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LOW-FIELD NMR SENSOR TECHNOLOGY

FOR INDUSTRIAL APPLICATIONS

- Analysis of Snacks Products using Multinuclear Low-Field NMR Sensor Technology
- Determination of Salt and Fat in Food Products using a Low-Field NMR Sensor

NanoNord

Analysis of Snacks Products using Multinuclear Low-Field NMR Sensor Technology

A White Paper by Prof. Niels Chr. Nielsen & Dr. Michael Beyer, NanoNord A/S – Denmark

Multinuclear low-field NMR spectroscopy using the NanoNord TVESKAEG™ NMR analyzer is described as a versatile tool for compositional analysis of snacks/crisps/seasoning products as part of industrial process and quality control without the need for chemicals with hazardous health or environmental effects. It is demonstrated that highly accurate information may be obtained on the concentration of sodium and chloride being very important for product flavor, nutrition, and for correct dosing of seasoning during production. The sensor may additionally offer accurate information on, e.g., the content of fat. Description of the method, features of operation, and comparison with external laboratory measurements are provided.

Introduction

Process and quality control become increasingly important in diverse areas of food industry, including the snacks, chips, and associated seasoning markets. Here detailed compositional analysis of the amount of salts (including sodium and chloride) and fat represent important measures for the quality, texture, and healthiness of the products as well as the economy associated with production through correct administration of ingredients. This renders the availability of fast, reliable, and affordable measurement technologies important.

Nuclear magnetic resonance (NMR) spectroscopy represents an ideal tool to provide the desired information but is often regarded as very expensive and demanding in terms of operation, data interpretation, and sample preparation. In recent years, this picture has changed through the introduction of low-field NMR instrumentation, however, typically with exclusive focus on hydrogen which - albeit truly the most sensitive nuclear spin species - does not provide the information required.

In this White Paper, we intend to alter this image through description of a price-friendly low-field NMR instrument with multinuclear and automation features which may render NMR the method of choice in a variety of industrial settings.

The multinuclear TVESKAEG™ NMR Sensor

With focus on the use in industrial production lines and analytical laboratories, we introduce the NanoNord TVESKAEG™ NMR sensor offering the capability for on-the-fly NMR analysis of virtually all NMR relevant nuclear spin species. In relation to the snacks/crisps/seasoning market this may include nuclei such as ^{23}Na, ^{35}Cl, and ^{1}H which in one setting may be exploited to measure the contents of sodium, chloride, and potassium ions as well as obtaining information about the content of fat in the sample. The instrument, illustrated in Figure 1, may be configured to take samples in as liquids or powders in an NMR tube or liquids automatically through a sample hose using an integrated peristatic pump.

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.

The TVESKAEG™ NMR sensor uses nuclear magnetic resonances (NMR) spectroscopy as the source to quantitative and qualitative information about atoms (nuclei) in the investigated sample. The technology is widespread in analytical and research laboratories in a wide variety of areas spanning from materials science through chemistry and biology to food and medical areas. A well-known area is MR (magnetic resonance) scanners at hospitals. 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 health effects or negative environmental footprint, and is thereby not associated with any hazards and risks beyond what characterizes the native sample.

Analyzing snacks/chips/seasoning with the TVESKAEG™ NMR instrument

The focus of this study is the determination of sodium, chloride, and fat in crisp samples, supplemented with perspectives for similar analysis of ingredients such as seasonings. The analysis involves 37 crisp/seasoning samples from 5 different crisp and seasoning producers. The samples involved 33 crisp products, 1 peanut, 1 corn meal, and 1 pellet sample. All of these samples were measured at NanoNord on two Tveskaeg instruments as well as at two external laboratories.

a. *Sample preparation and NMR measurement*

   Salt analysis in crisp samples is based on samples where the crisps are diluted in a well specified amount of water (specifically 1:10 w/w) with the salt ions detected in the liquid to provide the desired information on free ions. The diluted samples are analyzed with the spectrometer either using a 9.2 mm sample tube, or by pumping them through the instrument using the peristatic pump unit available on the TVESKAEG™ Benchtop Pump version of the instrument. Information about content of fat is obtained from dry (native) ground crisp samples weighted into NMR sample tubes. Samples for laboratories were provided as requested by the laboratories, typically 20-100 g of ground sample for each parameter. NMR measurements were conducted on two different TVESKAEG™ instruments.

b. *Comparative external laboratory measurements*

   To validate NMR measurements, we consulted two commercial accredited analytical laboratories to measure various parameters for the full sample set or subsets of these. The laboratories provided information about sodium, chloride, and fat.

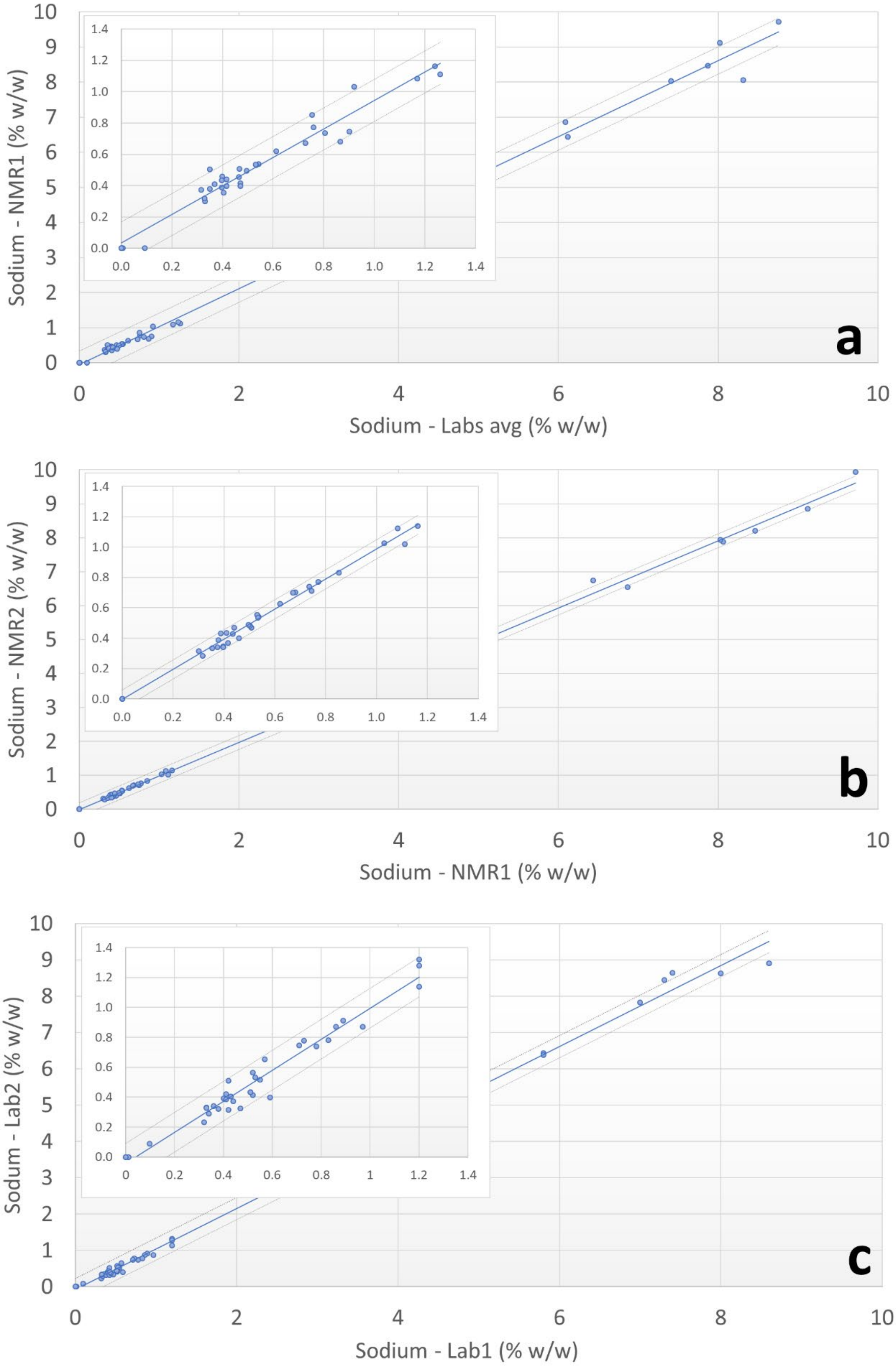

Figure 2. Correlations of sodium measurements performed by TVESKAEG™ ^{23}Na NMR and laboratory measurements with a) NMR vs average of two external laboratory measurements, b) two NMR instruments, and c) two laboratories. Inserts represent expansion of low range regions for crisps samples only. Correlation coefficients are typically better than 0.98. The 95% Confidence intervals corresponding to ± 2·SD are visualized with grey lines. Observed absolute standard deviations for low (full) range in %w/w are a) 0.07 (0.19), b) 0.03 (0.1) and c) 0.07 (0.15).

c. *Sodium*

Figure 2 illustrates measurement of the content of sodium in crisps and seasoning samples with the top panel showing the correlation between the NMR measurement (vertical axis) and the average of measurements from the two external laboratories (horizontal axis) as well as correlation between measurements for two different NMR instruments and between the two external laboratories. All analytical results obtained from laboratory- and NMR analysis are shown as weight % of the product.

It is evident from Figure 2a that NMR gives values matching very well with values provided by external laboratories with an overall correlation coefficient of 0.996. It is also worth noting from Figures 2b and 2c that NMR measurements conducted using two different TVESKAEG™ NMR sensors are mutually more consistent than more tedious measurements provided by two different commercial laboratories.

For each sample the ^{23}Na NMR signal resulted from 1 min 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 with 1:10 diluted chips/seasoning samples using 9.2 mm NMR tubes but could have been recorded with the same precision in an automated setting using the integrated peristaltic pump setup. We note that the standard deviation of measurements is reduced by $\sqrt{2}$ upon doubling the experiment time.

d. *Chloride*

The sodium measurements provide valuable information on the salt content of the crisps samples, being valuable for correct dosing of flavors and for fine calibrating the taste of the final product. Alternatively, information on salt concentration may be obtained through quantitative measurement of free $^{35}Cl^-$ ions, with representative results depicted in Figure 3.

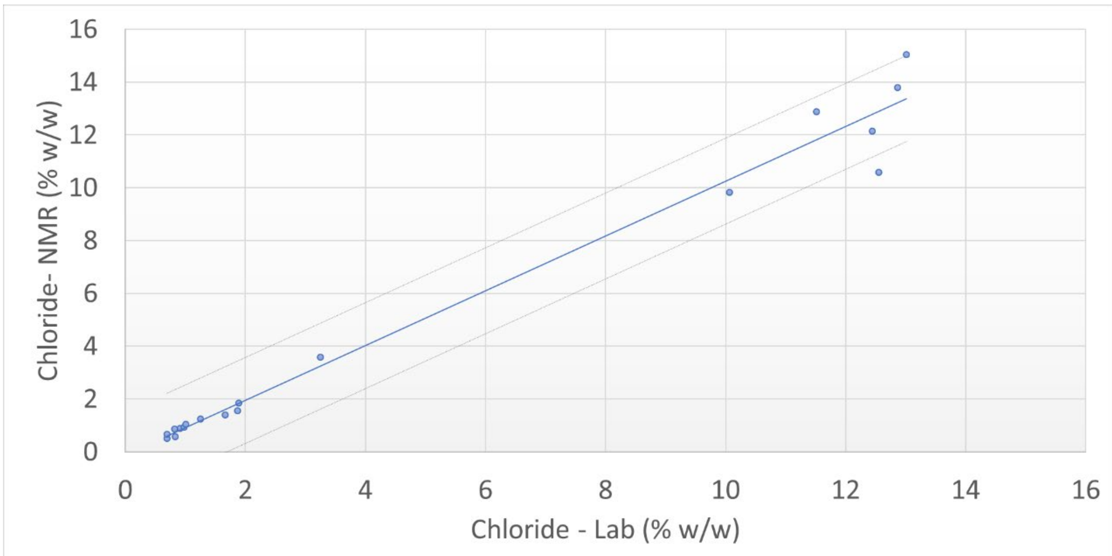

Figure 3. TVESKAEG™ ^{35}Cl NMR measurement of free chloride ion content in crisp and seasoning samples (15 min sampling time) correlated with measurements conducted at an accredited external laboratory.

Also, in this case a good correlation between NMR and laboratory measurements is observed with a correlation coefficient of 0.98 and an absolute standard deviation less than 120 mg/L corresponding to 0.012% w/w for 15 min measurement time. It is interesting to consider the complementarity of ^{23}Na and ^{35}Cl NMR in relation to an intuitively desired information about NaCl in the sample. Here one should be aware that Cl^- might also originate from other ingredients than NaCl (e.g., KCl) and that it may potentially bind to charged residues in proteins (often observed in the case of crisps samples, while in our observations less pronounced for seasoning samples)). In our experience, this implies that a more consistent measurement of NaCl and salt typically will be provided through the faster and more sensitive ^{23}Na measurement and comparison with ^{35}Cl measurements may be a source of more detailed information about the surroundings of the ions in the sample.

e. Fat

In the food industry information about the content of fat in products may be of great interest to adjust formulations and maintain desired final product specifications. Low-field NMR spectroscopy provides easy and fast access to such information as illustrated in Figure 4 showing correlations between TVESKAEG™ ^{1}H NMR measurements and information provided by an external laboratory for a subset of the crisp and seasoning samples investigated in this study. For these measurements we used dry/native ground crisp 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.

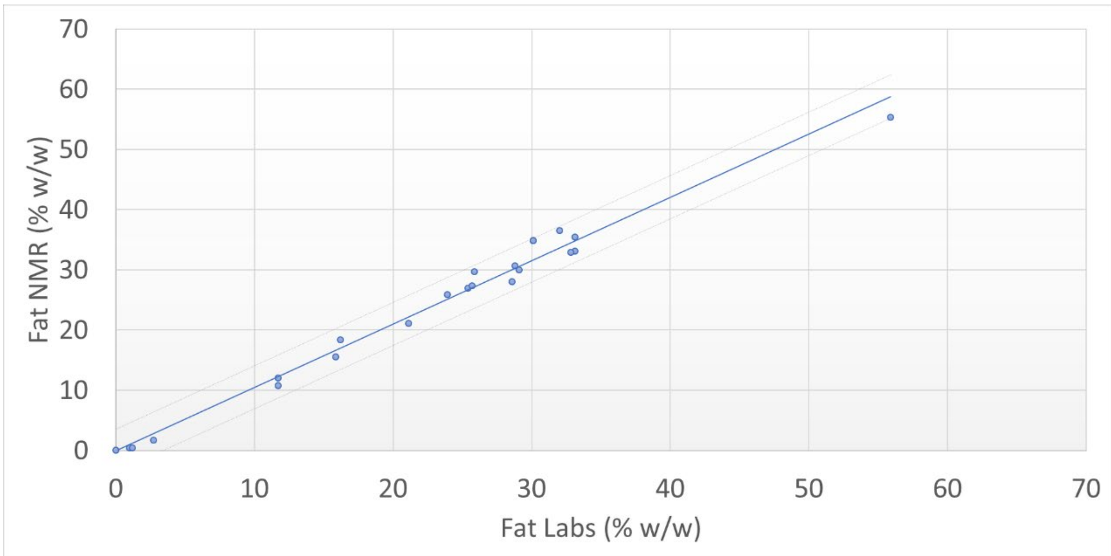

Figure 4. Correlation between TVESKAEG™ ^{1}H NMR and external laboratory measurements of the content of fat in crisps and seasoning samples. The samples with fat content below 5% w/w are seasonings – the sample with the highest fat content is ground peanuts.

Conclusions

We have in this White Paper described a versatile and efficient sensor based on NanoNord NMR technology to provide detailed and accurate compositional information of snacks products with relevance for production control and quality of the product. The NMR results compare favorably with measurements from external accredited analytical laboratories.

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

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.

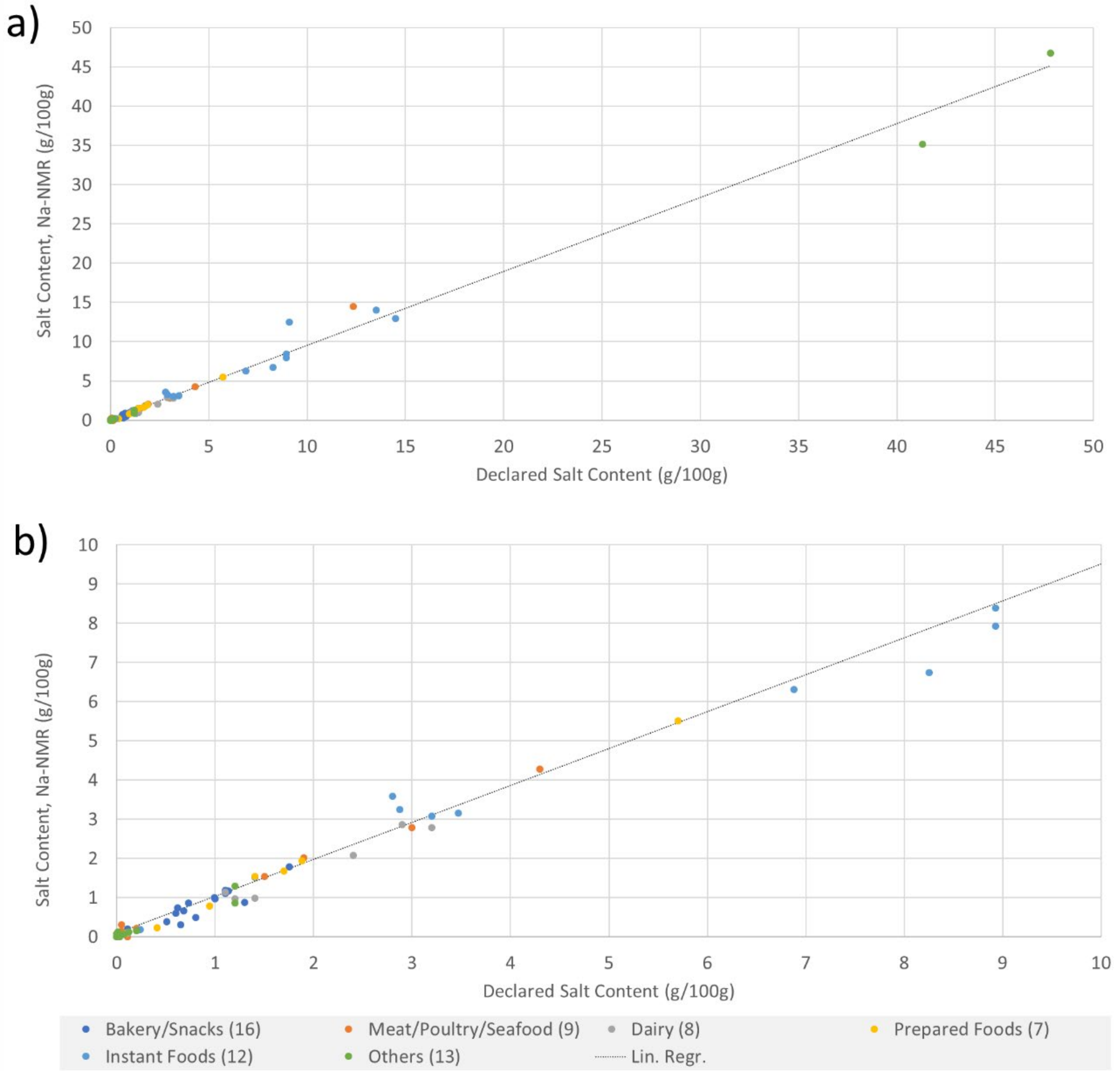

Figure 2. Results from 1-minute sodium measurements performed by TVESKAEG™ ^{23}Na NMR correlated with packet declarations for a variety of food products as marked with different colors with all samples in a) and expansion for samples with less than 10% sodium in b). The correlation coefficient is 0.99.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

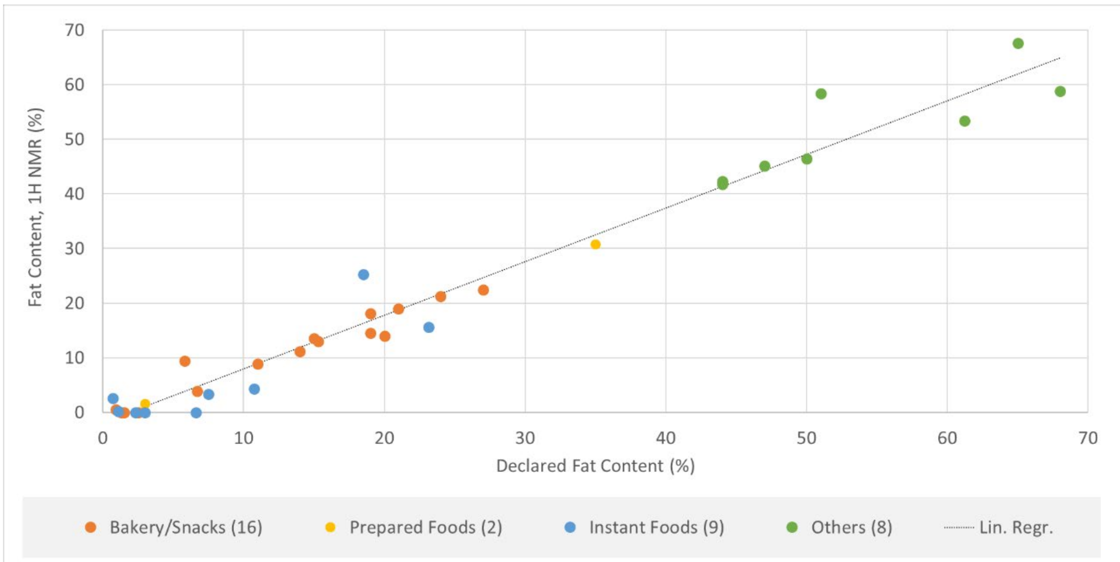

Figure 3. Correlation between TVESKAEG™ ^{1}H NMR and external laboratory measurements of the content of fat in dry food products with coloring reflecting different kinds of food products. The correlation coefficient is 0.98. The observed absolute standard deviation of all samples in %w/w is 3.6.

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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