

THE DETERMINATION OF WATER IN RAW SUGAR USING THE KARL FISCHER METHOD

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Abstract

A Karl Fischer method for the determination of moisture in raw sugar is described. The method entails the use of formamide to dissolve the sugar, the moisture in the resulting solution being titrated directly with the Karl Fischer reagent. The reproducibility and accuracy of the method are discussed and the results are compared with the moisture content obtained by oven drying at 105°C for three hours. Results obtained by this Karl Fischer method were found to be up to double those obtained by oven drying. The theoretical aspects of the Karl Fischer titration are also discussed.

Introduction

In order to study the conditioning of sugar it is necessary to be able to determine the total moisture in sugar. Several methods for the determination of the moisture content of sugars have been proposed. These include the standard oven method of drying for three hours at 105°C¹¹, the vacuum distillation method of Hill and Dobbs⁶, the cobaltous bromide adsorption method of Gardiner and Keyte⁵, methods using nuclear magnetic resonance, infra-red heating, vacuum oven drying, infra-red spectrophotometry, dielectric and high frequency electrometric techniques, the calcium carbide reaction and the Karl Fischer (K.F.) method. Reviews can be found in the International Commission for Uniform Methods of Sugar Analysis Proceedings.

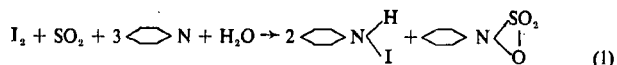
Due to the lack of suitable information on the reproducibility and accuracy of the K.F. moisture determination for sugar it was decided to investigate this method. Unfortunately an absolute method for the determination of water in sugar is not available for comparison purposes. The K.F. results are compared with results from the standard oven drying procedure¹¹ which is most frequently used for routine determinations of sugar moistures. It is known that the accuracy of the oven drying determination suffers because of the deterioration of the sugar at the temperature used.

The K.F. method proposed by McComb⁸ was used in this work. This entails dissolving the sugar in formamide and titrating the moisture in the resulting solution.

Experimental

Apparatus

The reaction of K.F. reagent with water is as follows:



The pyridine-sulphur trioxide complex formed in Reaction 1 can now react with a compound containing an active hydrogen. The presence of methanol prevents the reaction of the complex with another molecule of water.

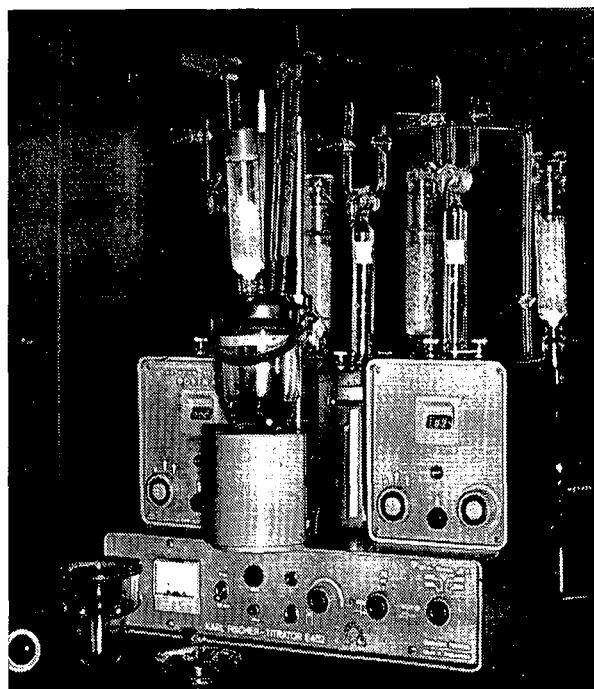
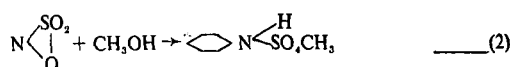


FIGURE 1: Automatic Karl Fischer Titrator.

A fully automatic Metrohm K.F. Titrator E 452 shown in Figure 1 was used in this work. The electrode circuit in this instrument is similar to that used by Foulk and Bawden⁴ and is shown in Figure 2.

This apparatus makes use of the "dead stop" technique, discovered by Foulk and Bawden⁴, to detect the endpoint. In this technique use is made of the polarisation of two similar platinum electrodes due to oxygen being absorbed on the anode and hydrogen on the cathode. A small potential is applied across the electrodes and is balanced by the back electromotive force of polarisation with the result that no current flows. If oxidising or reducing agents are added to the system the electrodes can become

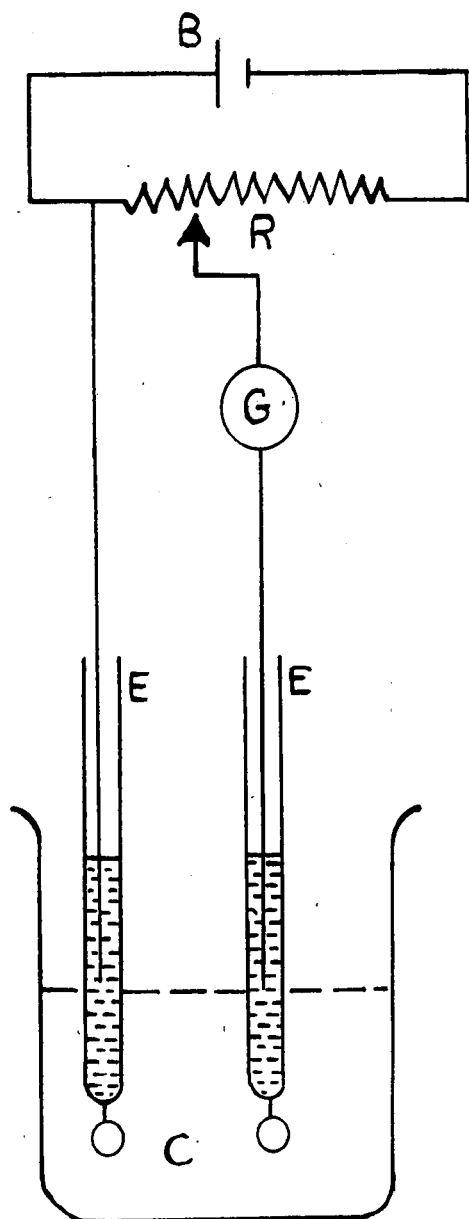


FIGURE 2: Wiring diagram for dead-stop apparatus⁴ —
 B Constant voltage supply.
 G Galvanometer.
 R Rheostat.
 E Platinum electrodes.
 C Solution.

depolarised (i.e. reaction of the reducing agent with oxygen on the anode, or reaction of the oxidising agent with hydrogen on the cathode). For a current to flow both electrodes have to be depolarised. In K.F. work the iodide ion acts as the reducing agent and iodine as the oxidising agent. For the forward titration there are, initially, iodide ions in solution which only depolarise the anode. As soon as all the water has been titrated the cathode is depolarised by the small amount of excess iodine and a current flows which is registered by the galvanometer G located as illustrated in Figure 2. The cell voltage vs ml. K.F. reagent for a titration when using a constant current of $100\mu\text{A}$ is illustrated in Figure 3².

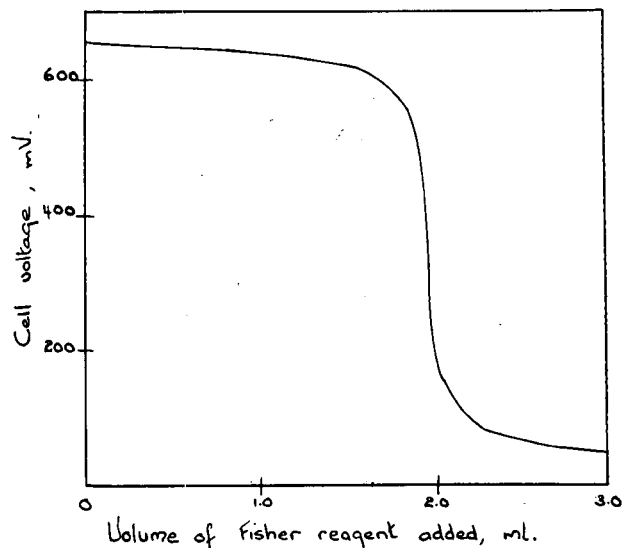


FIGURE 3: Voltage across electrodes during a titration, a constant current of $100\mu\text{A}$ being passed².

Reagents

K.F. reagent with a water equivalent of ca. 4 mg/ml marketed by May and Baker was used in this work. Methanol used for standardisation purposes, with a moisture content of ca. 0.01%, was supplied by Merck Chemicals. Commercial formamide, marketed by British Drug Houses, had a water content of ca. 0.01% which was found to be suitable.

Procedure

5 g raw sugar was weighed into the clean dry 50 ml titration vessel supplied with the instrument. The titration vessels used were dried in an oven for at least one hour at 110°C and cooled in a desiccator over calcium chloride. The vessel was attached to the instrument and 40 ml formamide was added from the automatic burette. The slurry was stirred with the aid of a magnetic stirrer for one hour after which time all the sugar had dissolved. K.F. reagent was then titrated directly against the moisture in the solution until the electrodes had remained depolarised for at least twenty seconds⁷. The clean dry titration vessel containing the 5 g sugar was attached to the instrument directly after completing a titration to ensure that the solution adhering to the electrodes was water free.

The direct titration with K.F. reagent was preferred to the back titration with standard water-in-methanol solution for the following reasons.

1. The use of another reagent, the standard water-in-methanol solution, is avoided.
2. The effect of possible side reactions is reduced by not having the large excess of K.F. reagent.
3. The direct titration is more rapid than the back titration.

The endpoint for the direct titration is reported to be as sensitive and accurate as for the back titration procedure⁹.

The formamide was found to be extremely hygroscopic and for this reason the experiment was performed without removing the titration vessel from the instrument. A blank titration was carried out under the same experimental conditions as for the

TABLE I
Comparison of oven moistures with Karl Fischer moistures using the formamide method

Percent Moisture

Sample	Karl Fischer			Oven Drying			Difference A-B	$\frac{B}{A} \times \frac{100}{1}$
	1st Determn.	2nd Determn.	Mean A	1st Determn.	2nd Determn.	Mean B		
GD 5/9	0.442	0.438	0.440	0.282	0.301	0.292	0.148	66
ZSM 5/9	0.414	0.418	0.416	0.283	0.260	0.272	0.144	65
FX 10/12	0.381	0.357	0.369	0.263	0.261	0.262	0.107	71
ZSM 12/12	0.288	0.280	0.284	0.156	0.152	0.154	0.130	54
FX 17/12	0.408	0.424	0.416	0.353	0.358	0.356	0.060	86
FX 21/12	0.427	0.419	0.423	0.330	0.328	0.329	0.094	78
ZSM 23/12	0.324	0.308	0.316	0.158	0.161	0.160	0.156	51
ZSM 4/1	0.338	0.326	0.332	0.233	0.243	0.238	0.094	72
FX 7/1	0.336	0.316	0.326	0.271	0.256	0.264	0.062	81
ZSM 7/1	0.287	0.287	0.287	0.222	0.206	0.214	0.073	75

sample to correct for any moisture pick-up from the atmosphere during stirring.

The K.F. reagent was standardised against ca. 0.15 g sodium tartrate dihydrate dissolved in 20 ml methanol. Duplicate analyses on the same sugar sample were carried out on the same day. The oven moistures were determined on the same day as the K.F. moistures.

Results

The results obtained by the K.F. method and the oven drying method are reported in Table I. The figures in column eight are the differences between the mean K.F. and the mean oven results, and the figures in column nine are the oven moistures expressed as a percentage of the K.F. moistures.

The standard deviation of the K.F. method was found to be 0.0095 and for the oven drying method 0.0087. The standard deviations for duplicate analyses were calculated according to the formula¹³:

$$S^2 = \frac{\sum W^2}{2k}$$

where W is the range and k the number of samples.

Discussion

From the standard deviation it can be seen that the reproducibility of the two techniques is about the same. The 0.0095 deviation represents approximately 0.5 mg water when using 5 g sugar for the experiment. For a K.F. reagent with a water equivalent of 4 mg/ml this deviation is equivalent to 0.10 ml.

Initial experiments with blank titrations carried out on both methanol and formamide indicated an expected reproducibility of this magnitude for K.F. work. The reproducibility of the K.F. results obtained in this work compares favourably with that reported in the literature^{12, 14}. Errors in K.F. work may be caused by reaction of K.F. reagent with compounds other than water, deterioration of the slight excess of K.F. reagent at the end point and moisture pick-up from the atmosphere.

From Table I it can be seen that the oven moisture content is in some cases as low as half the K.F. moisture. The higher K.F. results may be due to moisture contained within the sugar crystal which does not all migrate to the surface during the period of oven drying and is consequently not determined by the oven drying procedure. The presence of moisture contained within the sugar crystal has been observed by Powers¹⁰. Another reason for the high K.F. results might be the reaction of K.F. reagent with sucrose or other products in the raw sugar. Reaction with sucrose can be discounted since this phenomenon was not observed by Zerbán and Sattler¹⁴ working with pure sucrose solutions. Douwes Dekker³ recommended the K.F. method for the determination of moisture in final molasses, although his findings showed that K.F. results can be as much as 1.3% higher than those determined by vacuum drying. Even if these differences were due to reaction between K.F. reagent and non sucrose constituents of the molasses, their

TABLE II
Comparison of oven moistures with Karl Fischer moistures using the methanol slurring method

Percent Moisture

Sample	Karl Fischer			Oven Drying			Difference B-A	$\frac{A}{B} \times 100$
	1st Determn.	2nd Determn.	Mean A	1st Determn.	2nd Determn.	Mean B		
FX 13/1	0.210	0.211	0.211	0.288	0.285	0.287	0.076	74
FX 14/1	0.266	0.265	0.266	0.272	0.275	0.274	0.008	97
ZSM 14/1	0.185	0.187	0.186	0.195	0.200	0.198	0.012	94
ZSM 13/1	0.152	0.151	0.152	0.170	0.165	0.168	0.016	90
GD 11/1	0.283	0.285	0.284	0.348	0.360	0.354	0.070	80
IL 11/1	0.194	0.195	0.195	0.257	0.254	0.256	0.061	76
ZSM 9/1	0.177	0.181	0.179	0.196	0.205	0.201	0.022	89

effects on the accuracy of determination of moisture in a raw sugar of which at most 4% is molasses, would be far too small to account for the differences shown in column eight of Table I.

The possibility that oven drying determines only the moisture on the surface of the sugar crystal was subsequently investigated using a modification of the method of Bennett¹. The method entails the slurring of 10 g of the raw sugar with 30 ml methanol, adding excess K.F. reagent and back titrating the excess K.F. reagent after reaction with the water present, using standard water-in-methanol solution. The experiment was performed as rapidly as possible to avoid titrating moisture which may migrate to the surface from within the crystal. The back titration procedure was preferred for this experiment as the moisture which could migrate from inside the crystal would react with small excesses of iodine, making detection of the direct titration endpoint difficult. Standard water-in-methanol marketed by May and Baker containing ca. 5 mg water per ml. was used for this work. The results are reported in Table II.

The standard deviation for the back titration was found to be 0.0014 and for the oven drying 0.0046. The reproducibility of the back titration is exceptionally good. This could be due to the fact that the slurry is titrated immediately and no errors can arise due to atmospheric moisture migrating into the titration vessel during the one hour stirring time. From Table II it can be seen that the K.F. moistures are lower than the oven moistures, K.F. moistures being from 74 to 97% of the oven results. The differences between the K.F. and oven results reported in column eight (Table I) could be due to deterioration of the sugar during the drying period which would register as a loss in weight and therefore an increased moisture content. Perhaps a more likely cause of this difference would be the migration of part of the moisture within the crystal to the surface during the three hour oven drying period. This moisture would not have been determined by the Karl Fischer method.

Acknowledgements

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Discussion

Mr. Comrie: In Table II, where the oven dried samples gave a higher moisture content than the Karl Fischer method, the drying period was three hours at 105°C.

Had the samples been dried to constant weight, would the moisture content be even higher due to moisture migrating to the surface?

Mr. Oosthuizen: When the oven procedure is used to determine the moisture content of a sugar a constant weight is not reached due to the deterioration of sugars at the temperature used.

Mr. Jennings: What is the value of the moisture content as determined by the Karl Fischer method after oven drying?

Mr. Oosthuizen: A considerable quantity of the moisture in the sugar is removed by oven drying.

If you then use Karl Fischer the determination will be on the small amount of moisture remaining so the error will be large.

Mr. Comrie: There are three types of moisture namely, free, bound and occluded.

The free and bound moisture will probably affect the storage of sugars in silos, but will the occluded moisture remain in the crystal?

Mr. Oosthuizen: I intend to study this when a more sensitive method of detection is available.

If sugar was placed in a desiccator with phosphorus pentoxide and all the moisture that could possibly migrate from the crystal was removed, and the moisture that remained was determined it could possibly be termed the occluded moisture, or the moisture that would not migrate to the surface.

However, it is possible that occluded water does migrate from the crystal, so that in a silo, when the sugar has been conditioned, you are left only with moisture on the surface.

Mr. Rault: Is the water mechanically occluded in the crystal or is it part of the crystal structure?

Mr. Oosthuizen: The moisture is trapped—that is, the crystal is built around pockets of moisture.

Mr. Alexander (in the chair): Using a microscope, pockets of saturated syrup can be observed in candy and coffee crystals.

Mr. Howes: At the refinery we store up to 100,000 tons of raw sugar and this paper will assist us in interpreting storage losses.

Although we appeared to show a loss of 500 tons due to moisture in one year, this figure might well have been 1,000 tons had a more accurate determination been made.

With regard to moisture in the crystal, I do not think that there is moisture of hydration in a sucrose molecule. In pan boiling there must be scope for decreasing the amount of moisture held within the crystal.

Mr. du Toit: The difference between the Karl Fischer and the direct drying of a normal crystal and a finely ground crystal might indicate the presence of occluded moisture.

Dr. Graham: These results are disappointing as the Karl Fischer method has been considered recently as a possible alternative to the oven drying method, which is somewhat lengthy.

B
Referring to $\frac{\quad}{\quad} \times 100$ in Table 1, it would be
A

interesting to know if there is any correlation between the values shown and the pol of the sugar.

If there is a correlation, the Karl Fischer method could be used and corrected back to a familiar safety factor level.

Mr. Jennings: Regarding correlation, all the sugars used were high pol so the variation was not great.

The refinery had hoped to use the Karl Fischer method for moisture in refined sugar, where the differences between total moisture and surface moisture are greater.

It has been done overseas but with mixed success.

Occluded moisture is tied up with the amount of conglomerate so the problem can be overcome by better boiling.

Mr. Francis: Owing to the large amount of conglomerates in our sugar our total moisture content is high.

But overseas, where the moisture is lower, the Karl Fischer method is being used, although time was needed to get reproducible results. One problem is leakage into the equipment from the atmosphere.

The British Sugar Corporation use Karl Fischer for routine determinations but use the manual rather than the automatic apparatus as the former is entirely of glass construction and there is less chance of leakage.

Does Mr. Oosthuizen think that the Karl Fischer method can be used for routine raw sugar moisture analysis and would it have to be carried out by a highly qualified chemist?

Mr. Oosthuizen: If most of the troublesome moisture has been removed from sugar stored in a silo then the slurry method can be used to measure surface moisture, and the procedure is not too involved to be used on a routine basis.

For research purposes manual equipment, which can be easily modified, would be more suitable than an automatic instrument, which it would be advisable to use for routine work.

Mr. Francis: Where conglomerates are not high then bound and free moisture are almost the same and that is when the Karl Fischer method can be used.

Mr. MacGillivray: If the differences in the two methods are compared in Table I and Table II, Karl Fischer figures are higher in the first table and lower in the second. In both instances the oven drying appears to determine part of the moisture within the crystal, whereas the Karl Fischer method appears to determine all of it in the first table and none in the second.

Would the oven drying procedure be a guide to the storing quality of sugars if the part of the moisture within the crystal determined is the part that might cause trouble in storage?

Mr. Oosthuizen: If it is true that during the three hour drying period the moisture that could cause trouble is determined then I agree with that.

Mr. Muller: Gas circulating through the titration vessel should prevent moisture migrating into the vessel.

Mr. Oosthuizen: Although this was done, reproducibility did not improve because the trouble is due to atmospheric moisture while the titration vessel is being connected to the equipment.

Mr. Jennings: Sugar analysis never quite adds up to one hundred, probably because not all moisture present has been determined. Even if our approach to safety factor might have to be changed I think another method of moisture determination should be introduced.

All three papers today have suggested ways to improve the accuracy of analytical determinations and every effort should be made to introduce such methods.

I understand that Mr. Bruijn has been working on a gas chromatographic method of determining moisture in sugar.

Mr. Bruijn: We have the same difficulty as Mr. Oosthuizen with atmospheric moisture but whereas a half a milligram upsets his calculations, in the gas chromatographic method we deal with .01 of a milligram and that makes the problem more serious. However, we are trying to improve the method.

Mr. Alexander: By using the Karl Fischer method and determining the moisture on the surface of the crystal it might be possible to get a more meaningful safety factor.

The principle of the safety factor is that you are protecting sugar by ensuring that the layer of syrup surrounding the crystal is sufficiently concentrated so that the osmotic pressure is too high to allow multiplication of micro-organisms in the film.

We have recently been applying syrup films to crystals and have discovered that the use of safety factor as a guide to storing quality of a sugar is unreliable because only the moisture content and polarisation are taken into account, the composition of the syrup film not being determined. If the syrup contains inverted material a brix below 75°C can be used in order to obtain the correct safety factor.

Safety factor as used at present is not a completely reliable indicator.