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Proposal of a new reference method for determining water content in butter oil

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Abstract

Determination of the relatively low water content in butter oil by desiccation methods is practically impossible. It is therefore carried out by Karl Fischer titration. To increase the solubility of butter oil in methanol, the main component of the working medium, a non-polar solvent is necessary. In an existing reference method, chloroform (trichloromethane) is prescribed. The aim of this work was the replacement of this toxic substance. It is shown that 1-octanol is a good alternative. It has the additional benefit that butter oil solubility is higher in a mixture of methanol and 1-octanol than in a mixture of methanol and trichloromethane, which conserves solvent. In addition, the sample size can therefore be higher, and this is an advantage for more heterogeneous products. The method presented is proposed as a new reference. It is also applicable to other non-polar samples.
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Keywords: Butter oil; Water determination; Karl Fischer titration; Reference method

1. Introduction

Butter oils contain less than 1 g water per 100 g of product. The accurate determination of low amounts of water in such a non-polar matrix by desiccation techniques is practically impossible. The Karl Fischer titration is therefore the method of choice.

According to a draft of the International Organisation for Standardisation (ISO) and the International Dairy Federation (IDF) (2002), pyridine-free one- or two-component reagents with a water equivalent of 5 mg H_2O/ml have to be used. The titration has to be carried out with simple laboratory materials such as, conical flasks, glass burettes and rubber stoppers. The alternative use of automatic titrators is mentioned only marginally. As butter oil is not soluble in methanol, usually the main component of the working medium, chloroform, (trichloromethane) is prescribed as additional solvent.

The aim of this work was the development of a new method to determine water content in butter oil and similar products using modern titration equipment and avoiding the addition of toxic trichloromethane.

2. Materials and methods

The method was developed with a titrator DL 38 from Mettler-Toledo, Schwerzenbach, Switzerland, and then also tested with a KF Titrino 701 from Metrohm, Herisau, Switzerland. The two-component technique with Hydranal-Titrant 2 as titrating solution and Hydranal-Solvent with additional solvents (see Section 3) as working medium was applied. All chemicals were from Sigma-Aldrich Laborchemikalien, Seelze, Germany. The two-component technique was used because of the higher reaction rate. Hydranal-Solvent contains SO_2 and the base so that these reaction components are present in excess, thus accelerating the reaction. In the one-component technique all the necessary reaction components (but for the alcohol which is the working medium) are in the titrating solution. Hydranal-Titrant 2 was preferred to Hydranal-Titrant 5 (as prescribed in the earlier mentioned reference) because of its lower water equivalent of 2 mg H_2O/ml and the resulting higher reagent consumption with better resolution of the volume added. The titrations were carried out at 40 °C in a titration vessel with thermostatic jacket. The end point was determined by the voltametric method.

Some samples were provided by the Centraal Orgaan voor Kwaliteitsaangelegenheden in de Zuivel (COKZ), Leisden, The Netherlands. Other samples (Butaris and Bonita) were purchased in German shops.

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The method was also applied to plant oils (olive oil and sunflower oil) as well as to margarine and frying fats (Biskin Spezial, Rama Culinesse, Becel, Lätta) bought in German shops.

3. Results and discussion

Standard working media for the Karl Fischer titration contain methanol (or ethanol, see later) as solvent. To improve the solubility of non-polar substances, the addition of non-polar solvents is necessary. It is also principally possible to replace methanol in the working medium by another alcohol which must react in the same stoichiometric way as methanol in the Karl Fischer reaction. Thus, ethanol-based reagents have been introduced in the market (Schöffski, 1998). This alcohol is, however, too short-chained to dissolve butter oil. When 1-propanol is used as working medium, a residue is observed on the electrodes (Grünke & Wünsch, 2000; Langer & Isengard, 1998; Wünsch & Grünke, 1998). This deposit can be avoided by the addition of methanol (Langer & Isengard, 1998).

Experiments with a mixture (1:1 by volume) of 1-hexanol and methanol as working medium were carried out in comparison with a mixture of trichloromethane and methanol (1:1 by volume). Table 1 shows the results. The coefficients of variation of the results obtained for the commercially purchased products are much higher than those of the samples provided by COKZ, which denotes their heterogeneity. The values of water content found with the 1-hexanol-containing working medium lie in the same range as those with the working medium containing trichloromethane. The method would therefore be principally applicable. As with (pure) 1-propanol, however, a residue is formed on the electrodes which has to be removed after at least two consecutive determinations. This limits the number of analyses that can be carried out in the same working medium without opening the cell. This fact is rather inconvenient as conditioning is needed after each opening of the titration cell.

Experiments with 1-octanol were more successful. More consecutive measurements are possible in the same working medium as no or only a slight residue on the electrodes is formed. Table 2 gives the results. Again, the COKZ samples proved to be more homogeneous than the purchased products. The results when using 1-octanol are comparable to those with trichloromethane.

The method was tested with two different titrators. The DL 38 has a standard setting of 20 μA for the polarising current and of 100 mV for the stop voltage in the voltametric mode. The corresponding values of the KF Titrino 701 are 50 μA and 250 mV. The setting of the KF Titrino 701 was adapted to the values of the DL 38 for this comparative experiment. Table 3 shows the comparative results. Data obtained with the KF Titrino 701 tend to be lower than the values obtained with the Mettler-Toledo device. This may be due to an obviously tighter titration cell. The drift observed for the KF Titrino 701 was usually clearly lower than that of the DL 38. But the results lie within the same range, so that the method can be transferred from one titrator to the other.

The solubility of butter oil is higher in a mixture of methanol and 1-octanol than in a mixture of methanol and trichloromethane. The sample size can therefore be increased, a measure that may lead to lower scattering of the results for heterogeneous samples. This effect could be confirmed as demonstrated in Table 4.

Determinations are in principle possible at room temperature. The temperature of 40 °C was chosen to

Table 1
Water content in g/100 g of different butter oil samples determined at 40 °C using Hydranal-Titrant 2 and the working media Hydranal-Solvent/trichloromethane (1:1 v/v) and Hydranal-Solvent/1-hexanol (1:1 v/v), sample size 2 g, 10 replicates each

Sample	Hydranal-Solvent/ trichloromethane		Hydranal-Solvent/ 1-hexanol	
COKZ B386	0.0610±0.0032	(±5.2%)	0.0787±0.0076	(±9.7%)
Butaris	0.0963±0.0206	(±21.4%)	0.0944±0.0164	(±17.3%)
Bonita	0.1081±0.0206	(±19.1%)	0.0989±0.0221	(±22.4%)

Table 2
Water content in g/100 g of different butter oil samples determined at 40 °C using Hydranal-Titrant 2 and the working media Hydranal-Solvent/trichloromethane (1:1 v/v) and Hydranal-Solvent/1-octanol (1:1 v/v), sample size 2 g, 10 replicates each

Sample	Hydranal-Solvent/ trichloromethane		Hydranal-Solvent/ 1-octanol	
COKZ Nr.1	0.0427±0.0018	(±4.3%)	0.0442±0.0018	(±4.2%)
COKZ B386	0.0610±0.0032	(±5.2%)	0.0706±0.0031	(±4.4%)
Butaris	0.0963±0.0206	(±21.4%)	0.1167±0.0133	(±11.4%)
Bonita	0.1081±0.0206	(±19.1%)	0.0914±0.0200	(±21.9%)

Table 3
Water content in g/100 g of different butter oil samples determined at 40 °C with different titrators using Hydranal-Titrant 2 and Hydranal-Solvent/1-octanol (1:1 v/v), sample size 2 g, 10 replicates each (nine replicates only for COKZ T15 with Metrohm titrator)

Sample	Mettler–Toledo DL 38		Metrohm KF Titrino 701	
COKZ B383	0.0675±0.0052	(±7.8%)	0.0658±0.0038	(±5.8%)
COKZ B386	0.0706±0.0031	(±4.4%)	0.0674±0.0050	(±4.2%)
COKZ T15	0.0556±0.0052	(±9.4%)	0.0407±0.0043	(±10.5%)
COKZ T44	0.0497±0.0023	(±4.5%)	0.0511±0.0034	(±6.5%)
Butaris	0.1167±0.0133	(±11.4%)	0.0862±0.0101	(±12.3%)
Bonita	0.0914±0.0200	(±21.9%)	0.0682±0.0125	(±18.4%)

Table 4
Water content in g/100 g of different butter oil samples determined at 40 °C using Hydranal-Titrant 2 and Hydranal-Solvent/1-octanol (1:1 v/v), 10 replicates each

Sample	Sample size 2 g		Sample size 5 g	
COKZ T15	0.0556±0.0052	(±9.4%)	0.0450±0.0021	(±4.6%)
COKZ T44	0.0497±0.0023	(±4.5%)	0.0509±0.0014	(±2.7%)

Table 5
Water content of butter oil sample COKZ Nr.3 determined at 40 °C with different electrical end-point criteria using Hydranal-Titrant 2 and Hydranal-Solvent/1-octanol (1:1 v/v), sample size 5 g

Polarising current (μA)	Stop voltage (mV)	Replicates	Water content (g/100 g)	
20	100	11	0.0441±0.0034	(±7.71%)
30	150	11	0.0439±0.0025	(±5.79%)
40	200	10	0.0448±0.0018	(±4.06%)
50	250	10	0.0465±0.0017	(±3.69%)

gain time. The average titration time for 10 replicates of butter oil COKZ Nr.3 (sample size 5 g) at 30 °C was 262 s and 220 s at 40 °C, yielding water contents of 0.0440±0.0037 g/100 g and 0.0441±0.0034 g/100 g, respectively.

In a further experiment, the possible influence of the electrical parameters set for the end-point detection was investigated. As shown in Table 5 no significant differences were observed.

Eventually, the method was tested by several operators. Table 6 gives the results. Operator A had analysed the sample some days before the other operators. It is therefore possible that the water content of the sample was slightly changed during storage. It is remarkable that the results are very consistent, although some of the operators have no or not much experience with the Karl Fischer titration. The method can therefore be regarded as robust.

The method was also applied to sunflower oil, olive oil, margarine and frying fat. Determinations were possible with good precision, as is shown in Table 7.

4. Conclusion

Water content in butter oil can be determined by Karl Fischer titration using a mixture of methanol and 1-octanol in a volume ratio of 1:1 as working medium. Analysis time is shorter at 40 °C than at room temperature. The method can be carried out with different titrators and with different electrical end-point criteria.

Table 6
Water content of butter oil sample COKZ Nr.1 determined by different operators with different titrators (polarising current 20 μA, stop voltage 100 mV) at 40 °C using Hydranal-Titrant 2 and Hydranal-Solvent/1-octanol (1:1 v/v), sample size 5 g, 10 replicates each

Operator	Titrator	Water content (g/100 g)	
A	DL 38	0.0442±0.0018	(±4.2%)
B	DL 38	0.0547±0.0022	(±4.1%)
C	DL 38	0.0556±0.0026	(±4.7%)
D	DL 38	0.0527±0.0023	(±4.4%)
E	KF Titrino 701	0.0515±0.0023	(±4.3%)
F	KF Titrino 701	0.0500±0.0037	(±7.4%)

Table 7
Water content of plant oils, margarine and frying fats determined at 40 °C using Hydranal-Titrant 2 and Hydranal-Solvent/1-octanol (1:1 v/v), 10 replicates each

Sample	Sample size (g)	Water content (g/100 g)	
Sunflower oil	5	0.0199±0.0010	(±5.2%)
Olive oil	5	0.1008±0.0018	(±1.8%)
Becel Diätmargarine	0.03	18.10±0.18	(±1.0%)
Rama Culinesse	0.04	15.98±0.31	(±1.9%)
Biskin Spezial	0.03	16.12±0.42	(±2.6%)
Lätta	0.01	45.97±3.17	(±6.9%)

It is proposed that the method presented should replace the method using toxic trichloromethane (chloroform) as additional solvent in the working medium. The successful application to other products with high fat content indicates that the method may generally be applicable to such samples. This will be tested in further investigations.

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