LOW-FIELD NMR SENSOR TECHNOLOGY FOR AGRICULTURAL APPLICATIONS

A Low-Field NMR Sensor for Applications in Modern Agriculture: Farm Fertilizers, Livestock Feeds, and Milk Products

Determination of Salt and Fat in Food Products using a Low-Field NMR Sensor

A Low-Field NMR Sensor for Applications in Modern Agriculture: Farm Fertilizers, Livestock Feeds, and Milk Products

A White Paper by Prof., CTO Niels Chr. Nielsen, Dr. Michael Beyer, Dr. Morten Kjærulff Sørensen & CEO Ole Jensen, NanoNord A/S – Denmark

In this White Paper we demonstrate the use of the multinuclear NanoNord TVESKAEG™ NMR analyzer for fast and accurate measurements of a wide variety of products being part of modern agriculture and farming aimed at high yield and sustainable production. We demonstrate determination of nitrogen, phosphorous and dry matter in animal slurries/manure, nutrients in livestock feeds, and protein and fat in milk products as examples spanning the agricultural cycle.

Introduction

High yield and sustainable production are central themes for modern farming and agriculture servering to feed an increasing global human population under conditions of increasing regulation to reduce environmental footprint. Among other things, this may amount to optimizing the use of natural fertilizers for crop production, livestock feed components for animal production, and ingredients in food products for quality and healthy living. To optimize these and dozens of other elements in the agricultural life cycle it is of vital importance to have access to accurate data which can be correlated with production yields, quality, and regulatory requirments. This acutely calls for new sensor technologies, potentially combined with big data analysis. Ideally such technology should be affordable, fast and accurate, safe, robust, and easy to use without time consuming calibrations and the need for huge data bases for similar samples.

A stong candidate for such a sensor may nuclear magnetic resonance (NMR) spectroscopy which is a noninvasive measuring technology that has found widespread application in as diverse areas as physics, chemistry, biology, and medicine as a prime technique in advanced analytical laboratories, universities, and hospitals. In general public the technique is mainly known from hospitals in terms of MR scanners, representing a flagship in modern diagnosis – exploiting that magnetic resonance in contrast to optical sensors measures the full volume of the sample (in MR, patients) and not only the surface. In general NMR and MR instrumentation is highly expensive and very demanding in terms of laboratories and expert personnel. In recent years, however, efforts have been devoted to affordable industrially relevant low-field NMR instrumentation for a much wider range of analytical applications. In this note, we present and demonstrate the use of the NanoNord TVESKAEG™ NMR sensor to serve a variety of applications relating to modern farming.

Figure 1. Two variants of the NanoNord TVESKAEG™ NMR sensor, based on a 1.5 Tesla magnet and advanced radio-frequency technology. A BENCHTOP instrument (left panel) with options for sample stick (shown in insert) or peristaltic pump (on the front of the spectrometer) sample insertion. A FLOW instrument (right panel) to use for inline continuous measurement in a production line.

The multinuclear TVESKAEG™ NMR Sensor

The NanoNord TVESKAEG™ NMR sensor, shown in two variants in Figure 1, is designed for industrial applications with unique capability for on-the-fly fast and accurate NMR analysis of virtually all NMR relevant nuclei forming the elements of matter. In the left panel is shown a benchtop variant of the sensor, which can be used in simple laboratory-like settings for measuring a large variety of parameters on samples taken from the production and inserted into the instrument using 9.2 mm sample sticks (shown to the left) or via a peristaltic pump automatically taking the sample from any sample container. In the right panel is shown a flow version of the instrument, which is designed for in-line measurements (12.2 mm sample diameter) in a production system, as for example recently introduced as a component in Samson slurry tankers.[1] The robust and accurate sensor uses nuclear magnetic resonances (NMR) spectroscopy as the source to quantitative and qualitative information about atoms (nuclei) in the sample subject to investigation. When located in a strong magnetic field, nuclei with a nuclear spin behave like small magnets rendering it possible to communicate with them individually or collectively with radio-frequency pulses and thereby obtain specific information about them using a radio-frequency transmitter-receiver system. The analysis is non-invasive, does not need time consuming calibrations nor the use of chemicals with problematic health effects or environmental footprint.

Analyzing farming components and products with the TVESKAEG™ NMR sensor

Relating to farming and agriculture the TVESKAEG NMR sensor may be used for analysis in virtually all steps ranging from crop and animal production to food products served to the consumer. This is demonstrated in this White Paper with examples taking origin in the present great attention to yield and environmental aspects of animal slurry/manure as a natural fertilizer, optimization of animal growth with lowest emission, and nutritional and healthiness of food products. This includes determination of ammonium, total nitrogen, total solids (dry matter), and total phosphorous in animal slurry, determination of protein, fat, sodium, and phosphorous in livestock feed, and determination of fat and protein in milk.

a. *Sample preparation and NMR measurements*

   Quantitative measurements of ammonium, total nitrogen, total phosphate, and total solids in animal slurry/manure were performed on native, homogenized slurry samples inserted into a TVESKAEG™ BENCHTOP spectrometer for ^{1}H, ^{14}N, and ^{31}P measurements using 9.2 mm sample tubes. With similar performance the samples can be measured directly on bulk slurry samples, as pursued in a collaborative project between NanoNord and Samson with the TVESKAEG™ FLOW instrument installed for in-line measurements in slurry tankers.[1]

   Quantification of fat, protein, phosphorous, and sodium in representative livestock feed products were performed at dry powdered samples (fat), 1:3 livestock feed:water samples (phosphorous, salts; specifically sodium), and overnight predigested 1:8 feed:water samples (protein) administered to the TVESKAEG™ BENCHTOP sensor for ^{1}H, ^{14}N, ^{23}Na, and ^{31}P measurements using 9.2 mm sample tubes.

   For milk samples amounts of fat and protein was determined using native samples upon adding small amounts of relaxation agent (fat) or salt (protein) in 9.2 mm sample sticks for ^{1}H and ^{35}Cl NMR measurements using the TVESKAEG™ BENCHTOP sensor.

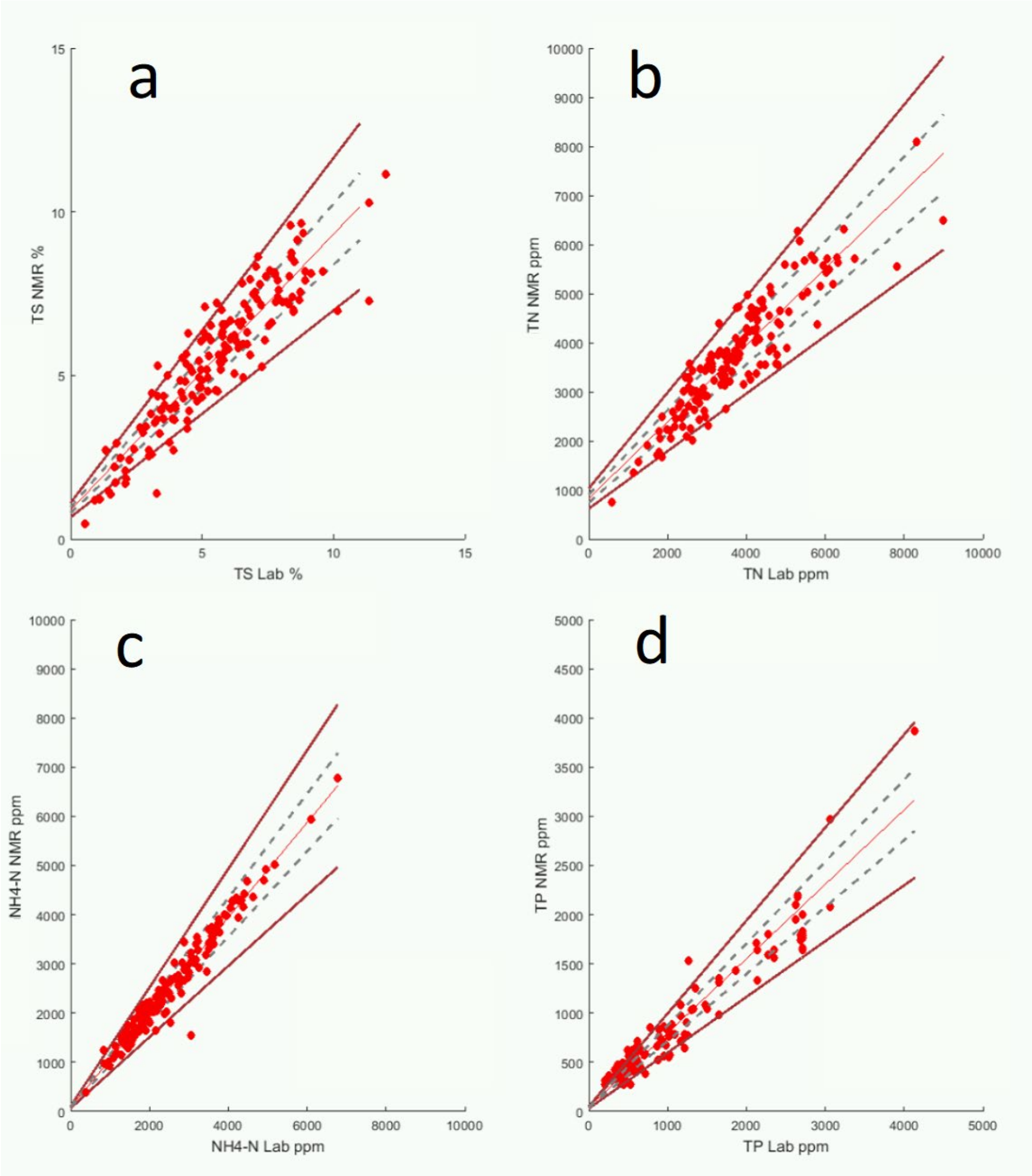

Figure 2. Quantification of (a) total solid (0.91%), (b) total nitrogen (572 ppm), (c) ammonium nitrogen (221 ppm), and (d) total phosphorous (314 ppm) in 132 animal slurry/manure samples using a TVESKAEG™ Benchtop NMR sensor correlated with laboratory measurements with standard deviations given in parenthesis. Measurement of total solids, total nitrogen, and ammonium nitrogen resulted from one 17 min measurement, while 1h measurement time was used for total phosphorous. The dots represent data points, while the dashed and solid line mark ±10% and ±25% variation from the best correlation. We note that variations reflect both laboratory and NMR measurements.

b. *Comparative information about content in samples*

In this study, we compare the NMR results with information provided by Agrolab, Sarsted, DE (animal slurry/manure) or on the product packaging information (stock feed and milk) to illustrate the principle of fast and accurate on-site measurements providing information compatible with external laboratory measurements or declared values. We note the comparative information is subject to measurement uncertainty (laboratory values) or averaging (declarations).

c. *Analysis of farm fertilizers: ammonium, total nitrogen, total solids, and total phosphate*
Using animal slurry as a natural fertilizer for optimal crop yield without compromising the environment through washout of nutrients require detailed information about nitrogen (N), phosphate (P), and in some cases potassium (K). Such information is important for farm operation with variations in the fields ability to take up the fertilizer, but also for export of animal slurry/manure to other farms or to biogas digesters prior to fertilization. Several countries have strict regulations on N and P content in animal slurry/manure in terms of field dozing and transport. However, it is generally believed that available measuring technology is not capable of handling the volume of measurements invoked through regulation or not sufficiently accurate for the purpose.

The applicability of low-field NMR for on-line NPK measurements was published in 2015.[2] In the present paper, we extend this analysis in collaboration with Agrolab, who conducted TVESKAEG™ BENCHTOP NMR experiments in parallel with normal chemical analysis for a large set of animal and digester slurries from different livestock types and different geographical origin (132 samples). Data resulting from this study is shown in Figure 2, correlating NMR measurements (vertical axis) with laboratory measurements (horizontal axis) for total solids (a), total nitrogen (b), ammonium nitrogen (c), and total phosphorous (d). For each sample data were accumulated using 17 min measurement time in total for the total solid, total nitrogen, and ammonium nitrogen, while the total phosphorous data were accumulated in 1 h. The measurement times may in practice be reduced, for example by a factor of four, at expense of a doubled standard deviation in the NMR measurements which is acceptable for many applications. We note that the reported standard deviations also include variations in the laboratory measurements, which can be substantial as reported in Ref. 2 by comparing results from 5 different laboratories. It should also be mentioned that the measurements work for solid manure as well as liquid-containing animal slurry and does require reference to data bases for different livestock types.

Analysis of animal slurry/manure, may as demonstrated here, be conducted on the farm/biogas/wastewater plant by TVESKAEG™ BENCHTOP NMR measurements in on-site laboratory-like measurements, or as demonstrated in a collaboration with Sansom using a TVESKAEG™ FLOW instrument on-line at the slurry tanker. This combination received a Silver medal for novel technologies at the Agritechnica 2019 exhibition.[1]

d. *Analysis of livestock feed: protein, fat, phosphorous, and sodium*
The composition of feed is of fundamental importance for the growth/yield, emission, and welfare of livestock. With the aim of continuous food optimization based on available feed resources, it is of great interest to have access to on-site measuring technology. Here we demonstrate the use of the TVESKAEG™ BENCHTOP for quantification of the amount of protein, fat, phosphorous, and sodium in livestock feed products. Figure 3 shows NMR data correlated with packaging declarations for a variety of different productions, with the panels representing (a) fat, (b) protein, (c) phosphorous, and (d) sodium. Overall good consistency is observed for the various components bearing in mind that the reference data may represent averaged values for very large quantities. Information about fat, protein, phosphorous, and sodium were obtained by 1 min ^{1}H, 5 min ^{14}N, 30 min ^{31}P, and 15 min ^{23}Na

measurements. The data demonstrates that a variety of different parameters describing livestock feed products may be obtained very easily to form basis for on-farm production optimization.

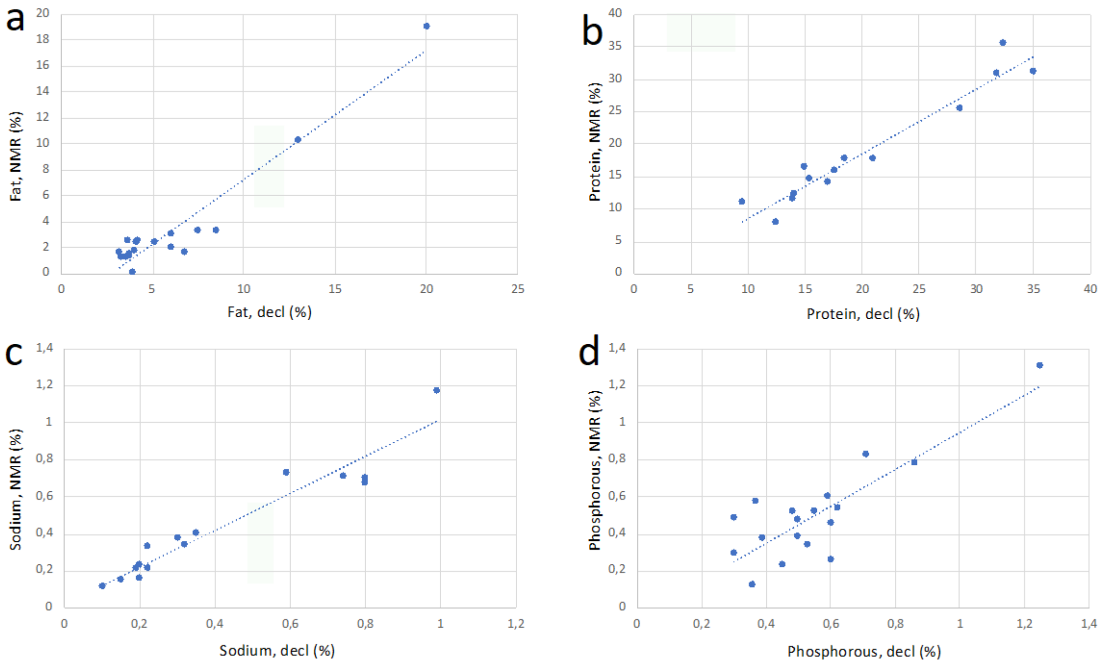

Figure 3. Correlation between TVESKAEG™ ^{1}H NMR and package declarations for content of (a) fat (0.92), (b) protein (0.93), (c) sodium (0.93), and (d) phosphorous (0.70) a diverse set of livestock feed products. Regression coefficients (R^2) for the correlations are given in parenthesis.

e. *Analysis of milk: fat and protein*

Quality assessment of food products resulting from farming may be of great interest for optimal quality, price assessment, breeding strategies etc. This may include determination of fat, protein, salts, and moisture in crop, animal, and milk products. The application of the TVESKAEG™ BENCHTOP sensor for such analysis is exemplified in Figure 4 showing correlations between fat and protein contents in milk products relative to package declarations. Overall a very good correlation is obtained, demonstrating the applicability of the low-field NMR for fast and accurate, on-site determination of food product quality parameters.

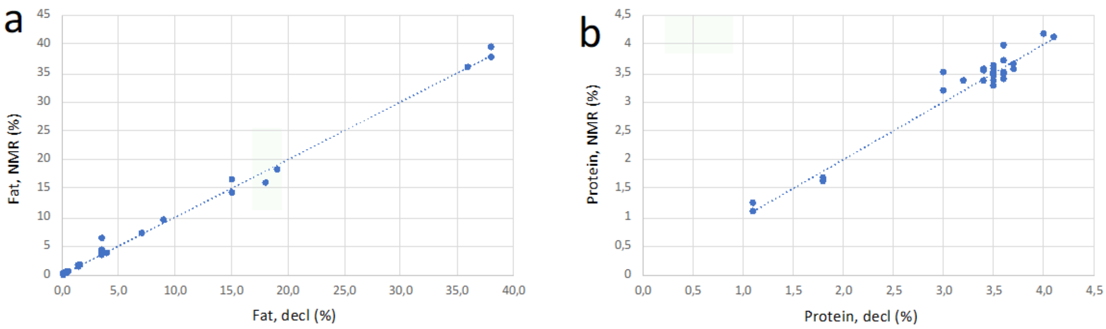

Figure 4. Quantification of (a) fat (0.995) and (b) protein (0.951) in liquid milk products resulting from 1 min ^{1}H and 4 min ^{35}Cl NMR measurements, respectively, performed using a TVESKAEG™ Benchtop NMR sensor correlated with packet declarations for a variety of milk products. The regression coefficient is given in parenthesis.

Conclusions

In this White Paper, we have described a versatile and efficient NanoNord NMR sensor to provide detailed and accurate information about the content of nitrogen, ammonium, total nitrogen, total phosphorous, fat, protein, and salt in a variety of farming components and products, ranging from on-site laboratory or in-line measurement of nutrients in animal slurry/manure, to compositional analysis of stock feed products, and food products being the outcome of farming. The method is fast, reliable and robust and does not require elaborate calibrations, nor the use of hazardous chemicals.

For more information, please visit www.nanonord.dk.

[1] AGRITECHNICA 2019, silver medal, new NPK sensor. Collaboration between Samson and NanoNord.

[2] M.K. Sørensen, O. Jensen, O. N. Bakharev, T. Nyord, and N. C. Nielsen, "NPK NMR Sensor: Online Monitoring of Nitrogen, Phosphorus, and Potassium in Animal Slurry", *Anal. Chem.* **2015**, 87, 6446-6450.

Determination of Salt and Fat in Food Products using a Low-Field NMR Sensor

An Application Note by Prof. Niels Chr. Nielsen & Dr. Michael Beyer, NanoNord A/S – Denmark

Low-field NMR spectroscopy offers great potential for cost-efficient analysis of food products. The fast and accurate NanoNord TVESKAEG™ NMR analyzer is well suited for such purposes and can be installed in production facilities or laboratories for production process control. In this application note we describe measurements of salt and fat in a highly diverse set of food products.

Introduction

Process and quality control become increasingly important in the food industry to reduce production costs, ensure correct declaration, and optimize quality, taste, durability/shelf life, and healthiness of the final products. This calls for affordable, fast, and accurate compositional analysis without excessive need for human operation, time consuming calibrations, or the use of hazardous/ environmentally undesirable chemicals.

Nuclear magnetic resonance (NMR) spectroscopy is a noninvasive measuring technology that has found widespread application in diverse areas of physics, chemistry, biology, and medicine as a prime technique in advanced analytical laboratories and hospitals. The general picture of being a highly expensive and demanding technique in terms of operation, sample preparation, and data interpretations is gradually changing due to introduction of low-field NMR instrumentation for a wider range of applications. In this note we present low-field NMR for analysis of salt and fat content in food products.

The multinuclear TVESKAEG™ NMR Sensor

With focus on the use in industrial production lines and analytical laboratories, we introduce the NanoNord TVESKAEG™ NMR sensor (Figure 1) offering the capability for on-the-fly NMR analysis of virtually all NMR relevant nuclei forming the elements of food products. The sensor uses nuclear magnetic resonances (NMR) spectroscopy as the source to quantitative and qualitative information about atoms (nuclei) in the investigated sample. The method exploits that nuclei with a nuclear spin behave like small magnets in a magnetic field implying that it is possible to communicate with them individually with radio-frequency pulses and obtain specific information about these through a radio-frequency receiver given they are located in a strong magnetic field. The method is non-invasive, does not need addition of chemicals with potential adverse health effects or negative environmental footprint, and is thereby not associated with any hazards and risks beyond what characterizes the native sample.

Figure 1. The NanoNord TVESKAEG™ benchtop NMR sensor, based on a 1.5 Tesla magnet and advanced radio-frequency technology, with options for tube (shown in insert to the right) and peristaltic pump (on the front of the spectrometer) sample insertion.

Analyzing foods with the TVESKAEG™ NMR instrument

Relating to the food industry the TVESKAEG NMR sensor may, among many other possibilities, use nuclei such as ^{23}Na and ^{1}H as a means to measure the contents of salt and fat. This is illustrated in this application note, where we with simple 1-minute measurements analyzed the sodium and fat content in a large number of food products directly available from supermarkets using TVESKAEG for NMR measurements and comparing the results with the declarations. Although simple in its setup, this study clearly demonstrates the versatility of the method for fast and reliable food analysis.

A variety of different food products were analyzed including 18 bakery/snacks products, 10 meat/poultry/seafood products, 8 dairy products, 8 prepared foods, 12 instant foods, and 14 products not falling into this category. For all 70 samples we conducted sodium measurements, while the fat analysis was restricted to samples not containing large amounts of water.

a. *Sample preparation and NMR measurements*

   In determining the amount of salt, we exploit that ions like Na^+ move freely in liquid and under these conditions provide easy measurable ^{23}Na NMR signals. Therefore, for such analysis we either use the product directly or partly diluted with salt-free water in case of flowable/liquid-like samples, or for dry/solid-like samples we dilute the samples in salt-free water typically in a ratio 1:10(1:11) w/w. The diluted samples are analyzed either using a 9.2 mm sample tube, or simply by pumping the sample from a normal sample container through the instrument using the peristaltic pump unit available on the TVESKAEG™ Pump version of the instrument. The measurement time is typically 1 minute. In this study, we specifically detect sodium, but note that the TVESKAEG™ analyzer also allows for detection of other ions such as chloride, potassium, bromide, lithium etc.

   Determination of the content of fat, as demonstrated here for non-flowable "dry" samples (to avoid dominant signals from water), is obtained by ^{1}H NMR on weighted samples inserted into an NMR tube, and with the measurement time being 1 minute or less.

b. *Comparative information about salt and fat content*

   In this study we compare the NMR results with information provided on the food product packaging to illustrate the principle of fast measurements providing information compatible with declared values. We note that an alternative approach is to use comparative measurements obtained from commercial analytical laboratories, which we pursue for more detailed analysis of series of specific types of food products. In most cases the deviation to declared values are very small.

c. *Sodium measurements*

   Figure 2 illustrates measurements of the content of sodium in the 70 analyzed samples with the top panel showing the correlation between the NMR measurement (vertical axis) and the product packaging provided information (horizontal axis) for all samples while the lower panel restricts the correlation to the samples having a sodium content of less than 10%. Different product types are marked with different colors. For each sample the ^{23}Na NMR signal resulted from 1-minute measurement time with an absolute standard deviation specified as less than 30 mg/L, corresponding to 0.003 %w/w. The measurements were carried out using the peristaltic pump for automated sample insertion. We note that the standard deviation of measurements is reduced by $\sqrt{2}$ upon doubling the experiment time. It is evident from Figure 2 that NMR provides results very well matching those provided on the packaging with an overall correlation coefficient of 0.99.

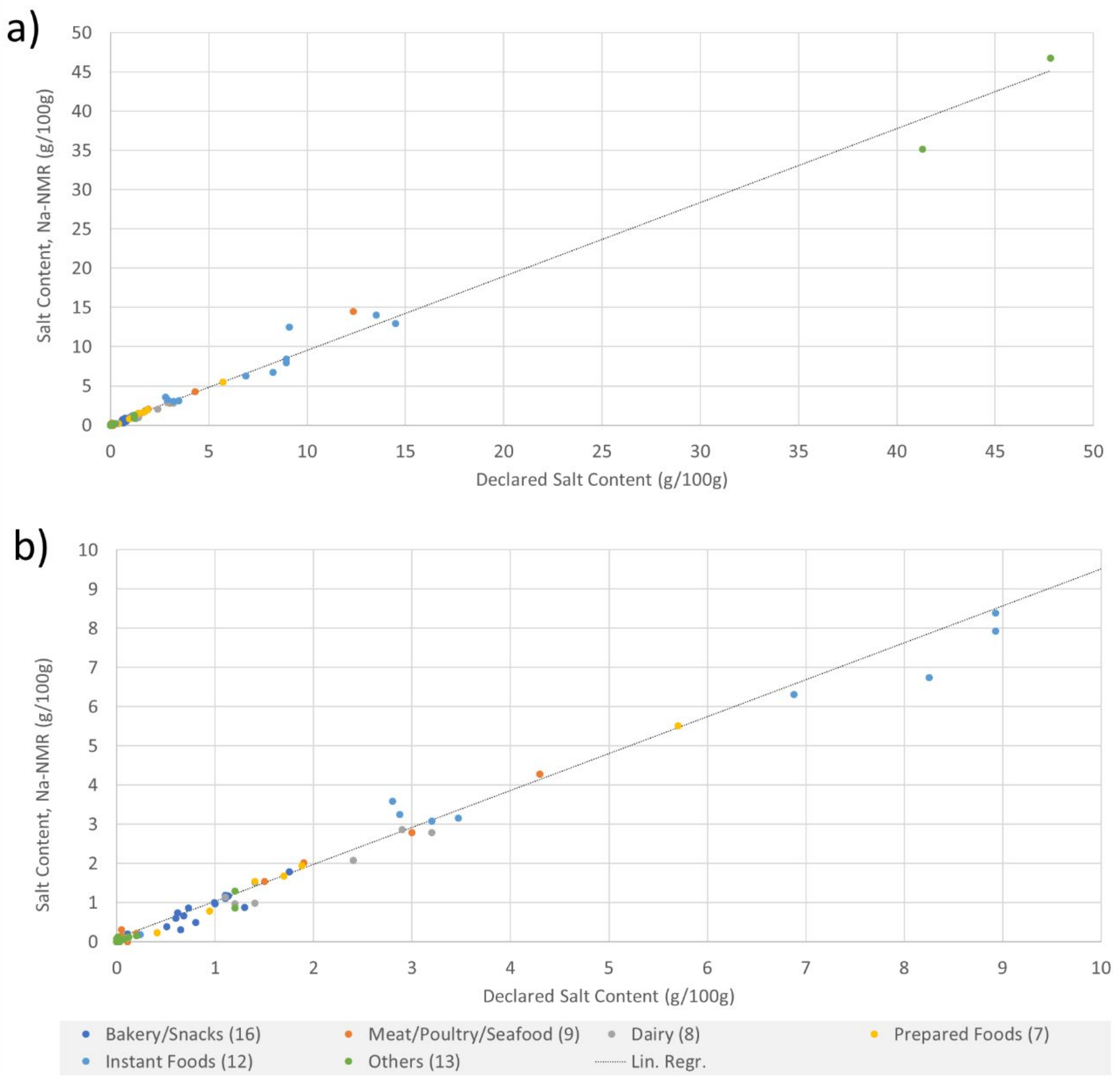

Figure 2. Results from 1-minute sodium measurements performed by TVESKAEG™ ^{23}Na NMR correlated with packet declarations for a variety of food products as marked with different colors with all samples in a) and expansion for samples with less than 10% sodium in b). The correlation coefficient is 0.99. Observed absolute standard deviations for all (less than 10%) samples in %w/w are a) 0.85 (0.26).

d. *Fat*

As another parameter of great relevance in food production, we demonstrate the use of the TVESKAEG™ NMR sensor to determine the amount of fat in food products. Such information is of interest for adjustment of formulations and ensure desired final product specifications in a global setting with increasing focus on obesity and healthy food products. TVESKAEG™

^{1}H NMR provides fast and accurate access to information about fat content for dry/solid-like samples as illustrated in Figure 3. The figure shows correlations between NMR measurements and information provided on the product packaging in a variety of food products. For these measurements we restricted ourselves to dry/native samples which were transferred into an NMR tube by simply pushing the open tube into the dry matter, closing the tube, weighting it (before and after) and analyzing the sample for less than 1 min. Overall we observe a good match between the NMR measurements and the information on the packaging noting, however, that declarations for some products may display seasonal changes and effects from variations in fat distribution over the product volume.

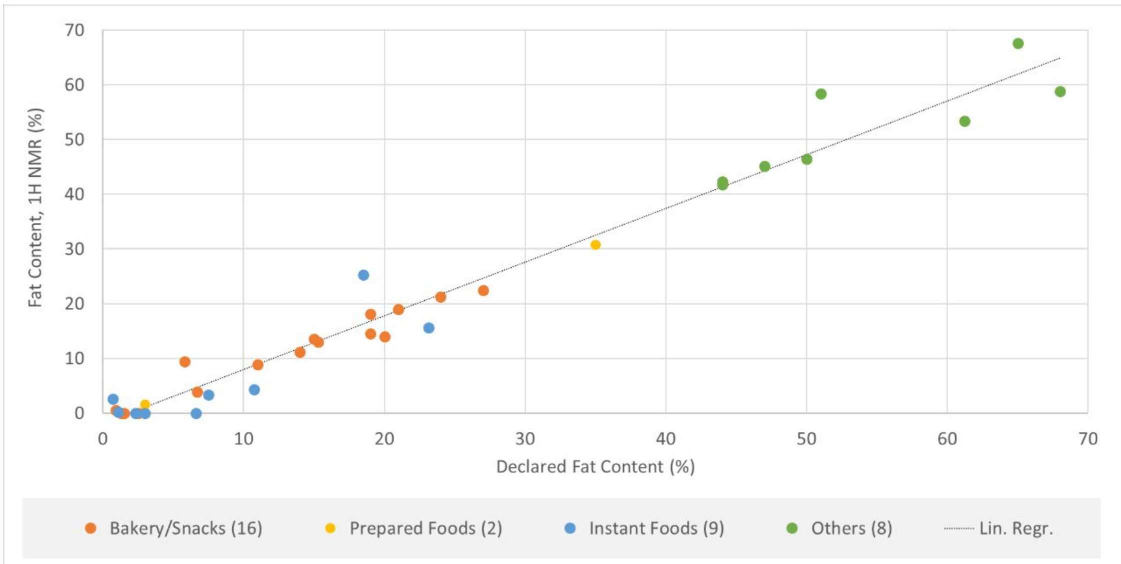

Figure 3. Correlation between TVESKAEG™ ^{1}H NMR and external laboratory measurements of the content of fat in dry food products with coloring reflecting different kinds of food products. The correlation coefficient is 0.98. The observed absolute standard deviation of all samples in %w/w is 3.6.

Conclusions

In this Application Note we have described a versatile and efficient NanoNord TVESKAEG™ NMR sensor to provide detailed and accurate information about salt and fat content in a large variety of different food products with relevance for production control and quality assessment. The method is fast, reliable, and robust and does not require elaborate calibrations, nor the use of hazardous chemicals.

For more information, please visit www.nanonord.dk.

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