University of Hohenheim
Institute of Food Technology
Food Analysis

Proposal of a New Reference Method to Determine the Water Content of Dried Milk Products

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Background

→ Diploma thesis
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Institute of Food Technology
Food Analysis, Prof. H.-D. Isengard

→ ISO/FDIS 5537: Dried milk - Determination of moisture content (Reference method)
Development of a new drying oven on the basis of the classic drying oven,
IDF (International Dairy Federation) standard

→ Comparison of two drying methods with the Karl Fischer titration

→ Critical view on accuracy and precision of the COKZ (Centraal Orgaan Voor Kwaliteitsaangelegenheden in de Zuivel)-oven

Samples

→ Dried milk products
→ Provided by Nestlé, Vers-chez-les-Blanc
→ 32 samples with different composition
→ Tested: 17 samples + pure α-lactose, lactose, baking starch
→ E.g. baby food, coffee whitener, protein concentrate, whey powder, (un-)skimmed milk powder
→ Differing in content of protein and fat
in content and kind of carbohydrates
and in water content

Binding types of water in milk powders

→ Water bound to proteins,
difficult determination,
structure of molecule changes

→ Crystallised water of α-lactose,
also difficult determination,
high temperatures destroy the sample

→ Water on the surface,
in pores and spaces of the food,
separation and determination is easy,
no change of the structure

Moisture content and water content

→ Conventional method: Determination of moisture content
by drying the samples at high temperatures (methods like the drying oven, drying by infrared light, microwaves or the halogen drying)

→ Problems:
mass loss is determined
→ evaporated water, volatile substances and also substances produced by reactions in the heat
→ other volatile substances lead to an increased loss of mass (of moisture?)
→ strongly bound water is not/not entirely determined

→ Karl Fischer titration detects the total water content of a sample by a selective chemical reaction

Determination of the moisture / water content in dried dairy products

Comparison of methods

→ Conventional drying oven

→ Drying oven, developed especially for milk powders

→ Karl Fischer titration

→ Precision

→ Selectivity

→ Handling

→ Time

Drying oven (“Reference Dryer”)

→ Reference method since 2003
→ Exactly 5 g of the samples dried at 87 °C
→ Constant gas flow (33 ml/min) through the samples
→ Drying time: 5 h
→ No control of the constancy of mass
→ Difference of mass moisture content

→ Results depend strongly on these parameters

Several variations of the RD standard method

→ Change of the drying temperature (80 °C, 102 °C)
→ Change of the drying time
→ Variation of the sample weight
→ Replicates on the same day and on following days
→ Increase of the gas flow
→ Change of drying time and temperature at the same time
(Comparison with the traditional method)

Karl Fischer titration

→ Most important and most frequently used method for the determination of water content

→ Total water of the sample (free as well as bound water) is selectively detected

→ Specific method, matrix interferences are eliminated

→ No method paraphrased as ´moisture determination´or ´drying loss´, real water determination method

→ Destination by a titration

→ Use of chemicals

Karl Fischer titration

Volumetric determination with two-component titration technique:

→ Working medium / solvent: solution of imidazole and sulphur dioxide in methanol

→ Titration agent: solution of iodine in methanol

→ Measured value: consumption of titration agent

→ End point indication: electrometric indication,
platinum electrodes in the solution,
constant current,
voltage is measured,
end point: voltage decreases below a set value

Karl Fischer titration

Variations of the standard procedure

→ Increase of the temperature

→ Different sample weights

→ Samples pre-dissolved in titration cell

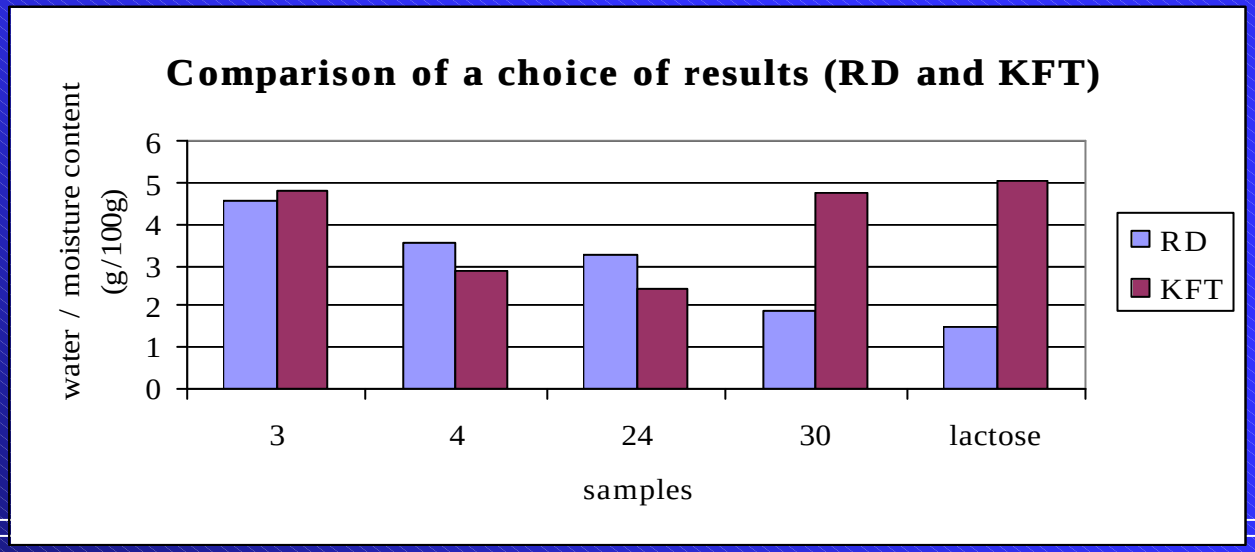
→ Different additional solvents:

- 1-octanol
- formamide
- t.-butylmethylether
- chloroform
- 1-propanol

Results

Comparison of a choice of results, Reference Dryer (RD) and Karl Fischer titration (KFT)

sample	n	⌀ ± s / g/100g (RD)	n	⌀ ± s / g/100g (KFT)
3	3	4.57 ± 0.82	10	4.81 ± 0.07
4	5	3.54 ± 0.41	10	2.88 ± 0.04
24	5	3.26 ± 0.25	3	2.43 ± 0.03
30	3	1.88 ± 0.34	3	4.75 ± 0.04
lactose	3	1.46 ± 0.07	4	5.05 ± 0.06



Results

variations of the RD standard method

→ variation of the *sample weight*, 87 °C, 33 ml/min, n=2

sample	weight / g	☞ / g/100g
no. 9	2	5.31
	3	4.21
	4	4.43
	5	4.10
	6	3.73

Results

variations of the RD standard method

→ variation of drying *time* and *temperature* : 102 °C, 5 g, 33 ml / min

sample	time / h	n	$\bar{x} \pm s$ / g / 100g
α-lactose	2	2	1.79
	3	4	2.37 ± 0.56
	4	6	2.65 ± 0.51
	5	6	3.00 ± 0.32
	6	4	3.17 ± 0.30
	7	2	3.35

α-lactose with standard parameters: 1.08 ± 0.07 %

α-lactose dried in traditional drying oven: 0.67 %

Results

variations of the RD standard method

→ sample no. 30 (high lactose content) dried in the RD (standard parameters), then titrated with Karl Fischer technique (0.1 g, 50 °C, pure solvent)

mass loss in RD: 2.20 g/100g (n=1)

water content by titration: 3.58 ± 0.10 g/100g (n=3)

Results

variations with the KFT

→ variation of the *sample weight*, pure solvent as working medium, 50 °C

sample	n	⌀ ± *s* / g / 100g (0.1 g)	VK	n	⌀ ± *s* / g / 100g (0.5 g)	VK
3	11	4.55 ± 0.06	1.23	3	4.87 ± 0.03	0.70
4	10	2.99 ± 0.04	1.40	10	3.00 ± 0.05	1.70
24	3	2.63 ± 0.02	0.70	3	2.49 ± 0.02	0.88
30	10	4.82 ± 0.06	1.43	4	4.89 ± 0.03	0.61
lactose	3	5.07 ± 0.06	1.25	3	5.10 ± 0.01	0.11

Results

variations with the KFT

→ variation of *working medium*: 0.5 g, 50 °C,

30 ml pure solvent compared to 10 ml formamide + 20 ml solvent

	pure solvent			formamide addition		
sample	n	⌀ ±*s*/g/100g	VK	n	⌀ ±*s*/g/100g	VK
3	3	4.87 ± 0.03	0.70	10	4.81 ± 0.07	1.36
4	10	3.00 ± 0.05	1.70	10	2.88 ± 0.04	1.49
24	3	2.49 ± 0.02	0.88	4	2.43 ± 0.03	1.27
30	4	4.89 ± 0.03	0.61	3	4.75 ± 0.04	0.75
lactose	3	5.10 ± 0.01	0.11	4	5.05 ± 0.06	1.11

Summary

→ Different results, depending on analytical method and composition (especially α-lactose)

→ Drying methods have week precision and reproducibility and are much more time consuming than KFT:

conventional drying oven: at least 6.5 h for 10 samples, relative standard deviation: 1-17 %, no mass constancy

Reference Dryer: at least 7.5 h for 8 samples, relative standard deviation: 2-30 % ⇨ no enhancement of precision

Summary

KFT: highest precision, proved by shape of titration curves,
preferentially used method
relative standard deviation: max. 4 %, normally 1-2 %,
10 samples can be analysed 1 hour

→ Advantage of KFT: detects all the water,
is applicable for all kinds of dried dairy products
independent of the lactose content

→ Question: Can this new drying oven method really be called a “reference method”?

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Prof. H.-D. Isengard for making this work possible

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Funke und Gerber for providing the Reference Dryer

Conventional drying oven

→ Well-known analysis of water content

→ Old prescription for milk powders:
heat up the samples at suitable temperature (102 °C) for special time / duration (2+1 h)

→ Difference of mass moisture content of the sample

→ No ´water content´:

→ Additionally to the water of the product, other volatile substances are released by high temperatures

→ Chemically combined water to the α-lactose is not entirely separated at 102 °C

→ Wrong results by water which arises by reactions in the heat

→ Maillard reaction: different products, brown colour of the samples


Trockenschrank: getrocknet
(102°C)
ungetrocknet
24
26
27
4
3
22
21


FUNKE
GERBER