, to say the least, very undesirable in a water to be used in the tanning industry, a bacteriological examination should be made. Such methods are to be found in any reliable text-book on applied bacteriology, for, as will be readily understood, this subject could not be suitably dealt with in a brief chapter.

Total Dissolved Solids.—250 c.cs. to 500 c.cs. of the filtered water, according to the amount of total solids suspected to be present, are carefully evaporated to dryness in a weighed platinum dish. The evaporation is best conducted over a small rose flame until only a small volume of water is left, and finally taken to complete dryness on a water bath. The residue is then dried in a hot air oven at 105° C. for three hours, when it is cooled in a desiccator and weighed. From the weight of total solids obtained, the quantity present in 100,000 parts of water is calculated.

Loss on Ignition of Total Solids.—The loss on ignition of the total solids gives an approximate indication of the amount of organic matter present.

The residue from the determination of the total dissolved solids is carefully ignited over a small rose flame until all organic matter has been driven off. This will be made evident by the disappearance of all black particles of carbonaceous matter. The basin is then allowed to cool, when the residue is treated with a few drops of a solution of ammonium carbonate. This is necessary, in order to reconvert any MgO or CaO formed back again into the

carbonate. The basin is again gently ignited to drive off the excess of ammonium carbonate, and then cooled in the desiccator and weighed. The loss in weight sustained by this ignition can, for technical purposes, be taken as representing organic matter.

According to Pearman and Moor,¹ the loss on ignition of a good water will seldom exceed 20 per cent. of the total solids.

Iron.—The non-volatile solids from the above determination is treated with a few drops of pure HNO_3 (free from iron), warmed, diluted with distilled water, transferred to a 100 c.c. Nessler tube and made up to the 100 c.c. mark with water. 2 c.cs. of a 5 per cent. solution of potassium sulphocyanide is added, when the presence of iron will be indicated by the formation of a blood-red coloration.

Should more than a moderate colour be produced, it will be necessary to dilute the 100 c.c. to 200 c.c. or more, so that 100 c.c. can be more accurately matched. Such dilution must be allowed for when calculating the result. The quantity present can be estimated colorimetrically by matching against a standard iron solution.

To prepare the standard iron solution, 0.7 gm. of pure ferrous ammonium sulphate (this salt contains one-seventh of its weight of iron) is dissolved in a few cubic centimetres of water, and the iron oxidised to the ferric condition by warming with a few drops of HNO_3 . The solution is then made up to 1000 c.cs. in a graduated flask with distilled water. 1 c.c. of this solution = 0.0001 gm. Fe.

By noting the volume of this solution required to produce the same tint as that in the water under examination, the amount of iron present can be calculated.

In order to obtain good results, the standard iron solution should be diluted to the 100 c.cs. mark on the Nessler tube before the 2 c.cs. of potassium sulphocyanide is added. Also, when judging the colours, the tubes should be held about an inch above a white surface, and the colour determined by looking down the tube.

The following examples will illustrate the method of determination:—

Example 1.—500 c.cs. of the water evaporated, etc., and the residue dissolved in HNO_3 and made up to 100 c.cs. in Nessler glass. On adding the potassium sulphocyanide a deep red colour, too deep for matching, was produced.

50 c.cs. of the solution was further diluted to 100 c.cs. with water and 1 c.c. of potassium sulphocyanide added.

This was then matched against the standard iron solution.

Iron solution required = 2.1 c.cs.

Now 1 c.c. standard iron solution = 0.0001 gm. Fe.

$$\therefore 2.1 \text{ c.cs.} = (2.1 \times 0.0001) \text{ gm. Fe.} \\ = 0.00021 \text{ gm. Fe.}$$

Now the 50 c.cs. of solution taken for further diluting corresponds to half of the original volume of water (500 c.cs.) = 250 c.cs.

\therefore 250 c.cs. water contain 0.00021 gm. Fe.

100,000 c.cs. water contain 0.084 gm.

Example 2.—500 c.cs. water treated for iron determination by the above method.

Iron solution required = 0.8 c.cs.

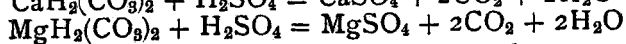
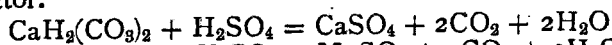
Now 1 c.c. of iron solution = 0.0001 gm. Fe.

$$\therefore 0.8 \text{ c.c.} \quad \quad \quad = (0.8 \times 0.0001) \text{ gm. Fe.} \\ = 0.00008 \text{ gm. Fe.}$$

500 c.cs. water contain = 0.00008 gm. Fe.

100,000 c.cs. " " = 0.016 gm. Fe.

Temporary Hardness.—The temporary hardness is due to the presence of dissolved bi-carbonates of calcium and magnesium, and is most conveniently estimated by *Hehner's* method. This consists in titrating the alkalinity produced by the bi-carbonates with $\frac{N}{10}$ acid, using methyl orange as indicator.



Although actually due to bi-carbonates, the temporary hardness is always expressed in terms of CaCO_3 .

100 c.cs. of the water is pipetted into a clean conical flask, two drops of methyl orange solution added, and titrated with $\frac{N}{10}$ H_2SO_4 or HCl . To obtain greater accuracy, the volume

of acid required to change the indicator from yellow to red should be determined by a blank experiment, using distilled water in place of the water under examination, with two drops of the *same* methyl orange solution. This amount is deducted from the total found in the actual titration, the difference being due to the temporary hardness in the volume

of water taken. Each cubic centimetre of $\frac{N}{10}$ acid required = 0.005 gm. of CaCO_3 , or using 100 c.cs. of the water for the

determination as already described, each cubic centimetre of acid is equivalent to 5 parts of temporary hardness per 100,000 of water.

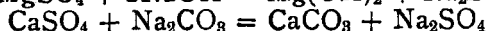
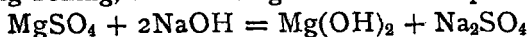
Bennett² recommends the following procedure when estimating the temporary hardness of very hard waters :—

100 c.cs. of the water is titrated at the boil with $\frac{N}{10}$ acid, using methyl red as indicator. Boiling is necessary in order to expel CO_2 . Another method, suggested by Winkler³ is to boil 100 c.cs. of the water with 1–2 gms. of pure boric acid, cool and then titrate in the ordinary way with acid, using methyl orange as indicator.

Alizarin is sometimes used as the indicator, with which, it is said, very accurate results can be obtained. A few drops of a 2 per cent. alizarin paste is added to 100 c.cs. of the water. It is then titrated with $\frac{N}{10}$ acid until the violet colour turns to yellow, when the water is boiled and the titration continued until the yellow colour is permanent. It is necessary in this case to make a blank experiment to allow for the acid required to change indicator.

Permanent Hardness.—The permanent hardness is due to the dissolved sulphates of calcium and magnesium, and the method usually adopted for their estimation in works' practice is that introduced by Pfeifer and Wartha. As a matter of convenience, the permanent hardness is also expressed in terms of CaCO_3 , in the same manner as the temporary. 200 c.cs. of the water is boiled in a conical flask with exactly 50 c.cs. of an equal mixture of $\frac{N}{10}\text{NaOH}$ and $\frac{N}{10}\text{Na}_2\text{CO}_3$ until the liquid is reduced to about two-thirds of the original volume. The solution should be boiled gently and loss by spirting guarded against by placing a funnel in the neck of the flask.

During boiling, the following reactions take place :—



After boiling, the liquid is cooled, transferred to a 200 c.c. graduated flask and made up to the mark with distilled water. After well shaking, it is filtered, and 100 c.cs. of the filtrate (corresponding to 100 c.cs. of original water and 25 c.cs. of the mixed alkali solution) titrated with $\frac{N}{10}\text{HCl}$ or H_2SO_4 , using here methyl orange as indicator. Then the number

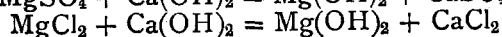
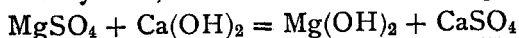
of cubic centimetres of acid required in titrating back the unused alkali subtracted from 25 c.cs., will give the volume of $\frac{N}{10}$ alkali used in decomposing the permanent hardness in

100 c.cs. of the water. Each cubic centimetre is equivalent to 0.005 gm. of CaCO_3 ; or, if the above details are adhered to, 5 parts of permanent hardness per 100,000 parts of water.

Sodium Carbonate.—This can only be present in waters which are free from permanent hardness, and in such waters the amount of acid required in titrating back the added alkali in the estimation of the permanent hardness as already described, will exceed 25 c.cs. The excess over and above 25 c.cs. will correspond to the Na_2CO_3 present in 100 c.cs. of the water. Each cubic centimetre of excess acid is equal to 0.0053 gm. of Na_2CO_3 , or 5.3 parts per 100,000 of water. It must be remembered that if sodium carbonate is present, it will also have been previously titrated when estimating the temporary hardness, so that the amount of acid corresponding to the carbonate found must be allowed for in calculating the temporary hardness.

Magnesia Hardness.—The hardness due to magnesium salts will have already been determined, either in the temporary or permanent hardness or both. It may, however, be determined separately by the following method :—

100 c.cs. of the water is neutralised with $\frac{N}{10}$ acid (the amount found necessary in the estimation of the temporary hardness), and boiled down to about 70 c.cs. By this means all magnesium (and calcium) salts due to temporary hardness are converted into permanent hardness, and the magnesium can be precipitated by the addition of lime water in the form of magnesium hydrate, the calcium salts remaining unaffected.



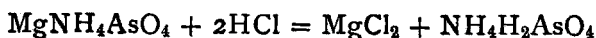
After transferring the boiled water to a 200 c.c. measuring flask, 100 c.cs. of freshly filtered lime water is added, and the whole heated to 100°C . on a water bath for quarter of an hour, during which time the mouth of the flask should be covered with a watch glass so as to prevent access of atmospheric carbon-di-oxide to the lime water. In the meantime, the actual alkalinity of 50 c.cs. of the same lime water should be determined by titration with $\frac{N}{10}$ acid, using phenol phthalein as indicator.

After quarter of an hour at 100°C . the flask is cooled down, and the contents made up to the mark with distilled water. The whole is well shaken and allowed to stand for a time, when 100 c.cs. of the clear supernatant liquor is pipetted out carefully and titrated with $\frac{N}{10}$ acid, using phenolphthalein as indicator. This titration will, of course, correspond to 50 c.cs. of original water and 50 c.cs. of lime water. The reading obtained, deducted from the $\frac{N}{10}$ acid value of 50 c.cs. of lime water, will give the number of cubic centimetres of acid corresponding to the lime water used up in precipitating the magnesia in 50 c.cs. of the water. From the reading obtained, the magnesia per 100,000 parts of water can be calculated—

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0.002 \text{ gm. MgO.}$$

One of the several methods suggested by Jensen ⁴ for the volumetric estimation of magnesium in water is as follows :—

The total solids from a known volume of the water is dissolved in HCl, and the calcium salts precipitated with ammonium oxalate and filtered off in the usual way. The filtrate is evaporated to dryness and ignited to decompose the ammonium salts. The residue is dissolved in a small quantity of dilute HCl, filtered and rendered alkaline with ammonia. The magnesium is then precipitated as magnesium ammonium arsenate by the addition of a slight excess of sodium arsenate solution. After standing overnight, the precipitate is filtered off, washed with dilute ammonia and then 50 per cent. alcohol, until the washings are free from ammonia. The washed precipitate is dissolved in a known volume of $\frac{N}{10}$ HCl, and the excess of acid titrated back with $\frac{N}{10}$ Na_2CO_3 , using methyl orange as indicator.



Each cubic centimetre of $\frac{N}{10}$ acid used up corresponds to 0.002 gm. MgO. To detect magnesium chloride, which is a very undesirable constituent in boiler waters, Bosshard and Burawzow ⁵ recommend evaporating a known volume of water to dryness and extracting the residue with a mixture of equal volumes of *dry* alcohol and ether. This dissolves only the MgCl_2 and CaCl_2 . After filtering, the solvent is

evaporated off and the residue re-dissolved in water. The CaO and Cl are determined in this solution, and, after calculating all the CaO into CaCl_2 , any remaining Cl is taken as being present in the form of MgCl_2 .

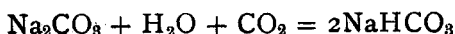
Carbon-di-Oxide.—According to Winkler, free CO_2 can be detected qualitatively as follows:—10 drops of a 1 per cent. alcoholic solution of alizarin are added to 100 c.c.s. of the sample.

Small quantities give a copper-red colour.

Moderate quantities give a reddish-yellow colour.

Large quantities give a yellow colour.

Quantitatively, CO_2 may be determined by titrating 100 c.c.s. of the water with $\frac{N}{10}\text{Na}_2\text{CO}_3$, using phenol phthalein as indicator. This titration depends upon the fact that sodium bi-carbonate, which is neutral to the indicator, is produced according to the re-action—



The titration is continued until a final pink colour is obtained.

The addition of the $\frac{N}{10}\text{Na}_2\text{CO}_3$ is made very slowly, one drop at a time only, and with constant shaking.

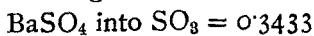
$$1 \text{ c.c. } \frac{N}{10}\text{Na}_2\text{CO}_3 = 0.0022 \text{ gm. } \text{CO}_2$$

Chlorides.—Chlorides are best determined volumetrically by means of a standard solution of silver nitrate, $\frac{N}{50}$ being a convenient strength. This is prepared by dissolving exactly 3.3932 gms. of pure AgNO_3 in a little distilled water, and making the solution up to 1 litre. 1 c.c. of this solution = 0.00071 gm. Cl or 0.00117 NaCl.

100 c.c.s. of the water are measured into a conical flask and two drops of a 5 per cent. solution of potassium chromate added as indicator. The silver nitrate is carefully added from a burette until the solution turns a permanent red colour. The volume of silver nitrate solution required multiplied by the factor given above, will give the amount of Cl or NaCl, as the case may be, in 100 c.c.s. of the water, from which figure the quantity in 100,000 parts of water can be calculated.

Sulphates.—Sulphates may be estimated directly by precipitating as barium sulphate and weighing in that form.

250 c.cs. of the water is made acid by adding an excess of HCl, and then concentrated down by boiling to about 70 c.cs. 10 c.cs. of a hot 5 per cent. solution of barium chloride is added and the liquid boiled for 5-10 minutes. The precipitate of BaSO_4 is filtered, washed with boiling distilled water, and dried in the steam oven. It is then ignited in a weighed crucible and weighed.



General Considerations.—For obvious reasons, water either for tanning or dyeing purposes should be as free as possible from organic matter. Especially also when it is to be used for soaking raw goods, etc. In such cases, it is not the actual organic matter which produces bad effects, but the fact that waters, rich in organic matter, form a good nutrient media for harmful and undesirable putrefactive organisms to develop.

Waters with excessive temporary hardness should be avoided, as these if used for washing limed goods are liable to produce an effect on the pelt known as "lime blast," owing to the precipitation of CaCO_3 and MgCO_3 on the pelt. The temporary hardness in water used for this purpose is generally eliminated by softening with lime added in the form of freshly-made lime water. Waters containing an excessive quantity of Na_2CO_3 also tend to cause "lime blast," and render the washing difficult. Bi-carbonates darken tan liquors, with the result that the leather produced in such liquors is dark in colour. Similar remarks apply to sodium carbonate. For a very complete account of the action of the mineral constituents of water in the extraction of tanning materials, the reader is referred to a paper by Nihoul,⁶ who has carried out some very valuable work on this subject.

From the dyer's standpoint, it must be remembered also that temporary hardness causes the precipitation of the basic dyestuffs, which, as well as resulting in a loss of dye, causes uneven dyeing of the leather. Water for this purpose can be neutralised with acetic acid.

Chlorides prevent the swelling of hide substance, but up to 6 parts per 100,000 of chlorides can be taken as a reasonable limit.

Iron, if present beyond the slightest trace, will produce a decided darkening in colour of tan liquors, with the consequent darkening of the leather being tanned.

REFERENCES

- ¹ "The Chemical and Biological Analysis of Water," 1899.
- ² *Coll.* (London Edition), 1915, p. 237.
- ³ *Zeit. angew. Chem.*, 1915, p. 48.
- ⁴ *Abstract, J.S.C.I.*, 1916, p. 1032.
- ⁵ *Abstract, J.C.S.*, 1913, ii. p. 245.
- ⁶ *Coll.*, 1902, p. 80.

NOTES

NOTES

CHAPTER II

ANALYSIS OF LIME

LIME to be used for depilatory purposes should be practically free from iron and contain only small amounts of silica and calcium carbonate. When examining a sample of lime the following determinations are made :—

Available Lime.—5 gms. of the powdered sample is shaken with a convenient volume (about 200 c.cs.) of a 10 per cent. cane sugar solution in a 500 c.c. graduated flask for half an hour, and the solution then made up to the 500 c.c. mark with distilled water. The whole is well shaken and filtered through a rapid filter paper. 50 c.cs. of the clear filtrate is pipetted into a clean conical flask and titrated with $\frac{N}{5}$ HCl, using phenol phthalein as indicator. The reading obtained will give the number of cubic centimetres of $\frac{N}{5}$ acid required to neutralise the free lime in 0.5 gm. of the original sample.

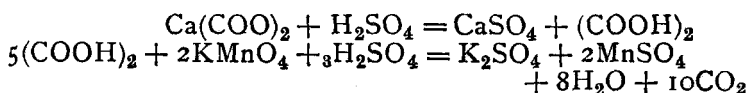
$$1 \text{ c.c. } \frac{N}{5} \text{ HCl} = 0.0056 \text{ gm. CaO}$$

Insoluble Matter.—5 gms. of the sample is dissolved in HCl and the solution evaporated to dryness in a platinum dish. The residue is ignited, gently at first to avoid spirting, and afterwards strongly, in order to decompose any silicates and to render the silica insoluble. After cooling, the residue is dissolved in dilute HCl, boiled, diluted with hot distilled water, and the solution filtered through an ashless filter paper. Any insoluble matter is well washed with water and the filter paper and residue dried in the steam oven. It is then ignited and weighed in a tared crucible. This will give the sand and insoluble matter in 5 gms. of the sample.

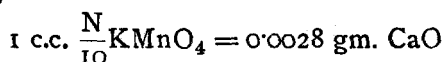
The filtrate and washings are cooled and made up to 500 c.cs. with water.

Iron and Alumina.—50 c.cs. of the above solution (corresponding to 0.5 gm. of the original sample) is transferred to a beaker and rendered alkaline with a slight excess of ammonia. It is then boiled for 5–10 minutes, and the precipitate, consisting of iron and aluminium hydrates, is filtered off, washed with boiling distilled water, dried, ignited and weighed as Fe_2O_3 and Al_2O_3 . In cases where a fairly large quantity of iron is present, it is advisable to detach the dried precipitate from the paper before ignition, as a partial reduction of the Fe_2O_3 to Fe may take place. The filter paper is ignited first, and then the precipitate added, and the whole again ignited for a short time. The crucible and its contents are cooled in the desiccator and weighed.

Total Lime.—The filtrate from the iron and alumina determination is heated to the boil and a further excess of ammonia added. The calcium is then precipitated by adding a boiling solution of ammonium oxalate as long as any precipitate is formed. It is most essential that both solutions should be boiling at the time of mixing, otherwise the calcium oxalate will be somewhat difficult to filter. After boiling for 10 minutes, the calcium oxalate is filtered off and washed thoroughly with boiling distilled water. A hole is then pierced through the apex of the filter paper and the precipitate washed into a clean flask. It is then dissolved in dilute sulphuric acid. The solution is warmed to 70°C ., and titrated with $\frac{\text{N}}{10}\text{KMnO}_4$ until the pink colour of the permanganate remains just permanent.



The $\frac{\text{N}}{10}\text{KMnO}_4$ is prepared by dissolving 3.158 gms. of the pure salt in water and making the solution up to 1000 c.cs. The solution should be standardised against either oxalic acid or ferrous ammonium sulphate, and stored in a coloured glass bottle.



As an alternative to the volumetric method, either of the following gravimetric methods may be used:—

The washed and dried calcium oxalate precipitate is ignited in a tared crucible until the weight is constant. By