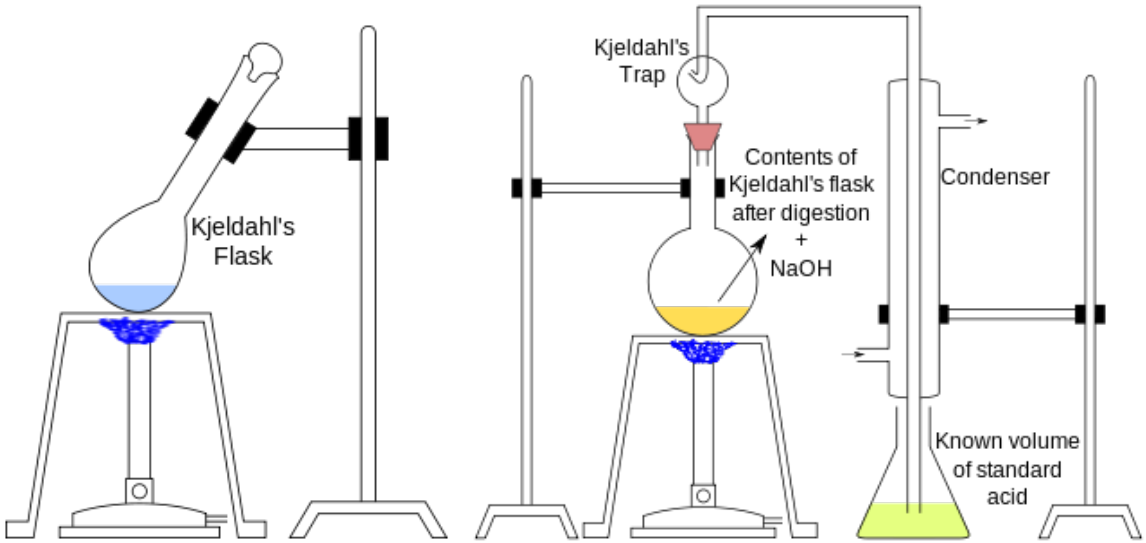
elementar
EXCELLENCE IN ELEMENTS

Kjeldahl and Dumas: Comparing Methods

Kjeldahl Method



1. Digestion in hot H_2SO_4
   - Hg-Catalyst?
2. Neutralization with NaOH
3. Distillation of Ammonia
4. Captured in Boric acid
5. Titration with HCl

Kjeldahl Method

Advantages

- Low initial investment: If not automated
- Established: Many standards
- Robust: Salty samples are no problem
- Larger samples sizes are possible

Disadvantages

- Labor-intensive: Two systems
- Slow: 100 minute analysis time
- Not environmentally friendly
- Only measures organic nitrogen compounds

Dumas Method

1. High-temperature combustion
   Sample -> CO_2, NO_x, H_2O, etc.
2. Reduction
   CO_2, NO_x, H_2O -> CO_2, N_2, H_2O
3. Gas separation
   CO_2, N_2, H_2O -> N_2
4. Detection with Thermal Conductivity Detector

Dumas Method

Advantages

- Fast: 4 minute analysis time
- Inexpensive : <1 € / sample
- Easily automated
- Environmentally friendly: No hazardous or toxic waste

Disadvantages

- Analyzer cost: No manual option
  - Still cheaper than automated Kjeldahl systems
- Possible problems with salty samples
  - Can be mitigated
- Limited number of standards
  - Not true!
- Measures all nitrogen compounds: Does not match Kjeldahl values?

National and International Norms: Grains

Norm	Organization	Title	Year First Approved
AGF 150	Association of Cereal Research [Arbeitsgemeinschaft Getreideforschung e.V.]	Determination of Protein Content [Bestimmung des Proteingehaltes]	2000
AOAC 990.03	AOAC International [Formerly Association of Official Analytical Chemists]	Protein (Crude) in Animal Feed	1990
AOAC 992.23	AOAC International [Formerly Association of Official Analytical Chemists]	Crude Protein in Cereal Grains and Oilseeds	1992
AOCS Ba 4e93	American Oil Chemists' Society	Generic Combustion Method for Determination of Crude Protein	1993
DIN EN ISO 16634-1	German Institute for Standardization [Deutsches Institut für Normung], European Norm & International Organization for Standardization	Food products - Determination of the total nitrogen content by combustion according to the Dumas principle and calculation of the crude protein content - part 1: Oilseeds and animal feeding stuff	2008
DIN EN ISO 16634-2	German Institute for Standardization [Deutsches Institut für Normung], European Norm & International Organization for Standardization	Cereals, pulses, milled cereal products, oilseeds and animal feeding stuffs - Determination of the total nitrogen content by combustion according to the Dumas principle and calculation of the crude protein content	2010
ICC 167	International Association for Cereal Science and Technology	Determination of crude protein in grain and grain products for food and feed by the Dumas Combustion Principle	2000

National and International Norms: Beer

Norm	Organization	Title	Year First Approved
AOAC 997.09	AOAC International [Formerly Association of Official Analytical Chemists]	Nitrogen in beer, wort and brewing grains. Protein (total) by calculation. Combustion method.	1997
ASBC Protein Methods	American Society of Brewing Chemists	Protein Methods	1992
EBC	European Brewery Convention	Total nitrogen in beer, wort and malt using the Kjeldahl and Dumas method	1999
MEBAK 2912	Central European Commission for Brewing Analysis [Mitteleuropäische Brautechnische Analysenkommission]	Combustion Methods Using Dumas [Verbrennungsmethode nach Dumas]	1993

National and International Norms: Fertilizer

Norm	Organization	Title	Year First Approved
AOAC 993.13	AOAC International [Formerly Association of Official Analytical Chemists]	Nitrogen (Total) in Fertilizers	1993
DIN EN 13654-2	German Institute for Standardization [Deutsches Institut für Normung] & European Norm	Soil improvers and growing media – Determination of nitrogen - Part 2: Dumas method	2001
LUFA 3.5.2.7	Association of German Agricultural Analytic and Research Institutes [Landwirtschaftliche Untersuchungs- und Forschungsanstalt]	Determination of Total Nitrogen in Fertilizer [Bestimmung von Gesamt-Stickstoff]	1995

National and International Norms: Meat

Norm	Organization	Title	Year First Approved
AOAC 992.15	AOAC International [Formerly Association of Official Analytical Chemists]	Crude Protein in Meat and Meat Products	1992
LMBG L06002 0	German Foodstuffs and Commodities Act [Lebensmittel- und Bedarfsgegenständegesetz]	Determination of the Nitrogen Content of Meat and Meat Products – Dumas Method [Bestimmung des Stickstoffgehaltes von Fleisch und Fleischerzeugnissen - Verfahren nach Dumas]	2003

National and International Norms: Milk

Norm	Organization	Title	Year First Approved
DIN EN ISO 14891	German Institute for Standardization [Deutsches Institut für Normung], European Norm & International Organization for Standardization	Milk and milk products - Determination of nitrogen content - Routine method using combustion according to the DUMAS principle	1995
LMBG L01006 0	German Foodstuffs and Commodities Act [Lebensmittel- und Bedarfsgegenständegesetz]	Determination of the Nitrogen Content of Milk and Milk Products – Dumas Method [Bestimmung des Stickstoffgehaltes von Milch und Milchprodukten - Verfahren nach Dumas]	1995

National and International Norms: Soil

Norm	Organization	Title	Year First Approved
DIN EN 16168	German Institute for Standardization [Deutsches Institut für Normung] & European Norm	Sludge, treated biowaste and soil - Determination of total nitrogen using dry combustion method	1998
DIN ISO 13878	German Institute for Standardization [Deutsches Institut für Normung] & International Organization for Standardization	Soil quality - Determination of total nitrogen content by dry combustion (elemental analysis)	1998

National and International Norms: Other

Norm	Organization	Title	Year First Approved
EU Pharm05: 2.5.33.	European Pharmacopoeia	Total Protein	2005
ISO 22241-2	International Organization for Standardization	Diesel engines — NOx reduction agent AUS 32 [AdBlue]	2006

Literature: Kjeldahl vs. Dumas Status 1997

- AH Simonne, et al. (1997): Kjeldahl/Dumas ratio is matrix dependent.
  - Milk: 1.01 (Kjeldahl finds more N)
  - Grain: 0.95 (Kjeldahl finds less N)
  - Fish: 0.80
  - Fruit: 0.73
  - Dumas can replace Kjeldahl if a Kjeldahl/Dumas factor is used.
- Based on data and technology from 1997 or earlier.
- No standard requires such a correction of the Dumas values!!

Simonne, A. H., Simonne, E. H., Eitenmiller, R. R., Mills, H. A. and Cresman, C. P. (1997), Could the Dumas Method Replace the Kjeldahl Digestion for Nitrogen and Crude Protein Determinations in Foods?. J. Sci. Food Agric., 73: 39–45. doi:10.1002/(SICI)1097-0010(199701)73:1<39::AID-JSFA717>3.0.CO;2-4

First Customer Comparison: Samples

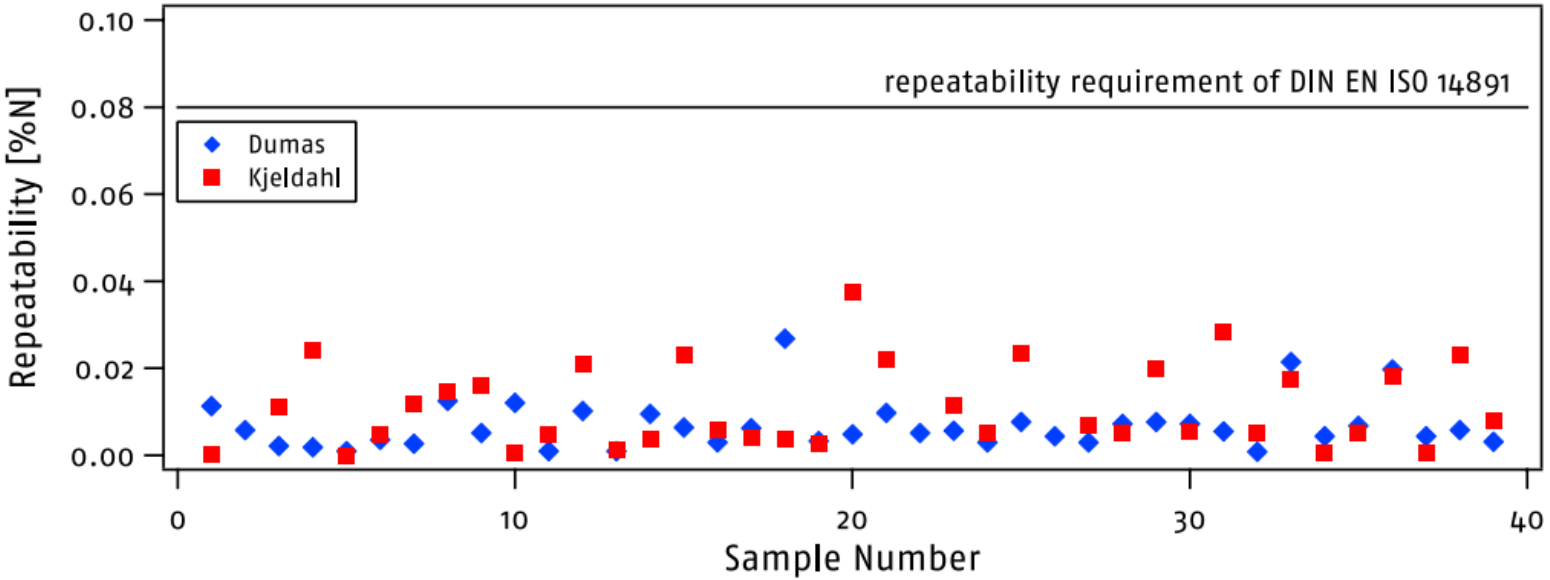
Table 1. A selection of sample types and the Kjeldahl values for %N and %protein.

	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

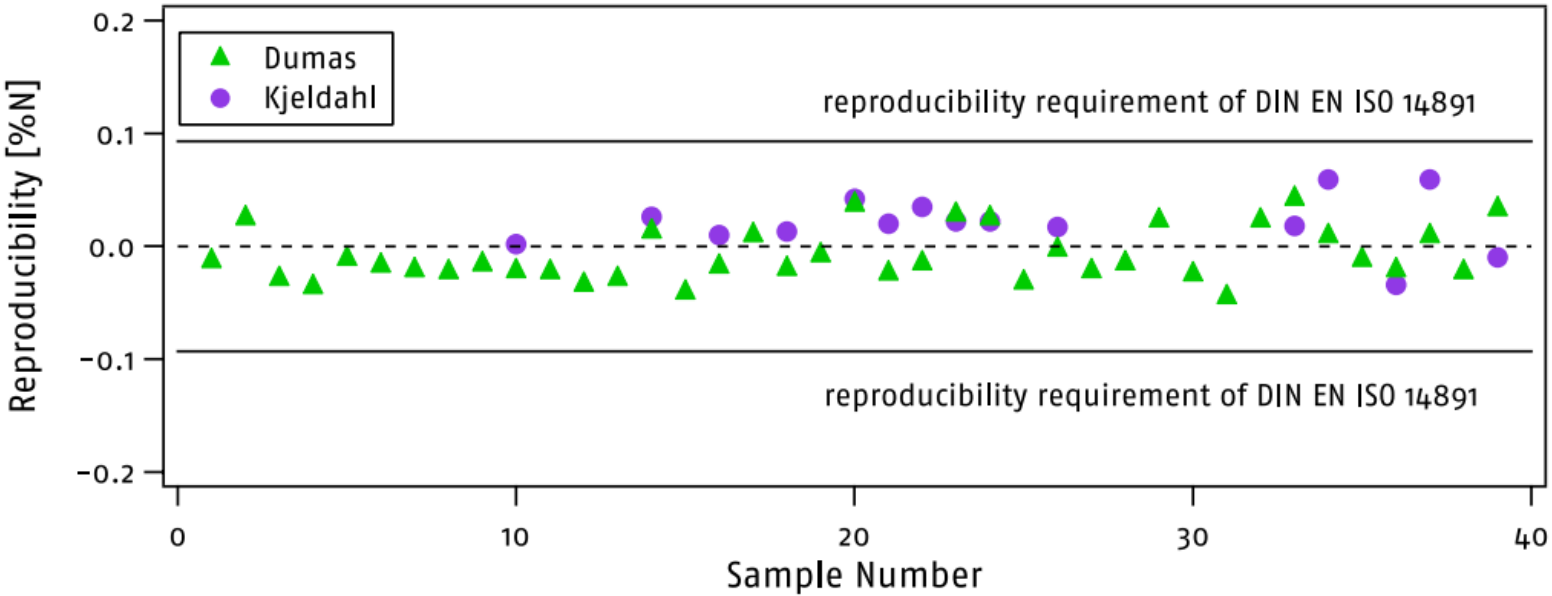
	SAMPLE	N [%]	PROTEIN [%]
21	Yogurt Drink Banana	0.646	4.12
22	Yogurt Drink Red Fruits	0.693	4.42
23	Sports Drink Chocolate	0.873	5.57
24	Sports Drink Strawberry	0.876	5.59
25	Protein Drink Vanilla	0.908	5.79
26	Sports Drink Vanilla	0.917	5.85
27	Sports Drink Chocolate	0.972	6.20
28	Protein Drink Vanilla	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

- Kjeldahl: 2x Analysis
- Dumas: 3x Analysis
- Some samples were also measured by an external lab using Kjeldahl
- Diverse samples: Yoghurt, Milk, Fruit drinks, etc.
- 2-9% Protein
- Needed a faster method!

First Customer Comparison: Repeatability



First Customer Comparison: Reproducibility



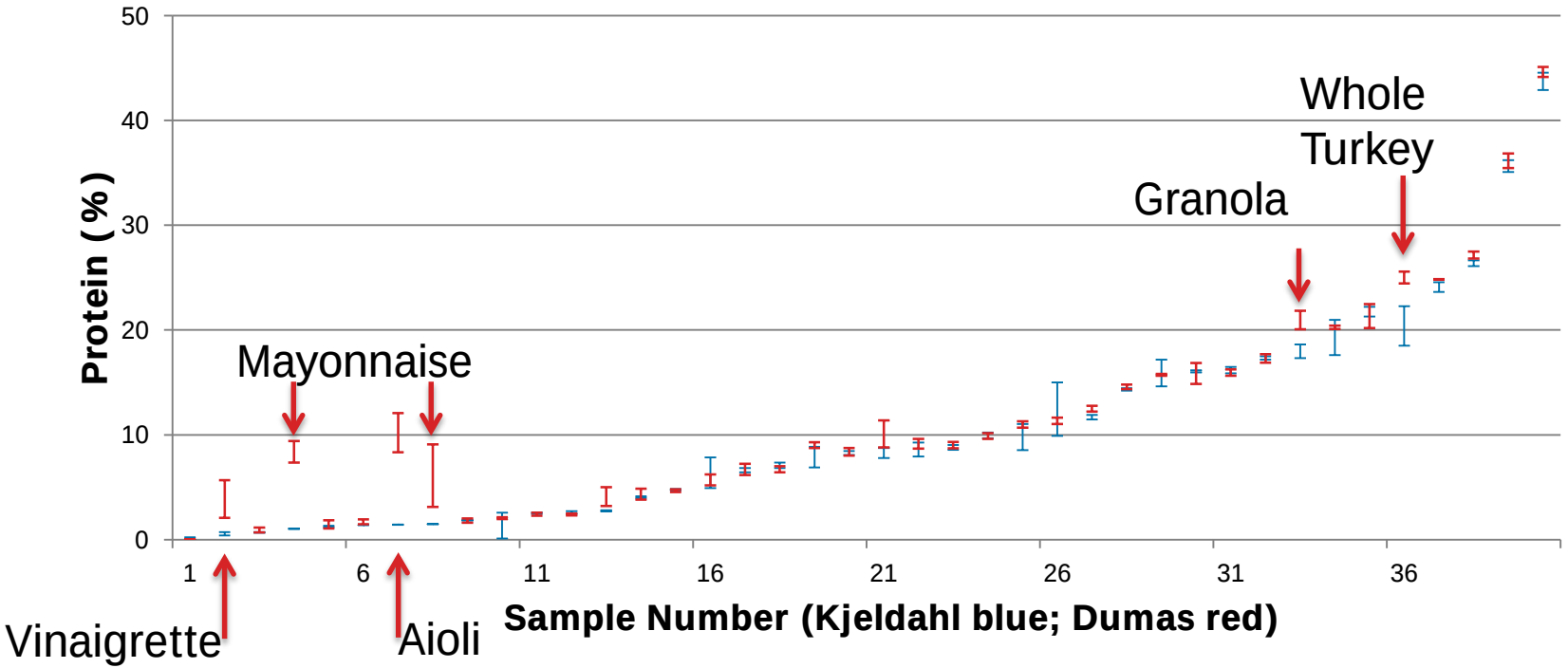
Changing from Kjeldahl to Dumas is comparable to having samples measured by an external lab!

Second Customer Comparison: Samples

#	Probe	#	Probe
1	Edible Tree Sap	21	Sausage Roll
2	Balsamic Vinaigrette	22	Beef Lasagne
3	Red Onion Marmalade	23	Low Fat Yorkshire Puddings
4	Lemon Mayo	24	Yorkshire Pudding
5	Tomato Chutney	25	Cheese Bread Roll
6	Brandy Sauce	26	Multigrain Bread Roll
7	Aioli	27	Coconut Bars
8	Mayonaise	28	Trout Pate
9	Green Soup	29	Cheese and Ham Sandwich
10	Curry Paste	30	Raw Cod
11	Pork & Lentil Soup	31	Minced Lamb
12	Porridge	32	Minced pork
13	Carrot Cake	33	Granola
14	Madeira Cake	34	High Protein Health Bar
15	Crushed Garlic	35	Ham
16	Chocolate Cake	36	Turkey Whole Bird
17	Doughnuts	37	Cold Smoked Swordfish
18	Yoghurt	38	Flapjack
19	Ciabatta Roll	39	Protein Pre-Workout
20	Macaroni Cheese	40	Protein Post-Workout

- Contract lab: All possible foodstuffs with one method
- Kjeldahl: 2x Analysis
- Dumas: 3x Analysis
- 0.1-44% Protein

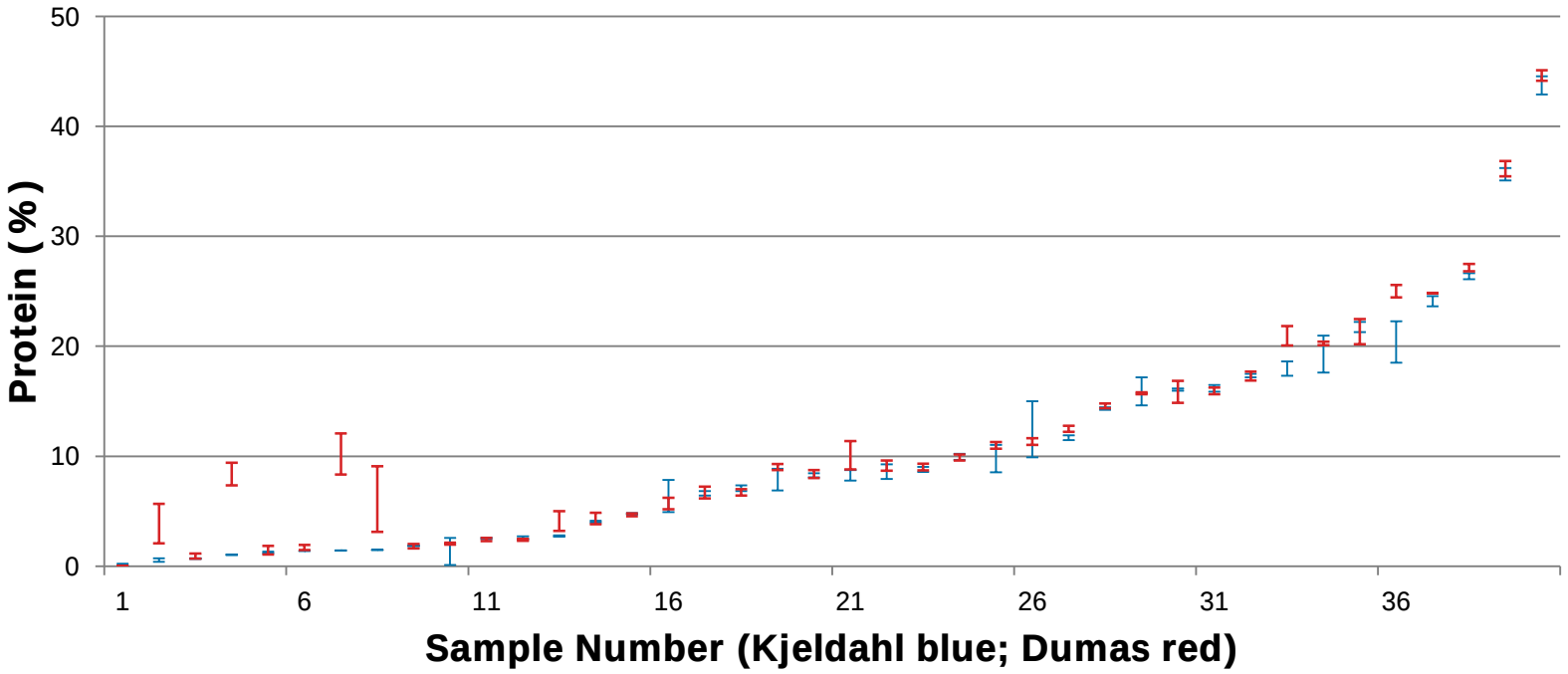
Second Customer Comparison: First Attempt



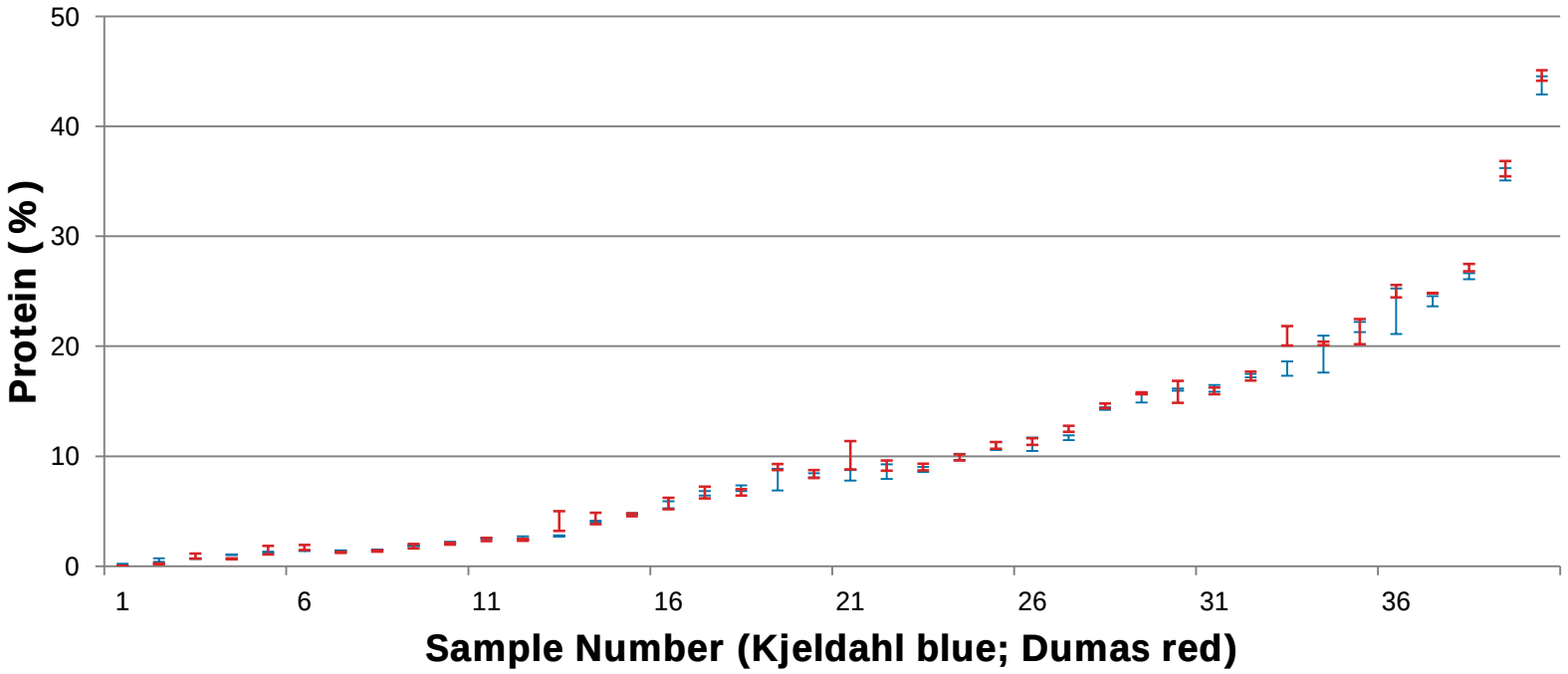
Fatty Samples with the Dumas Method

- Dumas analysis requires complete combustion
- Fatty samples can produce methane
- N-Values are too high because methane is also measured
- Best solution: Reduced sample weight (200 mg)

Second Customer Comparison: First Attempt



Second Customer Comparison: Improvements



Switching from Kjeldahl to Dumas

- The needs of a customer switching from Kjeldahl to Dumas are not very different to the needs of any customer.
- The sample size often has to be reduced.
  - Especially for fat containing samples
- Sample preparation (homogenization) might need to be more extensive.
- Repeatability is comparable.
- Requires a bit more training.
- If desired, Kjeldahl/Dumas conversion factors can be used.

- Less cost, less work, less space in lab