

Potential applications of Time Domain Nuclear Magnetic Resonance (TD-NMR) in chemical metrology: case studies with fat content measurements in milk powder

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Time Domain Nuclear Magnetic Resonance (TD-NMR) refers to a set of techniques that rely on the Nuclear Magnetic Resonance phenomenon but unlike NMR spectroscopy do not apply any Fourier transformation in the signals.

TD-NMR is widely accepted at present in some fields and there are international standards for some methods using the technique which are often used for commercial transactions as the ISO 10565 e 10632 for the determination of the oil content in seeds as well as the determination of the solid fat content (SFC) in animal and vegetable oils using ISO 8292 just to cite some of the ISO standardized applications.

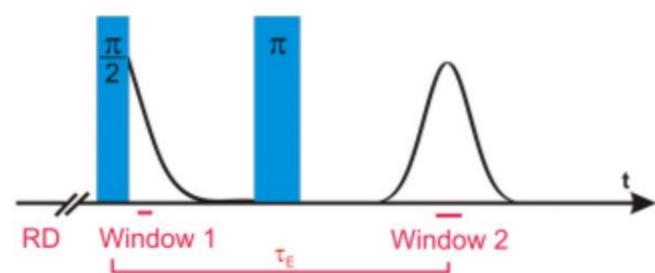
However, the full potential of the technique remains unexploited. In the era of the fourth industrial revolution when all data to support decision making processes in the industry has to be very quickly gathered and available to the fingertips of the managers, TD-NMR stands out among other analytical techniques because of its quickness, ease of operation and potential for informatization.

TD-NMR requires no sample preparation at all and in many cases it is even possible to perform analyses of materials inside sealed packages or intact fruit, for example. It can be used online in production processes and operated by untrained personnel while results, available in the few seconds to few minutes time frame, can be readily sent out to computer clouds and evaluated by the management of the production processes in order to immediately take actions that preserve the production efficiency and quality of the products.

Given the importance and the huge number of potential applications for the technique, this work has aimed to metrologically evaluate the technique in order to systematically understand the trueness and precision of the results and the measurement uncertainties related to these parameters as well as the cost-effectiveness of the analyses using the determination of fat in a simple food matrix as a model.

All the data in this work were acquired using a Bruker Minispec mq10 benchtop TD-NMR with a 40 mm probe operating at a 0.23 T.

The pulse sequence used in this work was a Hahn-echo:

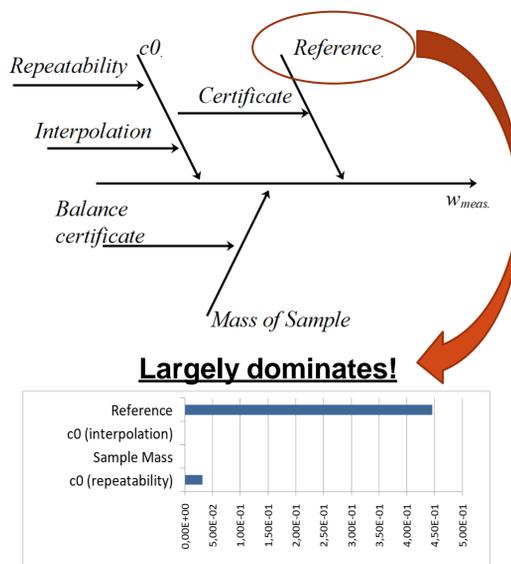


Briefly, this sequence excites the spins with a 90 degree pulse after which the spins will naturally start losing coherence by T2 relaxation. Then, a 180 degree pulse is performed in order to reverse the process in a spin-echo. The detection is then performed at the highest point of the echo signal (window 2 in the image above). Because different types of compounds present in the matrix have different T2, the time between the first pulse and the echo detection can be optimized to allow the measurement of a specific property. In this case, a time of 7 ms is used to detect fat in a solid matrix.

Traceability of the measurements is given by a calibration curve, which means that it actually depends on the reference material used to build the calibration curve.

In this work, NIST SRM 1849a was used as a calibrant with a reference value for fat of 30.43 g/100 g and an expanded uncertainty of 0.95 g/100 g ($k=2$). The model sample was a CRM candidate from Inmetro which has been characterized by an interlaboratory study with a fat content of 28.61 g/100 g and an expanded characterization uncertainty of 0.16 g/100 g ($k=2$) (stability and homogeneity studies not included). One of the points evaluated in this work was the stability of the magnet and the possibility of having the same calibration for an extended period of time. Manufacturers of these instruments claim that the same calibration can be used for over a year in some cases still with good performance due to the stability of the permanent magnet. To that end, a calibration curve was built using the CRM and the model samples were analyzed at the initial time and then after 15, 30 and 90 days without a new calibration curve.

Initial Time				
Sample code	w_{analyte} g/100 g	\pm	U g/100 g	RSD%
FI 18-a	28,604	\pm	0,89	0,07
FI 133-1	28,571	\pm	0,89	0,13
FI 088	28,644	\pm	0,89	0,06
FI 184	28,504	\pm	0,89	0,16
15 days later				
Sample code	w_{analyte} g/100 g	\pm	U g/100 g	RSD%
FI 18a	28,554	\pm	0,89	0,15
FI 133-1	28,600	\pm	0,90	0,35
FI 088	28,406	\pm	0,89	0,16
30 days later				
Sample code	w_{analyte} g/100 g	\pm	U g/100 g	RSD%
FI 18-a	28,616	\pm	0,91	0,55
FI 088	28,488	\pm	0,90	0,42
FI 184	28,630	\pm	0,89	0,02
90 days later				
Sample code	w_{analyte} g/100 g	\pm	U g/100 g	RSD%
FI 84	28,548	\pm	0,89	0,19
FI 184	28,628	\pm	0,89	0,04
FI 088	28,341	\pm	0,89	0,10
FI 018b	28,693	\pm	0,91	0,49

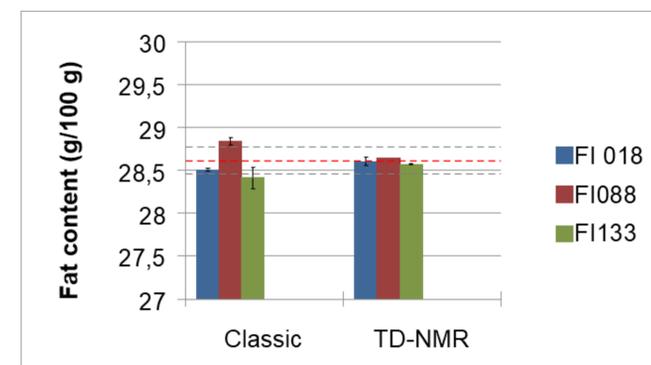


Cost of Analysis – versus classic method

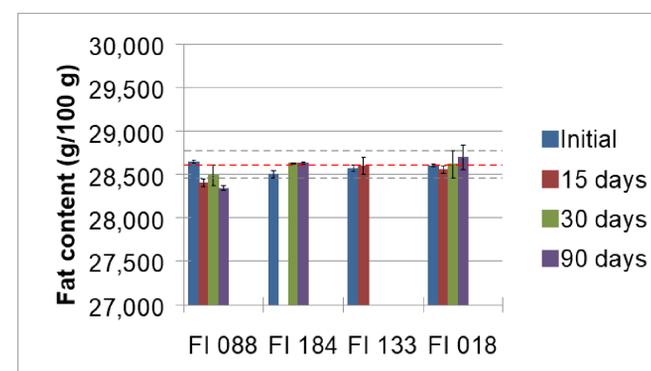
Classic Method	TD-NMR
At least 9-10 hours of work of a trained chemist to measure the samples	Samples measured in seconds
Use of ethanol, ethyl ether, hydrochloric acid, petroleum ether (around 800 mL total solvents per sample)	No use of solvents or sample preparation
Total analysis time: about 12 hours = 1 and a half day of work	< 10 minutes total analysis time (including placing sample in tube)
Total cost: US\$ 387.00	Total cost (including instrument depreciation): US\$ 255.00

Considerable initial investment

Repeatability and trueness of the TD-NMR measurements at the initial time as compared to the classic method:



Long term evaluation – 90 days using the same calibration curve. Results still equivalent to the reference value:



Using a very simple analytical model, this work highlights the potential of TD-NMR for metrological applications and some of its properties:

- better repeatability and trueness than the classic counterpart;
- much faster analyses;
- lower cost of analysis;
- no solvent disposal;
- no sample preparation;
- readily integrated to online results management software;
- excellent results with no need for specialized personnel;
- Calibration curve stability demonstrated for 90 days;
- Measurement uncertainties calculated and contributions from each input quantity determined.

Foster TD-NMR in industry : More reliable and traceable measurements at lower costs and higher throughput = **productivity increased**