APPLICATION NOTE

elementar
EXCELLENCE IN ELEMENTS

Dumas analysis in milk products

Introduction

The protein content of milk plays an important role in its taste and quality, as well as the properties of resulting products. Therefore, the protein content of milk and other dairy products is an important parameter for quality control.

There are three widely-used methods for determining the protein content of dairy products: Dumas, Kjeldahl, and Near Infrared Reflectance spectroscopy (NIR). The Dumas method involves burning the sample in a high-temperature oven (typically above 900 °C) followed by a reduction reactor, converting all the nitrogen in the sample to N_2, which is then measured. The Kjeldahl method digests the sample in a heated, strong acid for 90 minutes, converting all the nitrogen in the sample to ammonia, which is distilled and titrated. Both the Dumas and Kjeldahl methods are, therefore, actually total nitrogen determinations. The protein content is calculated by multiplying by an appropriate factor. The NIR method involves determining what wavelengths of light are absorbed by a sample and relating that to protein content. This method directly measures protein content, but requires sample-specific calibrations with another method.

Of the three methods, the Kjeldahl method is the slowest, most labor intensive, and has the highest operating costs. The fast, automated, reliable analysis by Dumas is a smart choice for any dairy product sample, either as a primary analyzer or for calibration of an NIR system.

MILK AND DAIRY PRODUCTS

rapid MAX N exceed

Instrumentation

With over 110 years of experience producing elemental analyzers and more than 50 years of experience producing dedicated Dumas N/Protein analyzers, Elementar recently released the rapid MAX N exceed analyzer, which combines high-throughput and ease of operation with reliable determination of nitrogen, even at low concentrations and in difficult samples. The 90-position autosampler utilizes stainless steel crucibles that can hold up to 5 mL of liquid or 5 g of solid. All positions of the random-access autosampler are always available, which combined with easy-to-use software means time-critical samples can easily be promoted to be the next sample measured.

The crucibles are introduced to the combustion furnace by a gripper arm which includes the oxygen inlet. By dosing the oxygen directly at the sample, less oxygen is necessary to get complete combustion, which is a key aspect of our unrivaled low price-per-sample. Further savings are realized by our proprietary EAS REGAINER® and EAS REDUCTOR® technology. This system utilizes a non-toxic, metal-free method for binding excess oxygen and regenerating the metals that reduce the nitrogen oxides from combustion to nitrogen gas for reliable detection. In this way, the reduction tube filling can analyze over 1000 samples before needing replacing, greatly reducing one of the major cost drivers for Dumas analysis without compromising analytical performance. Additional savings can be realized by using argon, instead of the typical helium, as a carrier gas.

Because the rapid MAX N exceed can measure up to 1 g of organic material, samples can be quite heterogeneous, such as milkshakes or yogurt with fruit, and still yield accurate, reproducible results. With a robust three-stage gas drying system, routinely measuring several grams of aqueous solutions, such as milk, present no challenges to the instrument. Because the same, upright crucibles can be used for liquids or solids, switching between liquid and solid samples requires no additional chemicals or materials, such as sample liners or absorbers.

A case study

The company Immergut has been producing milk and related products for over 100 years, and now has a product portfolio of about 300 products across several brands, spanning a wide range of milk- and fruit-based drinks. With increasing demands on their quality control lab, Immergut needed a faster alternative to their existing Kjeldahl protein determination. In the fall of 2016, a rapid MAX N exceed was installed in their lab and personnel were trained in its use and maintenance in just four hours. Over the course of 14 working days, nearly 800 samples were analyzed with the rapid MAX N exceed and comparison measurements were also made with the existing Kjeldahl systems (see Table 1). The Dumas measurements were completed in triplicate and the Kjeldahl values in duplicate (except where no repeatability is given, in which case only one determination was made). The Dumas and Kjeldahl measurements were all completed at Immergut's facility by their personnel. A subset of the samples was also sent to an external lab performing Kjeldahl analysis.

Immergut

Table 1. A selection of sample types and the Kjeldahl values for %N and %protein.

	SAMPLE	N [%]	PROTEIN [%]
1	Yogurt Drink Raspberry	0.307	1.96
2	Cream	0.309	1.97
3	Milkshake Cafe	0.342	2.18
4	Milkshake Vanilla	0.393	2.51
5	Milkshake Chocolate	0.434	2.77
6	Milkshake Strawberry	0.470	3.00
7	Lactose-free Milk	0.495	3.16
8	Healing Whey	0.496	3.17
9	Whole Milk	0.519	3.31
10	Yogurt Drink Strawberry-Banana	0.521	3.32
11	Goat milk	0.522	3.33
12	Soy Drink Chocolate	0.534	3.41
13	Low-fat Milk	0.561	3.58
14	Diet Drink Yogurt Strawberry	0.562	3.58
15	Soy Drink Nature	0.568	3.62
16	Yogurt Drink Passion Peach	0.603	3.85
17	Cappuccino Milk	0.603	3.85
18	Protein Drink/Nutrition Suppl. Van	0.628	4.01
19	Sports Drink Chocolate	0.628	4.01
20	Sports Drink Mocha	0.634	4.04

	SAMPLE	N [%]	PROTEIN [%]
21	Yogurt Drink Banana	0.646	4.12
22	Yogurt Drink Red Fruits	0.693	4.42
23	Sports Drink Chocolate	0.873	5.57
24	Sports Drink Strawberry	0.876	5.59
25	Protein Drink Vanilla	0.908	5.79
26	Sports Drink Vanilla	0.917	5.85
27	Sports Drink Chocolate	0.972	6.20
28	Protein Drink Vanilla	0.988	6.30
29	Coconut Water Pineapple	0.993	6.34
30	Coconut Water Natural	1.016	6.48
31	Coconut Water Pure	1.039	6.63
32	Protein Drink Vanilla	1.119	7.14
33	Protein Shake Cafe	1.129	7.20
34	Protein Drink Chocolate	1.154	7.36
35	Protein Water Passion Fruit	1.161	7.41
36	Protein Shake Strawberry	1.165	7.44
37	Protein Drink Chocolate	1.290	8.23
38	Protein Drink Strawberry	1.317	8.40
39	Protein Shake Vanilla	1.495	9.54

Comparison with DIN EN ISO 14891

In DIN EN ISO 14891 "Milk and milk products – Determination of nitrogen content – Routine method using combustion according to the Dumas principle", the precision requirements for repetitions with the same technique within labs (repeatability, r_{95}) and between labs (reproducibility, R_{95}) are given. The precision requirement is that two independent measurements should have an absolute difference in mass percent nitrogen less than the matrix-dependent accepted value. As a conservative estimate for the variety of samples in this study, the requirement for reduced fat milk (r_{95} of 0.080 %N and R_{95} of 0.093 %N) was applied to all samples. Figure 1 shows the difference of the two Kjeldahl measurements and the maximum difference of the three Dumas measurements for each sample. Both methods exceeded the repeatability requirement by a factor of two or better for all samples.

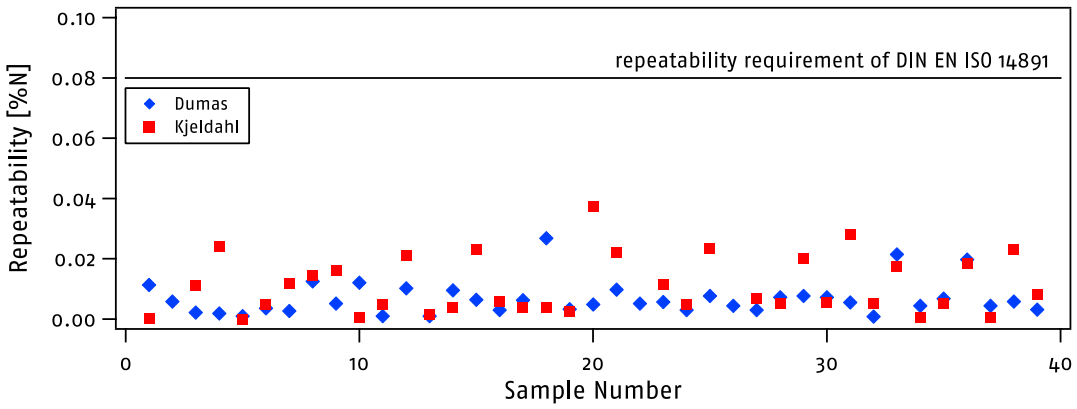

Figure 1. A comparison between the difference of two Kjeldahl analyses of each sample (red squares) and the maximum difference of three Dumas analyses of each sample (blue diamonds).

Although this case study involves different techniques, the reproducibility requirements of the standard would provide a reasonable benchmark for establishing the equivalence of these methods. Figure 2 shows the largest difference between a Kjeldahl value and Dumas value for each sample. For comparison, the largest difference between the Kjeldahl results from the external lab and Immergut is also shown. Both comparisons exceeded the reproducibility requirement by a factor of two or better for all samples. It should also be noted that neither the Dumas nor external lab values showed systematic variation from the Immergut Kjeldahl values.

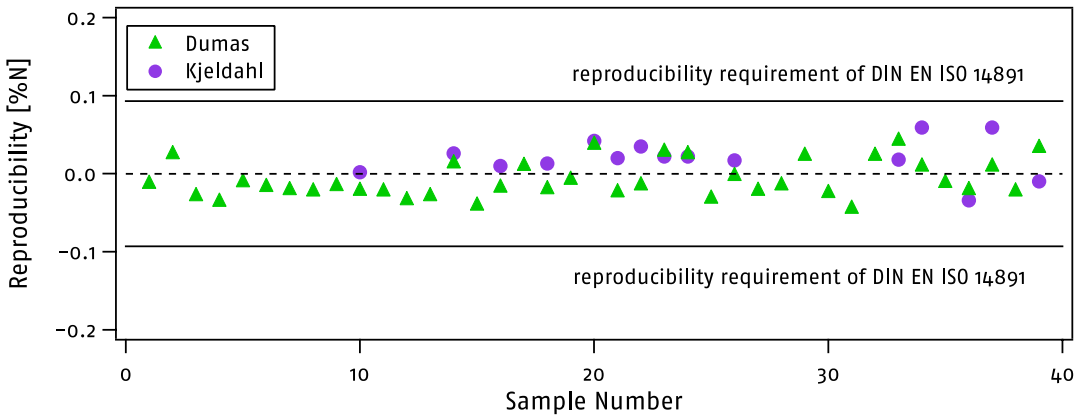

Figure 2. A comparison of the largest difference between a Kjeldahl and a Dumas value for each sample analyzed by Immergut (green triangles) and the largest difference between the Kjeldahl results from the external lab and Immergut (purple circles). For both series, values are positive or negative reflecting measurements above or below the Immergut Kjeldahl value, respectively.

Summary

For the determination of protein in milk and milk products, both the Dumas and Kjeldahl analysis techniques demonstrate high quality analytical performance. In the case of an example set of 39 products from the company Immergut, the average repeatability of a newly installed rapid MAX N exceed and the existing Kjeldahl technique were 0.007 and 0.011 %N absolute, respectively. The average reproducibility of the measurements between the Kjeldahl systems at Immergut and the rapid MAX N exceed and between Immergut and an external Kjeldahl analysis were 0.022 and 0.026 %N absolute, respectively. Although the analytical performance of both methods is well within the requirements of international standards, the rapid MAX N exceed performed better than Kjeldahl analysis in both comparisons.

In addition to superior analytical performance, Immergut was able to realize further advantages with the rapid MAX N exceed over Kjeldahl analysis, including lower operating costs (0.50€ per sample), improved throughput, and ease of use. With an average analysis time around six minutes, calibrations for NIR systems can now be completed in a timely manner, ensuring high-quality results in all aspects of production.

These advantages and improvements make the decision to purchase a rapid MAX N exceed a wise choice for any producer of milk and other dairy products hoping to reduce costs and increase productivity, while at the same time getting better quality results.

Elementar Analysensysteme GmbH
Elementar-Straße 1 · 63505 Langenselbold (Germany)
Phone: +49 (0) 6184 9393-0 | info@elementar.de | www.elementar.de

Art.-No. 05 005 273, 02 / 2017 A