

WATER DETERMINATION IN FOOD A CHALLENGE FOR THE ANALYSTS

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ABSTRACTS

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WATER DETERMINATION IN FOOD A CHALLENGE FOR THE ANALYSTS

1st International Workshop

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SESSION I

Introduction

Chair: E. Anklam

WATER CONTENT, ONE OF THE MOST IMPORTANT PROPERTIES OF FOOD

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Water content is a property that concerns practically every foodstuff. It has an influence on physical characteristics, technological processes, microbiological stability, shelf life, sensory properties and also has economic and legal aspects. Several methods exist for the determination of water in food. They can be divided into different groups, one main group comprising physical, and the other chemical techniques.

Within the physical methods we have again different approaches. The first group measures a product property that depends on the water content of the product. Such methods are densimetry, polarimetry, refractometry or electrical techniques like conductimetry or the measurement of the capacitance. If the sorption isotherm is known, water content can also be determined via water activity. The second group measures a specific property of the water molecules contained in the sample. These techniques comprise low-resolution nuclear magnetic resonance, near infrared and microwave spectroscopy. The third group aims at a separation of the water with consecutive determination. Such techniques are distillation methods and, above all, drying techniques. These, again, comprise methods like oven drying and more rapid techniques like microwave, infrared or halogen drying. Drying techniques do, however, not yield the water content as the result but the mass loss caused by all volatile material, observed under the conditions applied.

Chemical methods are based on the quantitative determination of a chemical reaction of water. Thus, water reacts with calcium carbide to form ethyne the volume of which can be measured. Water can be absorbed by phosphorus pentoxide to give phosphoric acid that can then be quantitatively electrolysed. By far the most important method is the Karl Fischer titration. An alkyl sulphite is oxidised to alkyl sulphate by iodine. The end point of the titration can be determined by an electrochemical effect. The Karl Fischer titration can also serve as a calibration method for other techniques.

WATER IN FOOD – A CONSUMER OVERVIEW

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Water is unique. It is the one chemical that is known to everybody. The reason is quite simple, without it man can survive a matter of days.

The change from hunter-gatherer to farmer was due in part, to the invention of food preservation. Reducing the amount of the water present made the food microbiologically stable; food treated with salt had an enhanced stability. Today we are aware that the quantity of both the total water and also the water activity of a food is of vital importance to the food industry to help predict the shelf life of a product.

As trade developed so did the opportunity for food adulteration. By the 18th century the addition of water to liquid foods, particularly beer and milk, was rife. New legislation introduced in 1870's and together with the rapidly expanding science of analytical chemistry, allowed some protection for the consumer for the first time.

The reliance for consumer protection is also based on food labelling. However if less than 5% of water is added there is no requirement for ingredient listing; the ingress of small amounts of extraneous water to high volume products has never been easier to disguise.

Water was, and remains an ideal adulterant; it is colourless, non-toxic, cheap, available and particularly before 1860's in most food products was difficult to detect.

Today, analytical chemistry is able to determine various forms of water by a variety of classical and instrumental techniques; rapid methods of analysis, often non-destructive, have been developed for process control and internationally accepted procedures with defined performance characteristics are used as reference methods.

The consumer requires the confidence provided by scientists working for the enforcement authorities to confirm the legality of food products. In turn, the scientist's need is for an increasingly sophisticated battery of analytical methods to identify deception.

CASE STUDIES IN THE APPLICATION OF AOCS MOISTURE METHODS

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The Official Methods and Recommended Practices of the AOCS are a large compendium of techniques which can be applied to oilseeds, crude and refined oils, lecithins, glycerol, and oleochemicals derived from fatty acids.

Currently approved methods for moisture are based on drying, fractional distillation, chemical, electrochemical or non-destructive techniques. Drying methods using drying oven, vacuum oven and hot plate have the drawback that other volatile materials may also be lost, giving rise to elevated moisture determinations. Distillation methods are more useful if the water content is greater than 1%. Moisture in oil and other liquid products can be measured using Karl Fischer reagent, either manually or using an autotitrator. Non-destructive methods using near infrared reflectance (NIR), transmission (NIRT) or nuclear magnetic resonance (NMR) require the use of a number of standards with known moisture content to calibrate the system. Coulometric measurements have been proposed for various oil products, but have not yet been given official approval.

For a number of applications, the accurate determination of the moisture content influences all other determinations in a proximate analysis. Most of the popular techniques are reliable but have reproducibility values (R) in the region of 0.5%. Since this is often higher than for the other techniques being applied, moisture measurement becomes the factor which limits the validity of the other values. Many oilseeds are graded and traded on their oil content and other values such as free fatty acid content. Oilseed meals are traded on their nitrogen (protein) content. The effect of the limits of moisture determination are central to the determination of these important values.

SESSION II

General

Chair: K.H. Grobecker

DRYING OF BIOLOGICAL MATERIAL AND ITS EFFECTS FOR THE USE OF BIOLOGICAL AND ENVIRONMENTAL REFERENCE MATERIALS

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The production of biological reference materials includes steps to ensure stability. In most cases product stability is achieved by a drying procedure. The intensity of drying influences sorption properties and hygroscopicity of the material. Especially as dried biological matrices represent a group of products with an affinity to water, accurate water determination is of utmost importance. A comparison of different methods of moisture and water determination allows conclusions about the significance of accurate and precise dry mass correction for the use of biological reference materials.

Exemplary results from thermogravimetric moisture and chemical water determinations as well as sorption data of reference materials, representing several food groups, will be presented and discussed.

WATER CONTENT, WATER ACTIVITY, WATER STRUCTURE AND THE STABILITY OF FOODSTUFFS

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Determination of water content, whatever the accuracy of the analytical method, is not sufficiently informative in relation to the stability of the investigated food product. Water activity (a_w) brings a supplement of information as it accounts for the availability of water for degradation reactions. The understanding of why certain products are more stable than others at the same a_w needs an elucidation of water structure. Of particular importance are the interactions (hydrophilic, hydrophobic) between water and the components of the foodstuff and the effect of the soluble molecules of the food on the hydrogen bonding in solvent water.

Studying water in foods should start with an analytical determination of water content for commercial and legal reasons which are evident. This has to be completed with the measurement of the thermodynamic activity of water in the food. Such a parameter (a_w) should hold an important place in the identification of the food product, especially as regards its shelf life. A further step in unveiling the behaviour of water in foods consists in determining water structure, at least the degree of mobility of water molecules in the studied food matrix.

This tripartite (analytical, thermodynamical, and structural) approach to water in foods will be examined, based on examples of sugars and sugar rich products.

WATER SORPTION OF WHEAT FIBRES

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Fibres play an important role in nutrition and food processing. In this investigation wheat fibres were examined which are neutral in colour and smell and with a mean length of 250 μm and a mean thickness of 25 μm . These fibres can bind additional water up to 750 %, which is useful in various aspects of the food industry, such as maintenance of freshness, quality standardisation, texture improvement and anti-caking support. To obtain an overview of this behaviour, sorption isotherms were established. To account for the hysteresis effect, both adsorption and desorption behaviour was examined. In the first case the samples were dried and then moistened in a desiccator above water and also above different saturated salt solutions. In the second case the moistened samples were dried above phosphorus pentoxide and above different saturated salt solutions. The sorption isotherms were interpreted.

Additionally, the water binding capability of the wheat fibres was examined in a baking experiment. The water activity was used as evaluation criterion for the maintenance of freshness of the baking goods. The results showed an improvement on baking goods combined with wheat fibres in comparison to baking goods without wheat fibres.

SESSION III

Karl Fischer titration

Chair: H.-D. Isengard

MAIN AND SIDE REACTIONS IN THE KARL FISCHER SOLUTION

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Since first published in 1935 the Karl Fischer titration method has gained great importance as a method for determining the water content in different substances especially in the fields of food industry and pharmacy. At present water determinations using Karl Fischer titrations are carried out about half a million times daily. Both the possibilities of applications and the constitution of the reagents are still in active development. However, until now the reactions taking place in the complex Karl Fischer solution are not fully understood. The mechanism of the main reaction itself is controversial. Essentially there are two different hypotheses: the direct oxidation of alkyl sulphite to alkyl sulphate and the oxidation of hydrogen sulphite to alkyl sulphate via formation of the unstable iodosulphonic acid and sulphur trioxide.

For further clarification of the mechanism both kinetic measurements of the iodine concentration and chromatographic determinations of the reaction products were performed. The new investigations show that various equilibria compete against each other depending on the reaction conditions. In alcoholic solutions mainly alkyl sulphite is oxidised, where a reaction via partial formation of sulphur trioxide is supposed. In methanol an exact 1 : 1 stoichiometry ($\text{H}_2\text{O} : \text{I}_2$) has been verified. In long-chain and branched alcohols and/or in the presence of higher water concentrations additionally HSO_3^- is oxidised.

In the aprotic dipolar solvents acetonitrile, DMF and propylene carbonate, HSO_3^- is oxidised by iodine. Through formation and subsequent hydrolysis of base- SO_3^- -adducts the stoichiometric factor for water is determined by type and concentration of the base, by the concentration of water and by the solvent itself.

Side reactions between the various components of the KF reagents are of direct practical importance both for the producer and for the user of the reagents. Besides the formation of iodinated species and dialkyl sulphite it was recently found out that in KF reagents sulphate and alkyl sulphate may be slowly formed even in the absence of iodine. Here the oxidation of SO_2 or HSO_3^- by atmospheric oxygen takes place via formation of sulphur trioxide.

NEW KARL FISCHER REAGENTS FOR WATER DETERMINATION IN FOOD

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In previous years a variety of new Karl Fischer reagents have been launched on the market. These reagents have been developed to fulfil the market's requirements regarding safety and the environment. They are based on ethanol instead of toxic methanol, or halogenated hydrocarbons are replaced by less problematic substances.

Water analysis in food requires special working techniques. Titration at elevated temperatures and the addition of solubilisers are often used to improve water extraction. It has to be checked whether similar techniques can be chosen using the new reagents. Coulometry is not a state-of-art food analysis technique. Aside from very special applications like the water determination in oils, volumetric titration is more usable for food samples.

The addition of toxic formamide cannot be avoided to improve the solubility of polar compounds like sugar. In this case it makes no sense to develop new applications for an ethanolic reagent. Methanol is preferred since it also improves the solubility of polar substances.

For water determination in non-polar matrices the replacement of methanolic reagents and halogenated hydrocarbons makes sense. Non-polar products are more easily dissolved in ethanol, chloroform might be avoided. For titration at elevated temperatures ethanolic reagents are also recommended since they can be heated to higher temperatures.

EFFICIENT, PRECISE AND FAST DETERMINATION OF THE WATER CONTENT IN FOOD BY THE KARL FISCHER TITRATION

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One of the most widely used techniques for determination of the water content in food is Karl Fischer (KF) titration. The primary advantage with respect to methods based on loss of weight is its high selectivity to water. On the other hand, KF titration is only possible when water in food samples is freely available. Water is present in different forms in food samples, e.g. as surface moisture in sugar, entrapped water in noodles or as capillary-bound water in vegetables. Thus, a suitable sample preparation method to release water completely has to be selected and carried out prior to the KF titration.

Water release from food samples can be achieved by direct dissolution in the titration cell, external dissolution/external extraction in an appropriate solvent (with subsequent direct titration of the solvent), and by evaporation in a drying oven. Some samples need hazardous auxiliary solvents such as formamide.

Although KF titration itself is a fast method (1-2 minutes for a single analysis), the sample preparation step is time-consuming, e.g. 1-2 hours when performing an external extraction. The use of a high-speed stirrer for internal homogenisation, in addition to fast control algorithms in automatic KF titrators, offers a fast, quick and efficient alternative to more traditional sample preparation techniques. Sample preparation and stirring time can be considerably reduced, and auxiliary solvents can be avoided. The whole analysis is completely automated. In this contribution the use of high-speed homogenisers in KF titration will be discussed in details.

OPTIMUM CONDITIONS FOR COULOMETRIC KARL FISCHER TITRATIONS IN DIAPHRAGM-FREE CELLS

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This lecture will deal with investigations of the optimum conditions for coulometric Karl Fischer titrations in cells without any barrier between the working and the auxiliary electrodes. The extent of formation of oxidisable (with iodine) reduction products formed in the cathodic reaction was found to be critically dependent on the pH of the reagent and the cathodic current density. Using continuous coulometry and methanolic reagents buffered with imidazole, the relative formation of oxidisable reduction products varied in the range 2-40%; i.e., 51-70 µg of water was found for a 50 µg water sample. If such reagents were buffered at pH 10 and contained suitable modifiers like 1-3 M of chloroform, carbon tetrachloride or hexanol the relative errors were typically in the range 0.1-0.5% provided that the cathode current density was kept in the interval 1000-4000 mA cm⁻².

The above-mentioned reagents have also been tested in a coulometric system, Metrohm 756, which is based on pulsed-current generation. The errors observed were somewhat larger but in general less than 1% which shall be compared with relative errors in the range 2-5% obtained with the commercial reagents from Riedel-de Haën and Merck.

The conditions for a 1:1 stoichiometric KF reaction using these new type of reagents have been thoroughly investigated and will be discussed in this lecture as well.

SESSION IV

Spectroscopic methods

Chair: M. Mathlouthi

CHARACTERISATION OF WATER IN AGRO-FOOD PRODUCTS BY TIME DOMAIN-NMR

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Until recently, Time Domain - Nuclear Magnetic Resonance (TD-NMR) has been used almost exclusively to quantify major constituents in agro-food and petrochemical products or to monitor their evolution during processing. In this context the technique is often referred to as "Low Resolution NMR". This situation has changed with the advent of more sophisticated instruments that can be used to perform NMR experiments previously only possible on much more expensive, high-field spectrometers. Time Domain - NMR is therefore now being used both for quality control in industry and for research purposes.

In TD-NMR, unlike other instrumental techniques such as Infrared spectroscopy, it is possible to generate a wide range of responses by using different sequences of radio frequency pulses to excite the protons in the sample. The resulting relaxation curves may vary as a function of the physicochemical properties of the product. This apparently unlimited number of possible signals is both an advantage and disadvantage for TD-NMR : on the one hand, it increases the range of potential applications of the technique, on the other, it complicates the development of new analytical procedures.

Chemometric techniques, such as Analysis of Variance (ANOVA) and Partial Least Squares Regression (PLS), will be shown to be a very useful way of getting around this problem in order to determine whether a particular TD-NMR or other signal contains any relevant information and to then extract and use that information. Techniques for the simultaneous analysis of several signals will also be presented.

Chemometrics has already been applied to TD-NMR signals by Davenel *et al.* who used Principal Components Analysis to study the relaxation curves of doughs during cooking, by Gerbanowski *et al.* applying PLS and Multiple Linear Regression (MLR) to relaxation curves and calculated relaxation parameters (T_1 , T_2 and initial signal amplitudes) and Airiau *et al.* using Principal Components Analysis and Evolving Factor Analysis to study the influence of a complexation reaction on relaxation curves and calculated relaxation parameters. Vackier *et al.* applied ANOVA, MLR and PLS to both relaxation curves and calculated relaxation parameters of gelatines while Clayden *et al.* applied Factor Analysis to ^{19}F Time Domain-NMR FID signals of PTFE samples with different crystallinities.

NEW DEVELOPMENTS OF NEAR INFRARED (NIR) SPECTROSCOPY FOR ONLINE MEASUREMENTS IN THE FOOD INDUSTRY

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NIR spectroscopy has been used in online monitoring since 1960. The first instruments were quite user unfriendly with respect to calibration and application. The improvements and development since those days covered not only the optics and the electrical components but also made a big step forward in data processing. New and improved possibilities in evaluation led to a better understanding of the process. Today the instrument signal is used in a closed control loop not only to monitor the process but also to control it.

At the beginning mainly the moisture parameter was determined in the material. Since then an enormous expansion has taken place to measure (on line in the process) many more parameters in foods such as starch, fat or oil, alcohol, sugar, protein etc.

Today's instruments are multiple component systems, which measure a number of different constituents simultaneously. The development process in gauge design will be explained with some instruments from different suppliers. Also new possibilities in calibration will be shown which make life easier for the operator.

Today the instruments are embedded in a quality system like that described in the ISO 9000 series of standards. These define a quality circle with inspection and testing at all critical points. NIR analysis therefore has an important part to play in the implementation of ISO 9000 in the food industry since it offers the opportunity to check each batch of raw materials against specifications, monitor or control the process and check the final product quality. Some examples of successful implementations will be presented.

HIGH-SPEED MOISTURE MEASUREMENTS BY THE MICROWAVE RESONATOR TECHNIQUE

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Among the several methods to determine the water content of materials, microwave measurement methods play an important role. Microwave methods are non-destructive, they are very sensitive, and they give fast and precise results. Therefore microwave methods are well-suited for in-line applications. Due to the well-defined electro-magnetical conditions the microwave resonator technique is the most precise microwave measurement method.

In this presentation the principles of the microwave resonator technique will be discussed. A method to compensate the influence of the material density is described. The effect of the product temperature on the measurement result is discussed. Several optimised resonant microwave structures used for in-line applications are shown.

In an example a high-performance in-line application demonstrates the suitability of the microwave resonator technique. In this application a special high-speed microwave system measures the moisture and density of the product simultaneously with a sampling rate of 10.000 measurements per second. While the moisture is only monitored (quality control), the density result is used to control the mean-weight of the product. Furthermore the spatial density distribution inside product samples is monitored to allow the rejection of samples with abnormal density distributions.

RESONANT MICROWAVE SENSORS FOR INSTANTANEOUS DETERMINATION OF MOISTURE IN FOODSTUFFS

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A range of microwave sensors suitable for the instantaneous determination of moisture in foodstuffs is presented. Several types of the sensors are available: The first type consists of a small container to be filled with samples of the substance, the second is a surface sensor to be mounted on the wall of a bunker or below a conveyor belt, and the third is a grooving probe to be inserted in a bulk of e.g. granular material like grain or even in a liquid. The sensors are based on open resonators at 2.45 GHz, which penetrate the materials with their fringing fields to a depth of several centimetres. The operation is mainly capacitive, but at microwave frequencies. Microwaves offer the advantage of being less sensitive to ionic conductivity within the measured substance than capacitive sensors at lower frequencies, which often masks the effect of the water content to be measured. They also have a higher penetration depth than infrared sensors. The dielectric properties of the moist substances shift the resonant frequencies and attenuate the resonance curve. Hence, under suitable loading conditions, two independent measurement values can be obtained. Those can be used to correct the moisture measurement for density changes. However, since the material may be situated in an inhomogeneous fringing field, this correction is not always possible. The various designs of the sensors and their signal processing will be explained in detail, their features will be outlined and measurements on selected foodstuffs will be given as examples in order to assess their capabilities. Sensor hardware could also be on display and demonstrated in operation.

SESSION V

Oven methods

Chair: D.N. Rutledge

INFRARED DRYING FOR FAST DETERMINATION OF THE MOISTURE CONTENT

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Infrared drying combined with gravimetric measurement is the most widely used alternative to the conventional oven drying method. Infrared dryers combine the reliability of the thermogravimetric method with the fast heating made possible by the absorption of infrared rays.

Infrared drying uses heat to cause evaporation of volatile components in the sample material. The loss of mass in the sample is calculated from the difference between the initial weight, measured before heating, and the final weight, at the conclusion of the drying procedure, to arrive at the percentage of moisture contained in the sample material. The term "moisture" refers to all of the volatile components that are given off when a sample is heated, resulting in loss of weight. Although in general usage the term "moisture" is equated with water, in this context it can also refer to other substances, such as fats, oils, alcohols and flavourings.

The decisive advantage of an infrared dryer is that it can be used in such a wide variety of applications. This flexibility is made possible by the dryer's fast measuring speeds. As a result, the dryer delivers results usually within 5-15 minutes. To achieve this advantage of speed over conventional oven drying methods, a different heating principle had to be called into play – namely, the absorption of rays.

MICROWAVE DRYING OF DAIRY PRODUCTS

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Oven drying is still the most frequently used moisture determination method. To obtain results more quickly, instruments based on more rapid heating techniques are used. One of these methods is sample drying by microwaves. The result of any drying method however, can only be the mass loss under the applied conditions. In only very few cases it corresponds exactly to the water content. The mass loss is caused by the evaporation of volatile matter present or produced during the drying process, not only by water. Particularly foodstuffs risk decomposition reactions with the formation of volatile substances on exposure to higher temperatures. The results of drying processes depend, therefore, on the drying parameters and are variable, whereas the water content is a defined property of the sample. If the true water content is to be determined by a drying process, the parameters must be adjusted in a way that the results equal those obtained by a direct and specific method like the Karl Fischer titration. The dependence on the drying parameters varies very much for different products. This necessitates a product-specific calibration. In many cases a set of parameters can be found to match the mass loss with the analysed water content, in other situations a differing, however reproducible result can be multiplied by a constant "fudge" factor to give the reference value.

For some dairy products the true water content was analysed by Karl Fischer titration and then the mass loss was determined by oven drying and microwave drying. It could be shown that, by choosing appropriate parameters, the results can be very close to the Karl Fischer values. It could be proven that microwave drying is a correct and effective method to determine not only a mass loss but also the true water content of the investigated products.

A SPECIAL VACUUM OVEN DRYING METHOD

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Text follows

**IMPROVEMENTS FOR THE DETECTION OF MOISTURE IN MILK POWDER:
A SPECIAL OVEN DRYING METHOD USING CONTROLLED AIR FLOW**

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The variation of the moisture content of dried milk determined according to IDF Provisional Standard 26A: 1993 and the EC method (1979) is affected by the humidity of the air in the laboratory where the test is carried out. COKZ has developed an apparatus for drying test portions of dried milk under adjustable, standardised conditions. With this apparatus the influence of the drying temperature and time, relative humidity and flow of air used for drying the test portion on the level and variation of the moisture content was studied. The constant mass of the test portion is obtained after 4-5 hours at a temperature of 87 °C and with continuous flushing dry air ($<0.01 \text{ mg H}_2\text{O L}^{-1}$) through the test portion. The moisture content obtained corresponds with the moisture content determined by the EC method.

SESSION VI

Application and comparison of methods

Chair: K. Schöffski

DETERMINATION OF WATER IN MILK POWDER – A COLLABORATIVE STUDY

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The method according to the International Dairy Federation, IDF Standard 26 A: 1993 corresponding to AOAC is currently the reference method for the determination of water in milk powder. It is widely used and generally accepted.

The method is based on drying a test portion to constant mass under given conditions. However, constant mass is a major problem of this method as it is hardly ever achieved.

The results are dependent on the relative air humidity in the laboratory and are therefore of poor reproducibility. For this reason a collaborative study on the determination of water in milk powder was performed in order to compare the results of alternative methods with those of the IDF-method.

The study was designed, organised and performed according to the international standard ISO 5725 Part 1-6 (1994). Special emphasis was placed on the validation of the ease of handling and the statistical evaluation of the results. The water determination in milk powder was performed using four different methods: The IDF drying oven method under atmospheric pressure, two different vacuum drying oven methods and Karl Fischer titration. Skimmed and whole milk powders from Austria, Finland and Spain have been investigated. Eight experienced laboratories from eight European countries participated in the collaborative study.

For the evaluation of the performance of the four analytical methods the following parameters have been assessed: instrument handling, repeatability, reproducibility and accuracy of the results. The vacuum oven method No.1 and the Karl Fischer titration achieved best results for repeatability and reproducibility. The Karl Fischer titration performed best regarding the accuracy of the results for the total amount of water in milk powders. The selected drying parameters of the vacuum oven method No.2 achieved results, which were close to the total amount of water in the milk powders obtained by the Karl Fischer method. Analytical confirmation by NIR spectrometry and the lysine test supported the accuracy of the results.

ALTERNATIVES TO OFFICIAL METHODS USED FOR WATER DETERMINATION IN HONEY

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The water content in honey is usually determined via the refractive index. With the help of the Karl Fischer titration using the two-component system and a temperature of 50 °C it is possible to determine the water content in honey quickly and precisely. The refractive-index method usually yields results lower than those found by the Karl Fischer titration.

The refractive-index method prescribes that crystalline honeys have to be liquefied at a temperature of 50 °C before determination, while for the Karl Fischer titration a temperature of 40 °C is sufficient (simpler handling of the sample). It could be shown that a pretreatment at too high temperatures makes the water content determined by the refractive-index method decrease more strongly in comparison to the Karl Fischer value.

A further method for the determination of the water content is the drying process by infrared radiation, where the mass loss results depend on the parameters chosen.

However, the determined moisture may not be equated with the water content of a sample, since the moisture includes all volatile components, which escape during the heating. In order to match the mass-loss results with the true water content measured by a reference method like in this case the Karl Fischer titration, the drying process parameters must be adequately adapted. It could be shown that after such a calibration, the water content can be determined in relatively short time and with small product deterioration.

DETERMINATION OF THE MOISTURE CONTENT IN HONEY SAMPLES

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The moisture content of 54 authentic honey samples from various geographical and botanical origins was measured by four different means: refractometry, direct drying, a special oven method and Karl Fischer titration. The first two methods are official methods for the determination of honey moisture. The prototype special oven method is similar to the conventional oven. However, a vacuum can be applied under controlled atmosphere (N₂) during the heating and cooling procedure. The Karl Fischer titration method determines the total water content.

These various methodologies used for the analysis of water slightly impacted the values obtained. Plotting the results of the refractometric method against the others, it was seen that overall Karl Fischer gave higher general values followed by direct drying, leaving the special oven method with lower values.

This work was part of a project on the evaluation of methods for the determination of the botanical and geographical origin of honey. No significant differences between the honey samples of different floral and geographical origin (from European Member States) could be observed.

MOISTURE DETERMINATION IN DAIRY PRODUCTS – ASSESSMENT OF AVAILABLE INSTRUMENTATION

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The determination of moisture in food products is essential for compliance with legislation and to guarantee product stability during the distribution chain. In drying processes the moisture content is the most important control parameter and in order to keep the product quality stable, strict control is necessary. Too high moisture can lead to browning reactions, caking, modifications in the product taste and other consumer perceivable product qualities. A too low moisture content tends to lead to oxidation and alteration of the taste.

Several methods were assessed in order to evaluate the accuracy and precision of different analytical techniques. This allows us to establish the performance of these methods for different areas of use like reference laboratory, in-line laboratory or on-line production control. We evaluated methods such as the air-dried oven at 120 °C, infrared balances, Karl Fischer titration and drying by desiccant P_2O_5 . Differences of these methods are explained by the different stages of absorption of the water (free water, bound water, crystallisation water) by additionally using water activity measurement. It is important to be aware of all the parameters influencing the performance of analytical methods in order to limit variations due to analytical errors.

COMPOSITION OF FOODS INCLUDING ADDED WATER USING MICROWAVE DIELECTRIC SPECTRA

A Project under the 4th Framework Programme: FAIR CT97-3020

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The added water content of fresh and untreated pork, poultry, fish and prawns was adjusted either by dipping in polyphosphate and salt solutions of known concentrations for controlled periods, or by injection (pork) with polyphosphate and salt solutions. Mixtures were prepared from treated and untreated fish and other foods (milk and flour). Liquid uptake was determined by the weight gain of samples. The proximate composition of the samples was determined (water, fat, protein, NaCl, and phosphorus (for polyphosphate content)). Complex dielectric spectra of each product were measured at known temperatures and at 31 frequencies in the range 0.2—12 GHz using an automatic network analyser (ANA) and a 3.0-mm open-ended coaxial sensor.

The spectra were subjected to various procedures:

- Principal component analysis using the individual complex components.
- Regression of the composition data against the principal components to obtain prediction formulae for composition including liquid uptake (Internal Cross-Validation).
- Regression of the composition data against raw spectral data and against other composition variables to obtain similar formulae.
- Discriminant analysis using principal components.

In order to design a simpler instrument the effect on accuracy was studied of reducing the number of frequencies in the spectrum and its range. The slight loss of accuracy engendered by using only 5 or 6 frequencies was acceptable. The accuracy of the method in predicting liquid uptake and composition was good. Using one of the compositional variables in the calibration made it equivalent to accuracy obtained by proximate analysis, which was the limiting factor. Measurements on solutions of glycerol, NaCl and water with precisely known composition demonstrated that the intrinsic accuracy of the instrument was far better.

A prototype instrument was built and validated using samples of prawns and herring.

DETERMINATION OF THE WATER CONTENT IN DIFFERENT SUGAR SYRUPS BY HALOGEN DRYING

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Nowadays quality control plays an important role in the manufacturing process. For that reason it is necessary to find accurate and fast methods to analyse products.

The water content can give useful information about the quality of products and production steps. Economic and legal aspects are also important. A well known method for the determination of the moisture content is infrared drying. The halogen dryer used for the following investigation has been developed from an infrared dryer. The different sources of radiation can have different effects on the drying process. The aim of the following study was to find a method to determine the water content in invert sugar syrup and fructose syrup by halogen drying. The interaction between water and sugar makes it necessary to use higher temperatures. Therefore, volatile substances caused by side reactions could simulate a higher water content. On the other hand a crust on the surface of the sample could prevent all of the water being determined. Karl Fischer titration was used as a reference method to ensure that the results of the halogen dryer represent the water and not the moisture content.

A suitable method could be found for both syrups. The possible errors caused on the one hand by undetermined enclosed water and on the other by detecting volatile substances other than water produced during the heating process compensate each other. The determination method is fast, accurate and easy to carry out.

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