Food and Beverage

Weighing
Titration
Moisture & water
pH value
Fat & oil analysis
Brix

Sweets and Savory Solution Guide

A Collection of Essential Analyses

METTLER TOLEDO

Editorial

Dear Reader,

Working in bread, confections, snacks, and pasta manufacturing is challenging yet rewarding. Natural products of varying composition need to be manufactured into consumer goods of consistent high quality to meet consumer expectations. This requires consistent and stringent quality assurance measures. Food safety trends and requirements further increase the demand for testing, error-free documentation and traceability. Strict hygienic specifications are prerequisite, thus requiring diligent execution of work tasks.

This guide presents selected METTLER TOLEDO solutions that support your chemical analyses from incoming ingredients inspection, to production monitoring and final product quality control. Most of the solutions describe routine tests. However, some material characterization tests apply to process technology development and new products design.

Consumers appreciate natural and healthy foods. Products such as bread, chocolate, potato crisps and pasta – to name just a few – are predestined to match such preferences. Thorough and accurate testing when manufacturing these products is one of the many steps to achieving consumer satisfaction.

Mettler-Toledo

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1. General Introduction

Around the world, grab-and-go food, including all manner of baked goods, confections, crisps, sweet and savory snacks, pasta, and more continue to rise in importance in fast-paced, modern cultures. Ensuring the quality, appearance and the palatability of products which often include raw and perishable ingredients, requires the right knowledge, technologies and tools. This will become even more true as food manufacturers continue to evolve their product lines with additional flavors, new sources of "sweetness", new grains, and shifts in fat sources to meet consumer demand for satisfying and increasingly healthier options [1].

To ensure product consistency and shelf-stability in this ubiquitous and wildly diverse category of comestibles, quality control technologies must be able to measure ingredient and batter and batch attributes such as moisture, pH, acidity and others, accurately and repeatably. This guide will provide suggestions and solutions you can use to help enhance safety and consistency in both your production facilities and quality control labs to produce happier customers, as well as the kind of improved process economics that help protect manufacturing profit margins.

State of the industry

Across most food industry segments, producers continue to be plagued by concerns such as the economic volatility that attends market shifts, increasingly denser food safety and quality regulations, imminent supply shortages, and rising feedstock and energy prices [2]. According to the International Dairy-Deli-Bakery Association, economic uncertainty is changing food-buying behaviors as well. "Channel surfing" is cutting the number of grocery store trips, while shrinking family size is reducing the volume of those trips. In October 2013, the association reported that 85 percent of global grocery purchasers said higher food prices affect their buying patterns and 52 percent noted price was a major consideration [3].

In this food- and snack-buying environment, which is expanding with everything from dried seaweed snacks to an almost continual parade of new energy bars, differentiation and relevance to the consumer are considered critical. Baked goods, confections, snacks and pasta may be poised to evolve into these market conditions, particularly if many customers' varied concerns for convenience, nutrition, pleasure and value can find common ground through innovative forms that share shelf-space alongside tried-and-true product formulas [4].

Addressing quality and safety

The bakery, confectionery, snacks and pasta industries rely on a broad supply chain network to obtain the ingredients they need to create their unique product blends, from milk, edible fats and oils to grains, sugars and additives like flavors, vitamins, stabilizers and anti-oxidants. As such, tracking, tracing, and assessing the quality and freshness of these items, while often a complex task, is absolutely critical to batch-to-batch consistency and product formulation. Thus, the segment is governed by many of the same national and international quality assurance regulations and legislations as many other foodstuffs.

Essentially, a complete regulatory framework starts with the feed and food chain, with a goal of improving food safety and ensuring the health of international trade. Various schemes are applied around the globe to ensure food safety and quality. The Global Food Safety Initiative (GFSI) claims to harmonize such schemes. It provides a platform for collaboration between some of the world's leading food safety experts from retailer, manufacturer, producer and food service companies, service providers associated with the food supply chain, international organizations, academia and government [5]. Service providers include auditors and standard owners such as BRC (the British Retail Consortium), IFS (International Featured Standards), SQF (Safe Quality Food Institute), among others.

Test requirements are stipulated for determining nutritional composition, microbiological status, residues, contaminants and other critical food properties. GFSI seeks to manage the convergence between various food safety management systems by maintaining a benchmarking process for them. The ISO 22000:2005 Food Safety Management System works to prevent presence of food-borne hazards at the point of consumption as well.

Regulatory guidelines also form a basis of several different types of chemical analyzes that are critical to baked goods and confectionery products' freshness, visual appeal, taste, texture, and shelf stability. Organizations such as the Association of Official Analytical Chemists (AOAC) and the International Organization for Standardization (ISO) exist to some extent to assert these methods, protect trade, and ensure that baked goods, confectionery, snack and pasta products remain safe from production through distribution to consumption [6].

The growth of functional foods

Regulatory requirements and tests related to food quality will continue growing in importance as desires for satisfying yet healthier products evolve to meet specific dietary requirements. Such special products are sometimes placed in the category of "functional foods". Functional food demands in snack items are being heightened by increased attention to disease risk factors and allergens. Food manufacturers are continuing to develop real-food solutions to address these concerns, and consumers are responding positively to their efforts [3, 7].

In 2012 alone, the Institute for Food Technologists notes that 78 percent of consumers made a strong effort to get more vitamins and 57 percent consumed more products with specialty nutritional ingredients, including vitamins C, D and B, protein, and fiber [8]. In this climate, the evolution of specialty products such as viable, appealing "gluten-free" baked goods, salt-reduced soups and sugar-free confections will continue to impact product development in this diverse food segment worldwide [8].

Cost-effective testing convenience

Modern quality control requires a systematic approach. With test methods requiring a certain sampling frequency, the evolution of new products, and cost pressure created by rising input costs, baked goods, confectionery, snacks and pasta manufacturers will likely continue to move towards faster, less-expensive, automated methods for carrying out quality tests. Any developments in analytical science that offer newer, more cost-effective test methods, however, must undergo scrutinizing comparisons with current tests, prove efficiency, provide consumer safety and meet globalized food standards.

Labs involved in development, production and quality control of baked goods, confectionery, snack and pasta continue to seek out ways to cost-effectively ensure compliance with their methods of analysis and sampling. The labs help to ensure consistent manufacturing of pleasing products with necessary characteristics including shelf-stability.

As they do, METTLER TOLEDO products such as balances, moisture and Karl Fischer analyzers, titrators, thermal analysis instruments, pH meters, refractometers, and density meters will continue to help them provide better value and quality consistency to consumers, added convenience for lab operators, and enhanced economics for manufacturers.

2. Products Concerned

This guide attempts to cover the wide variety of products from the bakery, confectionery, snacks and pasta production segments. Despite the diversity of consumer products, major ingredients are similar, and many of the production steps apply similar principles.

Thus, from the point of chemical analysis the same or similar parameters need to be tested. Such analyzes are performed along the entire production chain from raw ingredients to final product. We have divided the final products into savory and sweets to simplify the overview.

Classical water analyzes including hardness (calcium, magnesium), p- and m-value (alkalinity), chlorides, pH value and conductivity, exceed the scope of this guide and are not explained here. We refer to the water analysis application brochure 37 of METTLER-TOLEDO [10].

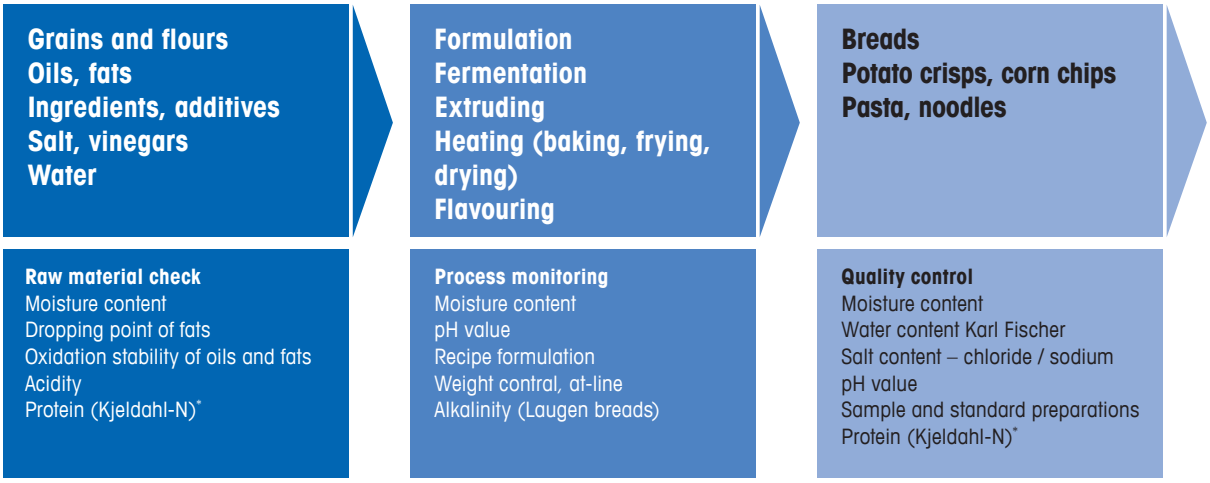


Figure 1: Savory overview

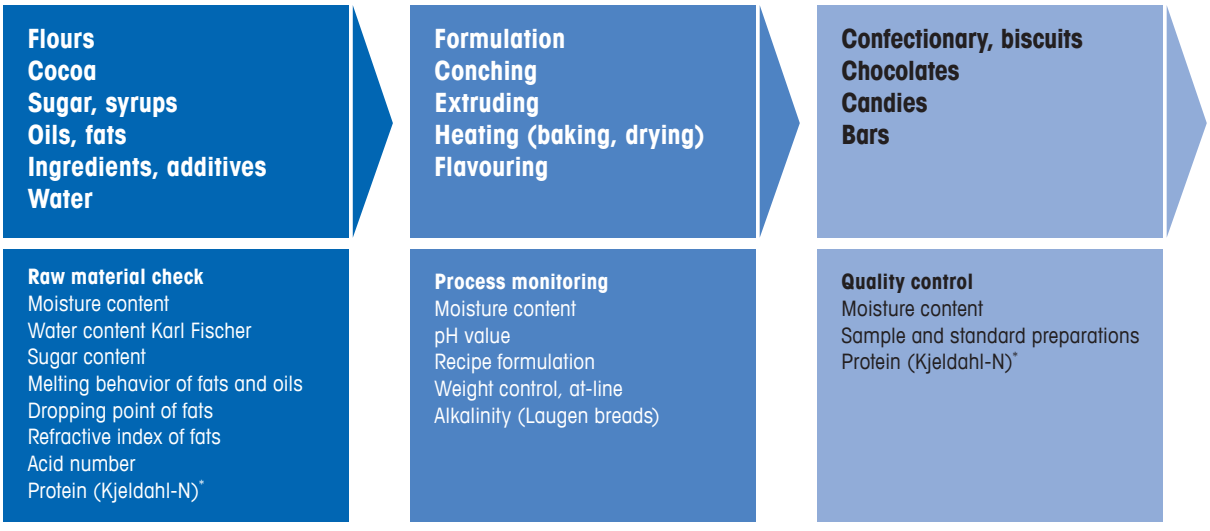


Figure 2: Sweets overview

(*) The protein content determination based on the Kjeldahl method of digestion, steam distillation and titration is not elaborated here. It is described in details in a dedicated application brochure [9].

3. Analyses

In this chapter we describe some general lab tasks and selected analytical parameters applied to analyze the aforementioned products. Some explanations about the parameters as well as some guidance on how to perform these tasks best are presented.

Method	Chapter	Method	Chapter
Sample preparation	3.1	Salt content chloride sodium	3.7
Moisture and water content Halogen Moisture Analyzer Karl Fischer	3.2		
pH value	3.3	Ammonia in raising agents	3.8
Sugar content (Brix)	3.4	Fat and oil characterization by DSC	3.9
Dropping point of fat	3.5	Recipe formulation	3.10
Acidity	3.6	Check weighing	3.11

Table 1: Selection of analyzes applied to dairy testing

3.1 Sample Preparation

Determining sample size and, in particular, sample weight is a fundamental step of sample preparation. A variety of samples from liquids to solids and pasty goods need to be prepared during a normal working day in a food QC lab. Sample size usually ranges from a few grams to some 50 grams. Thus, an analytical balance has to provide the right weighing capacity.

Standard solutions must also be prepared to calibrate spectroscopic or chromatographic analyses, such as the analysis of milk proteins by high performance liquid chromatography (HPLC). Reference materials, normally in the milligram range, are weighed. Here the analytical balance must be able to offer the required minimum weight capability as well.

An accurate and precise sample or reference material weight is of paramount importance as it is the first step of the measurement uncertainty tree. Mistakes made here propagate through the entire analysis. Basic weighing error risks include electrostatic charges of samples, references and tara vessels; spilling of sample material during the weighing; wind drafts and rapid temperature changes (e.g. by air conditioning); vibrations; operating errors and incorrect manual notes and calculations.

3.1.1 Reduce Weighing Errors

The typical approach to preparing sample and standard solutions is to weigh a certain amount of sample or reference, transfer to a volumetric flask, and dilute with solvent. Thus, how can we reduce errors in sample preparation? A few updates and changes to traditional lab equipment can make big differences in accuracy and productivity in sample and standards prep.

1. Dose directly into your tare container and avoid any intermediate receptacle and sample losses. ErgoClips can help. ErgoClips are ergonomic tare container holders, available for all kinds of vessels and vials. They keep containers well-positioned for weighing. ErgoClips fit with all METTLER TOLEDO Excellence XPE, XSE and XA analytical balances.

Figure 3: ErgoClip with flask on an XP56 analytical balance

2. If you cannot use ErgoClips, avoid the old-style weighing paper. Weighing papers can easily cause sample loss. Switch to new METTLER TOLEDO SmartPrep funnels. SmartPrep is an ergonomically designed funnel which directly improves the accuracy of prepared solutions. It perfectly fits all volumetric flasks. It features a large dosing area to avoid spilling and a smooth surface for efficient rinsing. SmartPrep is made of static-resistant plastic.

Figure 4: SmartPrep funnel

3. Gain automatic method guidance and data collection with LabX. Let LabX software guide you through the entire weighing process prompting each operational step on the balance display. LabX also collects all data error-free for later evaluation, archiving purposes or audits. LabX is the easiest way to avoid manual transcription mistakes and speed up lab work.

Figure 5: LabX software, standard preparation application

4. Place the analytical balance on a stable weighing table to avoid disturbance by vibrations. Avoid wind drafts from air conditioning and ventilation.

5. Do not expose the balance to direct sunlight in order to avoid deviations when weighing. Excellence analytical balances from METTLER TOLEDO provide FACT and proFACT, a fully automatic time- and temperature-controlled internal adjustment procedure, to help avoid this kind of atmospheric interference with results.

Figure 6: QB1 Quantos dosing systems, detail of weighing chamber with powder dosing head

6. Follow the SmartSample™ workflow. METTLER TOLEDO's SmartSample is a secure workflow ensuring results are unquestionably allocated to the right sample. The RFID option of Excellence analytical balances writes the sample weight to the RFID tag of the titration beaker when weighing is complete. The tag is later read by the autosampler and data is sent to the titrator. Because the RFID tag is attached to a unique beaker, the beakers can be placed in any sequence on the InMotion sample changer, with results still correlating safely to the appropriate sample data. No more beaker numbering; no more writing sample weights on beakers, papers or lab journals; and no more confusing of samples.

7. Apply Quantos dosing systems. Quantos is the latest development of METTLER TOLEDO for the dosing of powders and liquids. Fully automatic dosing of powders and liquids removes almost all sources of user error and gives highest level of accuracy and user safety.

With a few changes, significant improvements in weighing accuracy for samples and standards solutions can be achieved. This results in a significant increase in reliability, traceability, efficiency, and convenience.

3.1.2 Increased Safety

With LabX, quality managers and supervisors can create and administer all analysis methods, grant user privileges, and openly define numerous safety criteria. All settings and changes can be assigned to one individual balance, or deployed to all connected balances. This kind of protection helps ensure that samples are not tampered with and the right analyzes are performed.

For instruments see chapter 5.1

3.2 Moisture and Water Content

Moisture in bakery, confectionery, snacks and pasta products and in their ingredients is frequently analyzed before, during and after the manufacturing process to ensure the final product meets the desired overall properties and standards. Texture, taste, appearance, mouth feel and shelf-life are affected by moisture content. The final product must retain its properties up to the time of consumption. Therefore, ensuring optimal moisture content is a key aspect of quality control.

If water content must be measured specifically, Karl Fischer titration is applied. Here, special chemical reagents containing iodine and other compounds react directly with water.

3.2.1 Moisture Content

The drying oven is the typical reference method noted in food regulations. However, quality and process control of raw materials, semi-finished and final products usually needs information on moisture much quicker to enable timely interventions.

A much faster and effortless alternative to the drying oven are the Halogen Moisture Analyzers from METTLER TOLEDO. Also based on the LOD (loss on drying) principle, halogen moisture analyzers provide reliable results in minutes instead of hours. In fact, we have demonstrated the precision of our instruments by a cross-validation of the moisture analyzer vs. the drying oven for several samples such as crisps, snacks or pasta.

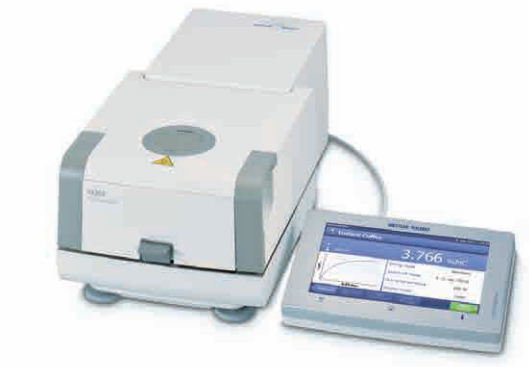


Figure 7: The Halogen Moisture Analyzer HX204

To summarize, METTLER TOLEDO halogen moisture analyzers are excellent choices for sweet and savory sample analysis because they are robust and easy-to-use, and they have proven reliable for 24/7 factory operation.

Sample	Moisture Analyzer			Drying oven		
	%MC (mean)	SD	Time [min]	%MC (mean)	SD	Time [min]
Cake mix	5.09	0.15	5	5.25	0.16	90
Chips	1.06	0.03	6	1.03	0.01	240
Cornflakes	4.15	0.04	8	4.19	0.01	240
Flour	11.00	0.08	7	11.00	0.09	120
Spaghetti	8.65	0.08	15	8.60	0.09	90

Table 2: Cross-validation of moisture analyzer to reference method drying oven (%MC = Moisture Content; SD = Standard Deviation)

Sample	Moisture Analyzer				Drying oven	
	Sample weight [g]	Drying program	Temperature [°C]	Switch-off criterion	Sample weight [g]	Temperature [°C]
Cake mix	5	Standard	160	3	5.5	130
Chips	5	Standard	135	3	5	102
Cornflakes	3	Standard	130	3	5	102
Flour	4	Standard	140	3	5	130
Spaghetti	4	Standard	145	3	5.5	130

Table 3: Methods used for moisture analyzer and reference method drying oven.

Tips for sample preparation and sample distribution:
The correct preparation of samples is key to repeatable and reliable results. Ensure even granulation and homogeneity of the sample, e.g. crush potato chips and spaghetti or mix the cake mix before measurement. Furthermore, an evenly spread sample on the sample pan results in a homogeneous distribution of heat throughout the sample being measured so moisture can diffuse evenly out of the sample and generate more repeatable results.

3.2.2 Water Determination by Karl Fischer Titration

Since the late 1970's several collaborative studies explain the suitability as well as limitations of the Karl Fischer titration when testing grains, breads, confectionery, pasta, etc. [11] [12].
Bread, confections, snacks, and pasta foodstuffs are insoluble in the usual solvents and release water only very slowly when put in the KF solvent. Thus, several sample preparation techniques are applied:

- Samples need to be disintegrated properly, e.g. finely crushed or milled.
- Additional solvents such as formamide are used, yet the formamide content shall not exceed 50% of the total solvent volume.
- Sufficient stir time (i.e. extraction time) in the titration vessel just before titration, typically 900 seconds.
- Stirring and titration at elevated temperature up to 50 °C and in the presence of formamide (*).
- External extraction of the sample with methanol or formamide (in some cases at elevated temperatures) for an extended period of 30 to 90 minutes.
- As an alternative, a drying oven may be applied to evaporate the water of the sample which is then transferred to the titration cell with a dry purge gas (*).

Figure 8: A Karl Fischer titratror: The volumetric titrator V30

(*)However, baked goods containing carbohydrates (sugars) may undergo thermal decomposition at and above 50 °C releasing water which then falsifies the result.

Remarks to the samples of table 4:

- Flour, biscuits, and potato crisps have all been crushed and titrated directly at 40–50 °C adding formamide to the solvent.
- Noodles, zwieback, dough and corn flakes have been tested applying the external heating oven at 120–190 °C. Nitrogen purge gas was applied to transfer evaporated water into the titration cell.

Sample	Water content (%)	RSD (%)
Flour	12.1	0.36
Biscuits	5.79	0.87
Potato crisps	4.83	0.72
Noodles	10.1	1.3
Zwieback	1.89	0.59
Corn flakes	6.14	0.69

Table 4: Water content in selected samples. Average water content and relative standard deviation (RSD) from six measurements [11]

For instruments see chapter 5.3 and 5.7

3.3 pH Value

The pH value indicates how much and how strong acids or leaches present in the sample are. Sample solutions with pH below 7 are acidic. If the pH is above 7, the solution is basic (also called alkaline). At pH 7.0 the solution is neutral. By definition, the pH value is related to the concentration of the hydronium ion H_3O^+ which is formed when an acid such as citric, lactic or acetic is dissolved in water. The pH value in dough influences the crumb's structure and palatability. This is especially relevant for rye breads. Thus, pH can be a quality limiting parameter.

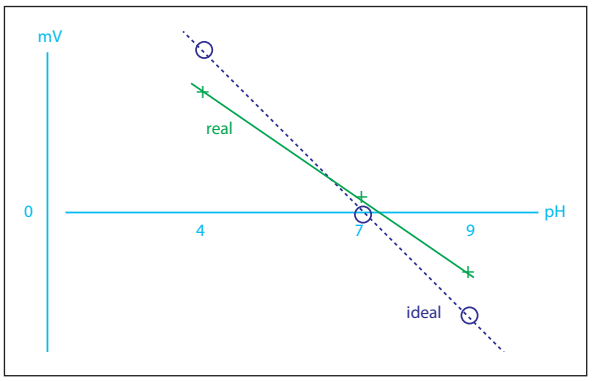


Figure 9: Schematic of a three-point pH calibration

The determination of the pH value requires a meter and a suitable electrode. Manufacturers usually offer a selection of models to cover actual customer needs. Small meters for simple routine tasks or elaborate models with color display, touchscreen, high resolution, data storage and many more features are available. The user can also choose from a variety of electrodes. Shape of the glass membrane (round, flat, puncture, etc) and shaft material (glass, PEEK, polysulfone) are two decisive factors.

Figure 10: Use of a portable pH meter with puncture electrode to check pH value of apples

The choice of pH electrode strongly depends on the consistency, temperature and composition of the bakery, confectionery, snacks or pasta products as well as their ingredients [13].

- For semi-solid samples like dough a puncture electrode is recommended.
- When cold and warm samples have to be measured, electrodes with short response time allow for efficient working. The Equithal® symmetric electrode design guarantees fast and stable readings when temperature fluctuates.
- Samples containing proteins require electrodes with a reference system which avoids the leaking of silver ions to the electrolyte. When electrolyte containing silver ions flows through the junction into the sample, proteins are precipitated and clog the junction. Clogging the junction leads to slow electrode response and unstable readings. The ARGENTHAL™ reference system stops the silver ions from discharging into the electrolyte.

- A further solution to avoid clogged junctions and achieve stable readings is an open or movable sleeve junction. Such types of junctions can be easily cleaned and kept free.

For more information and electrode selection go to www.electrodes.net.

Because of the importance of the pH value, we recommend applying a two or three point calibration. When the pH value of the samples can be below or above 7, three calibration points are good practice, typically pH 4, 7 and 9 (or 10). This ensures that pH values in a range from 4 to 9 or 10 are measured correctly. If the samples are mainly acidic, which is true for many food and beverage samples, a two point calibration between 4 and 7 is acceptable and yields reliable results.

Nowadays, pH buffers need to be traceable to generally accepted reference standards (e.g. NIST). Please respect the expiry date of the buffers ("best before…") to ensure reliable calibrations. We recommend using ready-to-use buffers in order to avoid any errors due to dilution or impurities. Discard used buffers. Backfilling them may contaminate the remaining buffer solution.

For instruments see chapter 5.4

3.4 Sugar Content (Brix) in Liquids

The sugar content of liquids such as concentrates, syrups and fruit juices, is a relevant quality parameter. There are many different sugars, e.g. sucrose, malt sugar, glucose, and HFCS. Strictly speaking, Brix only refers to sucrose content in aqueous solution. The unit Brix is defined as percentage by weight of sucrose in pure water solution. Therefore, the designation of Brix degrees is only valid for pure sucrose solutions in water. When determining the Brix degrees on malt sugar, glucose, honey or other sugars, the obtained results are not true Brix degree but related values only.

Nevertheless, this popular and often used unit is widely applied to express concentration of sugars in different samples. Most commonly Brix is determined by density or refractive index. Manual density measurement methods include pycnometer and hydrometer. For refractometry Abbe type refractometers are often applied, either an easy-to-carry handheld or a benchtop model. These manual methods, however, depend on operator readings which limit accuracy and precision of results, and may cause transcription errors, because the measurement data cannot be processed automatically.

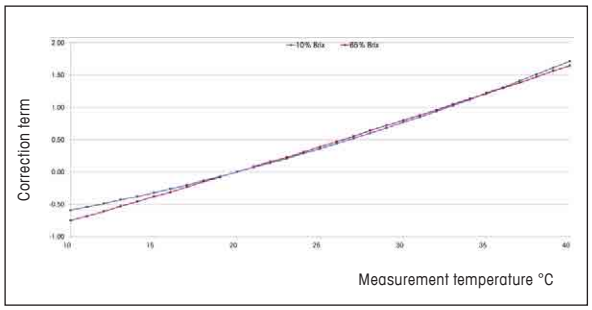


Figure 11: Temperature correction term to be applied to Brix value

Furthermore, very accurate results can only be obtained by thermostating the sample to the required temperature (e.g. 20 °C). This takes a long time with pycnometers or hydrometers. Digital density meters have a built-in Peltier thermostat wich sets the temperature of the sample to ± 0.02 °C of the target temperature within less than a minute.

Raw refractive index and density values are converted into degrees Brix using official conversion tables issued by ICUMSA (International Commission for Uniform Methods of Sugar Analysis) and NBS (National Bureau of Standards), respectively. As the reading depends on temperature, a temperature compensation is needed to get accurate results (Figure 11). For manual instruments this implies adding a correction term to the reading. Digital handheld density meters and refractometers offer a

Figure 12: A digital benchtop refractometer

built-in temperature correction, which obsoletes the manual error-prone compensation.
For very precise Brix measurements (e.g. concentrates, molasses) thermostated instruments are the best choice. The reading occurs at a user-defined target temperature (mostly 20 °C). Thus, any temperature compensation error is omitted.

Modern digital benchtop meters have built-in solid-state thermostats. This keeps the temperature of the measuring cell and the sample precisely constant at the selected temperature. Brix readings as precise as ±0.003 Brix are possible.

For instruments see chapter 5.5

3.5 Dropping Point of Fats

3.5.1 Dropping Point Fundamentals

Edible fats, fatty acid esters, and many other materials such as greases, waxes, polymers or tars, which are important raw materials for various industry segments, do not show a defined melting point. These materials gradually soften as the temperature rises and melt over a relatively large temperature interval. Generally, the dropping or softening point test is one of the few easily achievable methods available to thermally characterize such materials.

However, the manual determination of dropping and softening points requests long observation periods and is subject to operator bias. Automatic dropping point instruments have been available for many years. Even so, the choice of automatic instruments was limited.

METTLER TOLEDO has recently introduced a selection of modern, automatic melting, dropping and softening point instruments. These instruments apply a new, unique detection principle and operate under the easy-to-use One Click™ method.

Automatic dropping point determination: the unique detection principle

The dropping point measurement principle is based on a unique automatic video image analysis that allows direct insight into the dropping or softening point process. The image analysis technology was published as patent EP 2565633 from the European Patent Office in 2013.

Video based image analysis

Generally, the dropping point is the temperature at which the first drop of a molten substance precipitates from a standardized vessel with a defined orifice under controlled test conditions in a furnace.

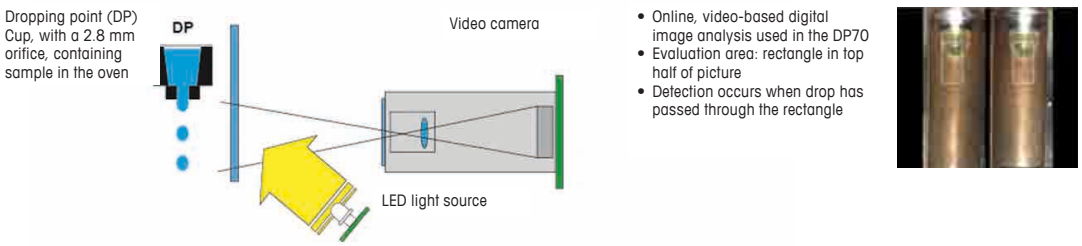


Figure 13: Principle of automatic dropping point measurement.
The video screenshot shows the dropping event of liquefied milk fat at 33.8 °C

Manual methods obviously require the visual inspection of the dropping point process, which is tedious as the attention of an operator is required to watch the test process. This can take considerable time. The drop point is a suddenly occurring event, as the liquefied drop is accelerated by gravity as it escapes the cup. Once this happens the operator needs to quickly note the temperature. In summary, manual dropping point testing is a time-consuming, error-prone process that is strongly influenced by operator bias.

Automated reading of the dropping point temperature
If human observation is replaced with a device that records and evaluates the dropping point event automatically, the quality of the result is greatly improved. In addition, no observation time in front of the apparatus needs to be spent by operators.

In METTLER TOLEDO Dropping Point Excellence instruments, a white balanced LED light is shone on the sample cup and holder inside the furnace. The reflection is recorded by a video camera. The entire drop point test is video-recorded and image analysis is used to detect the first drop that escapes the sample cup when it passes through a virtual white rectangle located underneath the cup orifice. While detecting this, the furnace temperature is measured and recorded at a resolution of 0.1 °C.

Melting point of milk fat and other edible fats
Edible fats are invariably mixtures of mixed triglycerides. Therefore, they exhibit a melting range rather than a melting point. The clear melting point is the temperature when the melt of the edible oil becomes completely clear. It is usually determined by capillary tube methods. However, the filling of capillary tubes with fats and oils may be difficult and laborious. Hence, the more empirically-based thermal value dropping point was found to be a suitable alternative for the thermal characterization of edible oils and fats.

3.5.2 Standardized Determination of Dropping Point

Sample preparation as well as the measuring method is thoroughly described in the AOCS Cc 18-80 standard. Including sample preparation it is a fast method and has become a tried and tested method of quality control for edible fats.

The dropping point method is applicable to edible fats that solidify sufficiently when held in a freezer for the allotted time. This can be ensured with the separate measuring cell of the DP90 Excellence Instrument, which can be easily stored in a commercially available refrigerator or freezer (Fig. 14). Once the measuring cell is cooled to the desired temperature, controlled heating in line with the programmed method starts and the dropping point is automatically detected by video-image analysis.

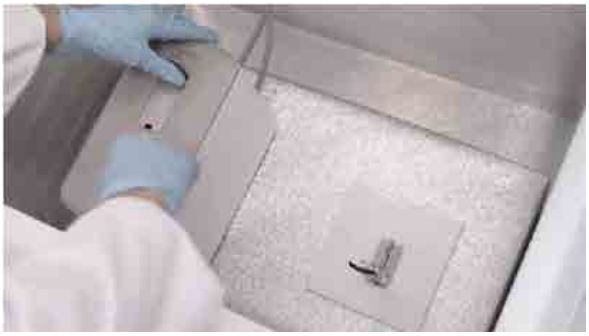


Figure 14: The external DP90 measurement cell in a freezer.

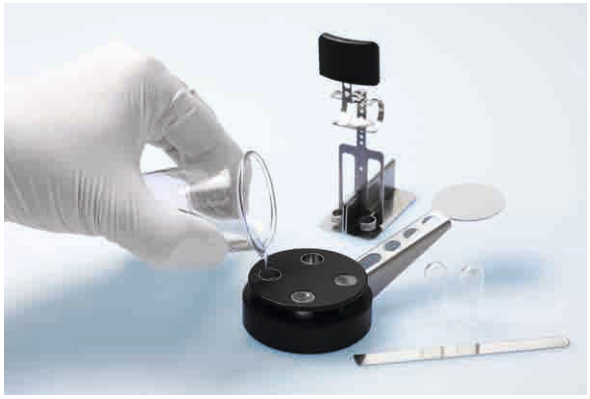


Figure 15: The DP sample preparation tool allows to fill the cups simultaneously with four samples.

To achieve comparable results, the AOCS standard demands melting the sample as a preparation step, in order to fill the standardized dropping point cup. The sample preparation tool of DP90 and DP70 Excellence Instruments can hold four cups which in turn can be quickly filled with the molten sample. Then, the tool is placed in a freezer. Before the analysis, the samples shall be allowed to solidify in the freezer for 1 hour. Optimum precision is obtained for samples with dropping points below 33 °C, when a freezer temperature of -20 °C or lower is used.

The sample holder shall be introduced into the instrument's furnace at a temperature that is 5 °C lower than the expected dropping point of the sample. A 1 °C/min heating rate shall be applied to heat the samples until the dropping point is automatically detected. Table 1 reveals the dropping points of a selection of edible fats that were determined with the DP90 Excellence system.

Sample	Dropping point [°C]	Standard deviation [°C]	n
Cocoa butter	29.8	0.17	4
Palm fat	53.0	0.18	4
Milk fat	34.0	0.22	4

Table 5: Dropping point of edible fats. The samples were prepared according to the AOCS Cc18-80 standard. The dropping point values are the mean values of 4 measurements

For instruments see chapter 5.6

3.6 Acidity

Titration has been applied for centuries to determine the content of acids in various samples. Before the first electrode was invented, colour indicators have been used to indicate the endpoint of the titration.

In particular, basicity i.e. caustic content and acidity represent classical parameters in quality and routine analysis of ingredients and intermediate products. The determination of acid/base content is generally regulated by national or international regulatory bodies such as the Association of Official Analytical Chemists (AOAC, USA) and the International Organization for Standardization (ISO).

The titration of acids is rather straightforward: The acid content is determined by controlled addition of an alkaline solution of known concentration (= titrant, e.g. 0.1 M sodium hydroxide solution) until a specific endpoint is reached. Color indicators usually used for acidity and basicity are phenolphthalein and methyl orange. For practical reasons, indicator solutions are prepared and some drops added to the samples. The recognition of the color change always depends to a certain degree on operators skills. Thus, reproducibility of results is challenging.

Nowadays, electrochemical sensors have replaced the classical color indicators in titration analysis, and the manual procedure is often made obsolete by the use of automated titration instruments. In fact, the titration is monitored by means of a pH glass electrode which is connected to automated titration instruments. Based on the potential measured in the sample, the addition of titrant is controlled i.e. larger or smaller portions (=increments) of titrant are added automatically by a motorized piston burette according to the signal change between increments until the endpoint is reached. From the titrant consumption and its concentration the acid (base) content of the sample can be calculated.

Figure 16: A compact autotitrator with printer for result documentation

The result is typically expressed in mol/L or mol/kg. Taking into account the molar mass of the acid (base) present in the sample, g/L or g/kg acid (base) can be calculated.

For instance, the caustic content of lye solution for the production of laugen breads (pretzels) is determined by titration with an acid titrant such as hydrochloric acid. The caustic content is expressed in g/L of sodium hydroxide, NaOH. On the other hand, the total acidity in vinegar and related products is determined by direct titration with sodium or potassium hydroxide. Since acetic acid is the main organic acid present in vinegars, the acidity is expressed in g/L acetic acid.

To comply with regulations, accurate and precise instruments are required in the laboratory to achieve reliable results. Among other parameters, this is guaranteed by METTLER TOLEDO's comprehensive equipment qualification including dedicated service and maintenance. An overview of automated titrators is given in chapter 5.7.

Autotitrators help to automate this entire procedure, providing:

- Automatic and error-free result calculation,
- Operator independent results and
- Full documentation.

3.7 Salt Content

Salt (sodium chloride NaCl) in food products enhances the taste, but may also adversely affect health. A clear relation between sodium intake and cardiovascular diseases has been shown by the World Health Organization (WHO) [23]. Measuring sodium content has therefore become imperative for food producers.

Salt determination can be performed using different analytical techniques; two typical and simple examples are described below.

Sample preparation is crucial for salt determination: liquid samples may directly be analyzed, whereas solid samples undergo sample preparation to extract the salt into solution.

Chloride determination

Argentometric chloride titration is a very common and frequently applied method to determine the chloride ions. Based on the chloride content, the amount of sodium chloride is calculated. However, chlorides of other origin are also included.

This reliable method leads to highly accurate and precise results from very low up to very high concentrations. The reaction is a precipitation and the titration reagent applied is silver nitrate. The added titrant forms insoluble silver chloride with the chloride ions contained in the sample.

$$Ag^+ + Cl^- \rightarrow AgCl$$

Important points to be noted for chloride titration:

- The method is calibrated via the titer. Thus, the titer determination of silver nitrate is crucial.
- In order to avoid supersaturation of the sample solution before the precipitate is formed, we recommend to adjust the pH of the sample solution to slightly acidic pH 4.5 using nitric acid.
- In highly concentrated sample solutions inclusions of sample and/or titrant may occur in the precipitate and thereby falsify the result. Rapid stirring during titration is an effective countermeasure.

Sodium determination

Ion selective electrodes (ISE) are an alternative method to measure the ion concentration in solutions. ISE respond to the concentration – more precisely to the activity – of the determined ions. The response follows the Nernst equation.

The Nernst equation describes the linear relation between the potential readings (in mV) and the logarithm of the ion concentration (activity respectively). The applicable concentration range is specified approximately between 3 mol/L and 10^{-5} mol/L.

The Sodium Analyzer is a dedicated device designed to specifically determine the sodium content by the multiple standard addition technique based on ISE measurements. The electrode potential of a defined volume of the sample solution (V_u) is measured. A small volume of a known standard solution (C_s) is added to the sample and the electrode potential re-measured, from which the potential difference (ΔE) results. The standard addition procedure is repeated several times. The sodium analyzer automatically calculates the sodium content of the applied samples (C_u) based on the potential differences.

C_u = Na^+-concentration of the sample
C_s = concentration of the standard
V_s = volume of the standard
Vu = sample volume
ΔE = change of potential in mV
S = slope of the electrode in mV

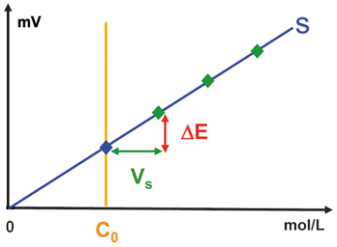


Figure 17: Multiple standard addition technique: Calibration graph and result reading

Some points be noted using sodium analyzers:

- Keep the ionic strength constant during the determination: Add ionic strength adjustment (ISA) buffer solution. The ISA solution also brings the pH value of the sample in the alkaline range.
- The added sodium standard must cause a significant increase in the measured potential of the sample solution. A 20 to 30 mV increase (ΔE) is ideal. After the user has entered the target value for the ΔE, the Sodium Analyzer proceeds the subsequent steps automatically and calculates the sodium content. It is recommended that the concentration of the sodium standard C_s is 5 to 10 times higher than the expected sample concentration.

For instruments see chapter 5.7

3.8 Ammonia in Raising Agents

A raising (or leavening) agent is a substance used in baked goods that causes them to rise. When water is added, the leavening agent reacts to produce carbon dioxide and eventually other gases that become trapped as bubbles within the dough to help it rise. Leavening compounds generally consist of an acid and an alkali in combination with a filler material. Typical examples are baking soda (sodium hydrogen carbonate $NaHCO_3$) and ammonium hydrogen carbonate (NH_4HCO_3, also called ammonium bicarbonate). The latter is designated as food additive E503. It is often one of the raising agents used in biscuit manufacture where the carbon dioxide and ammonia combine to raise the biscuit dough.

An alternative raising agent is yeast. Yeast is an organism capable of reproducing itself when added to bread. Whilst growing, yeast produces carbon dioxide (CO_2) gas which rises bread dough and creates the structure of breadcrumb. Yeast is not further considered in this guide.

Nowadays, leavening compounds and baking powders have become very relevant due to large scale production of bakery products. The correct amount and activity of raising agents is a key issue to achieve high quality bakery products. In particular, basicity (i.e. carbonate and bicarbonate content) and acidity (i.e. calcium phosphate and sodium aluminum sulfate content) of leaveners represent the quality parameters of baking powders.

Titrimetric analysis represents a reliable analytical technique for for the determination of acids and bases in raising agents. It is a well-known, robust and straightforward quantitative analysis for leaveners' quality control.

Figure 19: A bread in processing. The right amounts of leaveners and salt assure the right quality of the final product.

The titrimetric analysis of ammonia in raising agents consists of the following steps: The sample is first acidified with a known amount of sulfuric acid which leads to the release of CO_2 gas. Subsequently, excess acid is titrated back with sodium hydroxide solution until the endpoint is reached. The endpoint is generally indicated by a pH glass electrode. The difference between the added acid amount and the titrated acid excess indicates the amount of ammonia present in the sample. Figure 18 explains the procedure of this back titration.

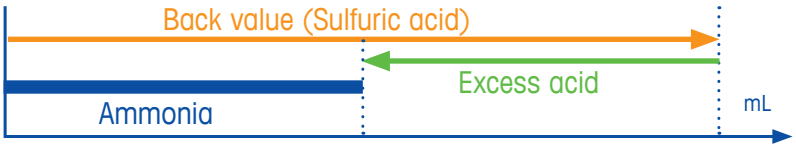


Figure 18: Back titration procedure

The content of carbonate and bicarbonate is determined by a direct titration with an acid titrant e.g. hydrochloric acid. Again the endpoint is indicated by a pH glass electrode. The consumption of acid relates directly with the amount of carbonate and bicarbonate.

Automated potentiometric titrators can be set to run the complete analysis from sample dissolution until result calculation and documentation. Compliance with regulations is well supported by modern, precise and accurate titrators and comprehensive equipment qualifications including dedicated service and maintenance.

An overview of automated titrators is given under chapter 5.7.

3.9 Fat and Oil Characterization by DSC

The investigation of fats and oils with a differential scanning calorimeter (DSC) is a widely used routine applications in food processing. The solidification properties of fats or the oxidation properties of fats and oils are of particular technological interest for the processing of such foodstuffs [14].

Crystallization behavior of fats

Fats often make up a critical component of sweets and savory goods. Seasonal and regional variability in milk fat composition causes differences in crystallization behavior, which can, inter alia, result in variability in fractionation efficiency and physical properties of butter. Examination of the triacylglycerol profiles led to the conclusion that the relative contents of higher-melting and lower-melting triacylglycerol combinations correlated well with crystallization behavior [15].

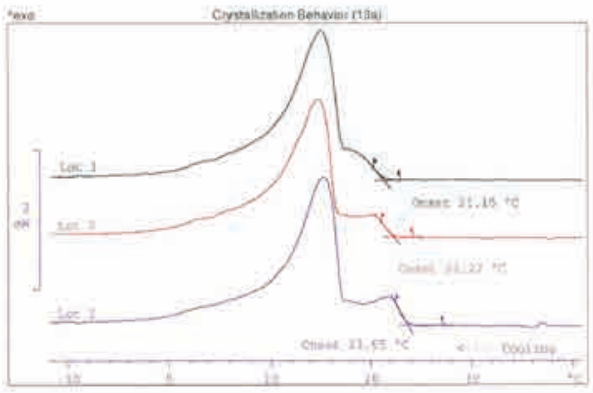


Figure 20: Crystallization behavior of cocoa butter [14]

The crystallization of cocoa butter and milk butter, for instance, is a process step of decisive importance for the quality of chocolate. It is only in this step that chocolate products obtain their desired properties such as glaze, breaking strength and melting behavior (e.g. 'softness').

Since natural fats such as cocoa butter contain numerous different triglycerides, these mixed systems do not have a melting point, but melt over a temperature range. This is the reason why melting behavior cannot be accessed by traditional melting point instruments.

The determination of the crystallization behavior requires a DSC with cooling device which is controlled by PC software. Samples of about 20 mg in size are prepared in hermetically sealed aluminum crucibles. A temperature program is applied which for example cools the liquid sample from 50 °C to -100 °C at a cooling rate of 10 K/min.

Using the evaluation software the resulting curve can be evaluated. It shows exothermic crystallization peaks which correspond to the crystallization. These can be evaluated regarding temperature at which the crystallization starts (onset).

Oxidation properties of fats and oils

The autoxidation of edible oils and fats can have a negative influence on the storage and processing of products which contain fat. At normal room temperatures, oxidation is relatively slow, but the reaction rate increases rapidly at elevated temperatures in the presence of oxygen. Above 150 °C, such as when roasting or frying, autoxidation sets in and at higher temperatures leads even to complete decomposition of the fat.

The stability of the fat (characterized by the temperature at which the oxidation starts) and the reaction kinetics of the oxidation can be determined by DSC measurements.

For this determination a fan cooled DSC which is controlled by PC software is required. Samples of about 5 mg in size are prepared in open aluminum crucibles. A gas supply delivers an oxidative atmosphere. Usually air containing approximately 20% oxygen is sufficient. For accelerated testing even a high pressure DSC can be used.

The temperature program applied is usually heating the sample from 30 °C to 250 °C at a rate of 20 K/min. At the point when the fat starts to degrade (oxidize), an exothermic peak evolves.

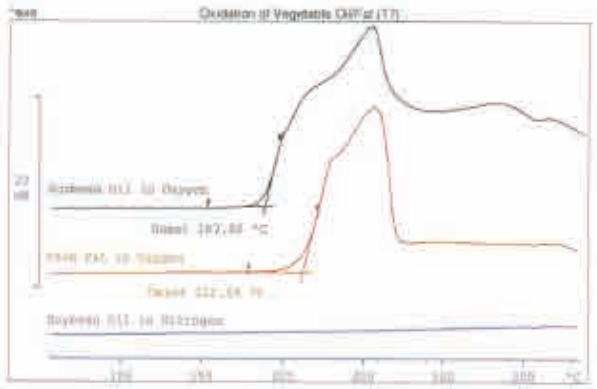


Figure 21: Oxidation of vegetable oils and fats [14]

Software can automatically switch off the heating at a certain degree of oxidation in order to protect the measuring cell from contamination with decomposed sample. The oxidation onset can also be automatically evaluated.

Figure 22: Manually placing a sample in the DSC furnace

More applications of DSC for the analysis of oils and fats

- Fatty acid composition and structure of the triglycerides in milk and butter fats
- Determination of the solid fat index (solid fraction, liquid fraction)
- Determination of the influence of process parameters on industrial crystallization
- Determination of the influence of the origin of fats and oils
- Determination of the influence of emulsifying agents (phospholipids) on fat crystal structures
- Behavior of cooking fat under different storage conditions

3.10 Formulation

Behind the success of a food product there is always a well-proven formula. Formulation is the process through which a formula is prepared by dispensing all the required raw materials and ingredients such as additives, flavors or spices, according to the expected quantities and right proportions up to the total required amount.

In bakery, confectionery, snacks and pasta manufacturing, formulation is widely used for any of the following purposes:

- new product development (R&D lab)
- product improvement and/or optimization (R&D lab)
- premix preparation for production (production batching)

Whether performed in a laboratory or in a production workplace, formulation is a highly critical process because any error such as inaccurate weighing, mixing of wrong ingredients or wrong calculations may lead to severe consumer, legal or financial issues. Batch-to-batch consistency is another concern. Precision balances help to manage these issues thanks to their versatility, accuracy and ease of use.

With a portfolio that ranges from 210 g up to 64 kg maximum capacity and readability down to 0.1 mg, METTLER TOLEDO precision balances provide a wide array of dedicated solutions that fit with every formulation process and accuracy demand in the lab.

Designed to be durable and robust, the MS and ML models are the right choice for simple formulations where just weighing the ingredients is the major task.

XPE and XS balance models represent solutions for enhanced and demanding formulation processes. These models include additional and dedicated functions to better support the user in every single step of the process. Data such as sample weights, calibration and operators, are fully traceable. Dispensing of ingredients is safely guided to avoid weighing errors. Automatic totalization and statistics are built-in. The balances connect seamlessly to barcode readers, label printers and PC based systems. In addition, the design is compact, provides IP54 in use protection and meets hygienic requirements.

For instruments see chapter 5.2

3.11 Check Weighing

Check weighing is widely used in bread, confections, snacks, and pasta manufacturing to quickly determine whether or not the weigh (or the average weigh) of a final product or product package meets the required target and lies within set tolerances. Such weight checking product inspections may be carried out for internal or legal purposes.

Internal product inspections are very often performed in the quality laboratory. The goal is to check the accuracy of production filling machines. As a consequence, filling machines may need a better setup or a maintenance visit. Pre-testing the filling of new products is another task in this area.

- This kind of monitoring of the filling behavior requires a simple statistical evaluation. It includes the average weight, the maximum and minimum values, the number of weighed samples and the overall standard deviation (absolute and relative).

Check weighing for legal purposes is carried out in-line or at-line in the production department while the filling process is running. It monitors the net content of manufactured packages helping to avoid legal and consumer issues that may arise if actual net weights fall below declared specifications.

- Automatic in-line checkweigher systems measure each package and provide full control of the entire batch (dynamic check weighing).
- As an alternative, precision balances placed at the line are manually operated. At defined time or production intervals, a package is selected and weighed.

Off-line methods do not allow complete, 100% inspection of the entire batch. However, the implementation of robust statistical quality control (SQC) measures and a consistent sampling plan provide high accuracy and repeatability.

METTLER TOLEDO support

- Comprehensive choice of precision balances
- SQC solutions with LabX and FreeWeigh.Net software
- Dynamic checkweighers and other product inspection systems

For instruments see chapter 5.2

4. Regulations and Standards

4.1 Regulations

Regulations regarding product safety become more and more demanding. An increasing number of regulations and stronger demands from retailers and finally consumers ask for extended testing and defining of critical control points.

A strong impetus comes from the US FDA's Food Safety Modernization Act (FSMA). FSMA was signed in to law in January 2011. Since then, this Act has influenced most other countries as well, due to the global food supply networks.

To assure the quality of food products from production to consumer, a chain of regulations is in place.

Global food safety Initiative GFSI			
Hazard analysis HACCP	Harmonized food quality systems IFS, BRC, etc	Harmonized QC systems ISO 22000	Harmonized audits and certificates FSSC 22000

Figure 23: Chain of regulations

4.2 Standards

GFSI

The Global Food Safety Initiative (GFSI) was launched in May 2000 and established as a non-profit foundation. Its mission is the continuous improvement in food safety management systems to ensure confidence in the delivery of safe food to consumers. GFSI includes all stakeholders of the food supply network, i.e. producers, manufacturers, distributors, retailers, standard owners, auditors, and governmental agencies.

GFSI maintains benchmarks accepted, approved and applied by the food supply stakeholders. It provides platforms for networking, knowledge exchange and sharing of information and best practice experience. One of these platforms is the annual Global Food Safety Conference.

GFSI is managed by the Consumer Goods Forum.

HACCP

Hazard Analysis Critical Control Point (HACCP) is a systematic preventive approach to safety of food and beverages. It was conceived in the 1960s for NASA's* first foods for space flights. HACCP addresses physical, chemical, and biological hazards from raw material production, procurement to manufacturing, distribution and final consumption. It focuses on identifying and preventing hazards rather than finished product inspection [16, 17].

* NASA = US National Aeronautics and Space Administration

1. Conduct a hazard analysis – Identify hazards, assess risk and list controls
2. Determine critical control points (CCP)
3. Establish critical limits – Specify criteria for each CCP
4. Establish a monitoring system – Define monitoring requirements for each CCP
5. Establish corrective action – Correct whenever monitoring indicates criteria are not met
6. Establish verification procedures – Ensure HACCP system is working as planned
7. Establish record keeping and documentation requirements – Recording keeping procedure

Table 6: The 7 principles of HACCP [16, 18]

Once CCPs have been defined, appropriate control measures are established. This may include at one point sodium content determination to assure preservation and the right taste, pH value measurements to monitor fermentation processes, packaging material identification by DSC*, microbiological tests to prove absence of harmful bacteria and many more.

* DSC = Differential Scanning Calorimetry, a thermal analysis technique

METTLER TOLEDO support

- Analytical instruments such as pH meters and electrodes, potentiometric and Karl Fischer titrators, thermal analysis instruments
- Pipettes and sterile tips.

Food quality systems

These quality systems focus on process and product certification schemes. They ensure that companies deliver food products in line with safety and quality specifications defined by customers. They are risk-based and apply a scientific approach. Another task is the standardization of the applied quality, safety and operational criteria.

Two typical examples are BRC Global Standards and IFS International Featured Standards. Both BRC and IFS have been initiated by retail companies. Another example is SQF Safe Quality Food, designed to meet the needs of retailers and suppliers.

Harmonized certification with FSSC 22000

The Food Safety System Certification (FSSC) is a food certification scheme for ISO 22000-based certification of food safety management systems. FSSC 22000 is acknowledged by GFSI and compliant with GFSI's latest Guidance Document version 6. It includes well defined requirements for:

- Companies of the food chain requesting certification,
- Certification bodies (CB) and
- Accreditation bodies (AB).

Audits of a company following FSSC 22000 put the company's safety management system in the center. They stress commitment of the company's management, effectiveness of the safety management system, and continuous improvement processes. The audit cycle is typically 3 years.

The Foundation for Food Safety Certification, an independently managed, non-profit organization which owns the FSSC 22000, sees a growing demand for certifications throughout the supply chain [19].

METTLER TOLEDO support

- Certified buffer and standard materials traceable to international references
- LabX software based solutions for audit trails, user management and automatic data transfer and storage
- Complete documentation of methods, calibrations and results either via printer or data network

ISO Standards 17025 and 9001

The ISO standard 17025 is a measure of quality and competence of a lab. It assesses if the lab is technically competent to perform certain tests with respect to accuracy, reproducibility, measurement uncertainty and other result quality aspects. It also assesses if good lab management practice is applied, i.e. sustainable operations, effective quality management system, suitable testing equipment and environment.

ISO 17025 directly applies primarily to testing and calibration labs. However, quality control labs perform tests and calibrations as well and thus, are included in the scope of ISO 17025. The application of ISO 17025 minimizes the risk of inaccurate results and avoids expensive and time consuming retesting. It can also improve the acceptance of results by third parties.

ISO 17025 is also the basis for an accreditation. The accreditation, executed by technical assessors or subject matter experts, recognizes:

- Specific technical competences of the lab, e.g. to carry out specific tests or types of tests,
- People skills and knowledge; and
- Procedures for calibration and maintenance of test equipment and for quality assurance of test and calibration data.

The ISO 9001 standard is, however, a rather generic standard for quality management systems. It applies to all organizations and recognizes the organization's ability to provide products according to preset specifications, customer requirements and regulatory requirements.

Certification against ISO 9001 considers the entire business and recognizes compliance with standards or specifications. The certification is executed by management system auditors [20].

METTLER TOLEDO support

- Webinar Evaluation of Measurement Uncertainty in Titration.
  Go to **www.mt.com/webinars**
- MuPac, a service offered by METTLER TOLEDO to evaluate measurement uncertainty of titration methods.
  Go to **www.mt.com/gtp-mupac** for more details.
- VPac Performance Verification for EasyPlus Titrators.
  See **www.mt.com/easyplustitration**

4.3 Test Methods

In the past, a "prescriptive approach" was taken which specified a certain method and its defined application. However, currently any suitable method is selected provided a defined set of criteria is fulfilled such as accuracy, specificity, precision, limit of detection, sensitivity etc. This freedom of methods selection, named "criteria approach", also takes into account developments in analytical sciences. From there, new methods and refinements of current methods flow into daily practice [6].

Reference method vs routine methods

Often in sweet and savory products, the parameter to be determined by the chemical analysis is not a chemical substance of known identity, but a mixture of substances captured by the method. Thus, many methods in food are „defining methods". Usually they are tedious and time-consuming to carry out.

In addition, many reference methods of sweet and savory products are „defining methods" as well. Reference methods are applied for official control and due to legal reasons.

However, sample frequency and cost of analysis require fast, cheap and automated routine methods. Routine methods need careful examination to prove the suitability. Extended result comparisons with the reference method explain and document result variability and potential systematic differences.

4.4 Sampling plans

In order to make acceptance/rejection decisions based on statistical and uncertainty evaluations, sample plans for multiple tests by routine methods have been specified and implemented in quality control labs. This best practice has replaced the former testing of a few samples only by a reference method.

Sampling plans also take into account involved risks derived from raw materials and processing to the consumer product. Risks can be classified, for instance, from negligible to intolerable, indicating how measures and frequency of control have to be geared.

Probability	most likely	3	moderate	high	intolerable
	likely	2	tolerable	moderate	high
	unlikely	1	negligible	tolerable	moderate
		0	1	2	3
			mild	remarkable	extremely severe
			Severity level of non-conformity		

Table 7: Classification of risks [6]

4.5 Support by Analytical Instruments

In general, regulations ask for more and more elaborate testing to make sure that quality and safety targets for food and beverages are met at all times. The documentation of such testing tasks including all data and results has to be error-free and without gaps.

Modern instruments help to achieve both targets.

- Extended automation possibilities based on autosamplers, accessories and method structures keep or even increase the efficiency in spite of increased sample numbers and manage sample throughput.
  A typical example is the InMotion™ autosampler and its paraphernalia providing automatic sample changing for up to 303 samples and many more helpful features.
  InMotion samplers can be used with titrators, density and refractometers.
- Balances and analytical instruments communicate via external software (e.g. LabX software) or directly via various communication ports (e.g. USB, RS232). This safe and secure automatic data transfer avoids transcription errors, saves time and provides traceability.

In either case, customers can decide on the automation level to match requirements. Thanks to METTLER TOELDO's modular solutions, future needs can be met easily as well.

5. METTLER TOLEDO Solutions

5.1 Analytical Balances

Product line	Solution	Example
Excellence Line	Analytical Balances • Reliable and fast results • Easy compliance • Highest safety • Sustainable investment • Ergonomic operation Typical models: XPE204, XS204 • Readability: 0.1 mg • Capacity: 0…220 g	
New Classic Line	Analytical Balances • For trust and comfort • Durable and robust thanks to metal housing Typical model: MS204 • Readability: 0.1 mg • Capacity: 0…220 g	

The XPE, XS, MS and ML series of analytical balances offer a large portfolio of models to meet nearly any user need.

5.2 Precision Balances

Product line	Solution	Example
Excellence Line	Precision Balances • Reliable and fast results • Easy compliance • Highest safety • Sustainable investment • Ergonomic operation Typical model 1: XPE6002S • Readability: 0.01 g • Capacity: 0…6200 g Typical model 2: XS16000L • Readability: 1 g • Capacity: 0…16200 g	
New Classic Line	Precision Balances • For trust and comfort • Durable and robust thanks to metal housing Typical model: MS4001S, • Readability: 0.1 g • Capacity: 0…4200 g	

The XPE/XS/MS/ML series include precision balances and scales with a capacity range from 210 g to 64 kg. Resolution reaches from 1 g down to 0.1 mg.

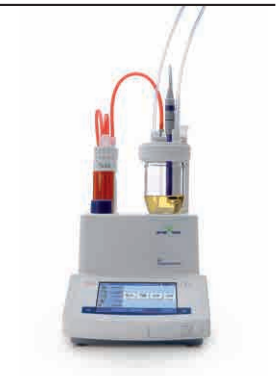
5.3 Moisture Instruments

5.3.1 Halogen Moisture Analyzers

Product line	Solution	Example
Professional Line	HX204 Halogen Moisture Analyzer Readability: 0.1 mg Capacity: 0…220 g • Record speed from start to finish • Premium performance for best product quality • Quality results, traceable reporting • Network connectivity	
Advanced Line	HB43-S Halogen Moisture Analyzer Readability: 1 mg Capacity: 0…42 g • Routine inspection made easy • Smart operation • Bright display • Rugged design	

METTLER TOLEDO offers an entire range of moisture analyzers to meet different performance requirements.

5.3.2 Karl Fischer Titrators

Product line	Solution	Example
Volumetric KF Titrators	The volumetric Karl Fischer compact titrators V20 and V30 have been designed for quick and precise specific water content determinations from a few 100 ppm to 100% water • Intuitive user interface • Personal home screen • Solvent Manager – prevents contact with chemicals With V30 only: • Flexible user management • KF automation with Stromboli (oven for solid samples)	

5.4 pH Meters and Electrodes

Product line	Solution	Example
Benchtop meter	S220 SevenCompact Universal instrument for measurements of pH, mV/ORP and ions	
Portable meter	SG8 SevenGo pro pH/ion Professional IP67 meter for pH, ion concentration, mV/ORP and rel. mV measurements (New products to be introduced shortly)	
	SG2 SevenGo pH Routine IP67 meter for pH, mV/ORP and rel. mV measurements (New products to be introduced shortly)	
pH Electrodes	InLab Solids Pro IP67 Robust pH specialist to puncture solid or semi-solid food samples (Find your sensor: www.electrodes.net)	
	InLab Routine Pro Refillable pH sensor, precise and fast (Find your sensor: www.electrodes.net)	
	InLab Expert Pro / InLab 413 SG Robust, maintenance-free pH sensors (Find your sensor: www.electrodes.net)	

5.5 Refractometers

Product line	Solution	Example
LiquiPhysics Line (benchtop models)	Refractometers RM40, RM50 METTLER TOLEDO digital refractometers are the perfect solution for Brix measurements and refractive index determinations. Our refractometers can also be expanded to measure density, pH, conductivity, color or optical rotation	
Portable models	Refracto 30PX Hand held refractometers allow you to determine the refractive index, Brix, Baume or specific gravity (SG) of a sample in the field or on-site	

5.6 Dropping Point Instruments

Product line	Solution	Example
DP Excellence Instrument	• Color touchscreeen • One Click® operation • Automatic dropping and softening point determination • Automatic video recording • Two samples can be measured at a time and the mean value is automatically evaluated • Outstanding temperature accuracy +/- 0.2 °C	
	DP70 • Compact instrument • Room temperature to 400 °C DP90 • Control unit with external measuring cell • Temperature range from 400 °C to -20 °C	
Accessories	DP70 and DP90 Excellence come with an accessory box that includes innovative tools for accurate and repeatable sample preparation	

5.7 Titrators

Product line	Solution	Example
Excellence Line	T90 Titrator, T70 Titrator • Intuitive user interface • Personal home screen • Flexible user management • Automatic burette recognition • Plug & Play sensors • Hot Plug & Play concept • Modular: tailored exactly to your needs • Automation options: Rondolino, InMotion Autosampler • PC software options: LabX express, LabX server, Regulation option (21CFR11), • Full qualification services available	
Sodium Analyzer	Sodium Analyzer Specific sodium determination – simple and accurate. • Reduce sample preparation work • Use safe and inexpensive chemicals • Easy operation thanks to smartphone-style user interface • No calibration is necessary thanks to the multiple standard addition technique • The integrated algorithm specifically designed for Na^+ delivers highly accurate and repeatable results	
Compact Titrators	G20 Compact Titrators • Intuitive OneClick™ user Interface • Personal home screen • Automatic burette recognition • Plug & Play sensors • Automation options: Rondolino • PC software option: LabX express • Installation qualification service available	
EasyPlus	Easy pH Titrator, Easy Cl Titrator • Affordable entry level titrator • Quick start and intuitive operation with app based iTitrate™ user interface • Only a few parameters to be set thanks to iTitrate™ intelligence • Internet support for easy self installation and application database • Unique VPac performance qualification service available	

5.8 Differential Scanning Calorimetry (DSC)

Product line	Solution	Example
TA Excellence	DSC 1 Modular system with built-in innovative technology perfectly suited for fat crystallization and oxidation studies. Can be expanded with valuable options like sample changer or microscopy.	

6. Conclusions

We have presented several essential analyzes and tasks pertaining to laboratories in bakery, confectionery, snacks and pasta products manufacturing companies. When performing these analyzes, accuracy and precision are absolutely non-negotiable. Any variation in the composition of a product could violate the product declaration, requiring, for example, batches of the product to be discarded. Any variation in taste could lead to disappointed consumers and lost revenue in the future.

Analytical instruments, balances and further solutions from METTLER TOLEDO empower you to perform these tasks with the confidence that your results will be accurate. Thanks to a unified and easy to understand interface concept, operation of instruments and balances is simple and straightforward. Depending on your needs, processes can also be automated to varying degrees, leading up to fully automated systems.

METTLER TOLEDO experts have contributed tips and hints to this guide advising you on best practices and ensuring you get the most out of your instruments and equipment. It's important to us that you achieve your target to manufacture quality bakery, confectionery, snacks and pasta products to satisfy your consumers.

7. Selected Application Methods

7.1 Melting of Chocolate – Measurement by DSC

(Thermal Analysis Application No. HB 1014, METTLER TOLEDO TA Application Handbook Food [14])

Sample Milk chocolate, Lindt chocolate bar

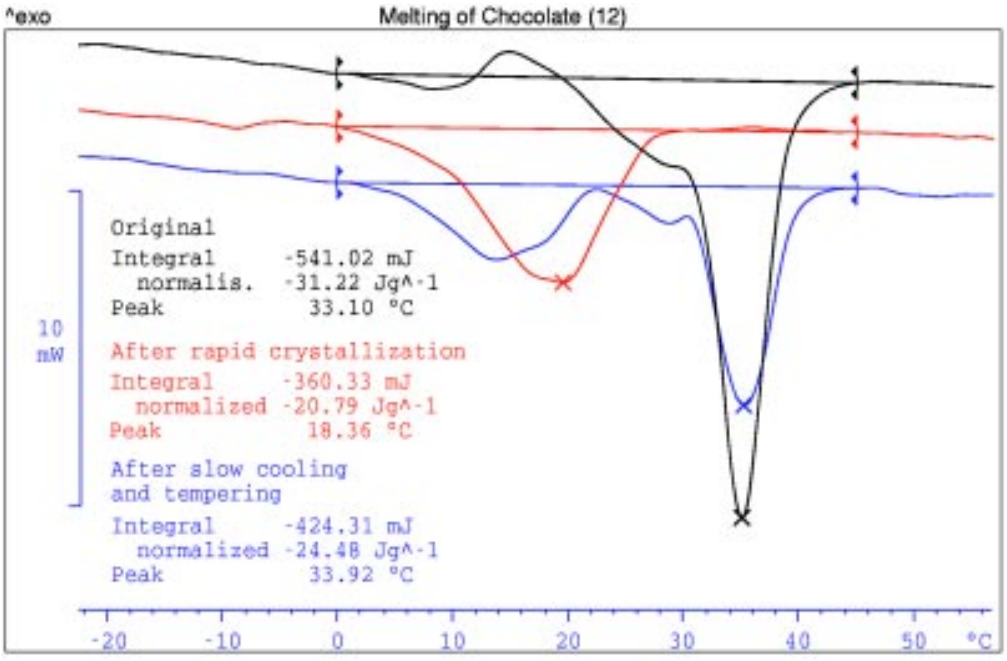
Conditions

Measuring cell:	DSC30
Pan:	Aluminum standard 40 µl, hermetically sealed
Sample preparation:	Sample was cut from a bar with a sharp knife and transferred to an aluminum pan without warming (heat from hands!). Sample weight 17.33 mg

DSC measurements with the same sample	Curve name in diagram
-30 °C [1]) to 60 °C at 10 K/min	original
60 °C to -30 °C at 20 K/min, isothermic 5 min	(not shown)
-30 °C to 60 °C at 10 K/min	after rapid crystallization
60 °C to 15 °C at 1 K/min	(not shown)
1 hour isothermic at 15 °C	(not shown)
-30 °C [2]) to 60 °C at 10 K/min	after slow cooling

[1]) Cooling from room temperature to -30 °C in approx. 5 min

[2]) Cooling from 15 °C to -30 °C in approx. 4 min



Interpretation In this experiment, commercial milk chocolate is used without any further preparation to demonstrate how the crystal modifications vary as a function of the crystallization conditions. The curve labelled 'original' shows the melting behavior of a sample of commercial milk chocolate stored at 5 °C after purchase. Between 10 °C and 20 °C an exothermic transition peak can be clearly recognized (rearrangement to the stable form). Above 30 °C (oral temperature) the melting range of the β-modification begins. This modification was achieved technically by gentle annealing. Because of the high heating rate (which was selected to obtain larger peaks), the individual melt fractions are not further resolved.

After faster cooling of the same melt to -30 °C at 20 K/min, the curve labelled 'after rapid crystallization' shows new melting characteristics. Only the unstable form is present. The total heat of fusion of the same sample has decreased from 541 mJ (original milk chocolate) to 360 mJThe rapidly crystallized chocolate no longer satisfies the sensory requirements.

The same sample was now cooled from the melt to 15 °C at a rate of 1 K/min, held isothermicly for 15 minutes and then cooled to -30°C. These annealing conditions are intended to simulate a 'slow and careful' crystallization. The melting behavior of this sample is shown by the curve labelled 'after slow cooling'. The α–form already starts to melt at 5 °C. There is virtually no further rearrangement (as a result of the high heating rate). Only about half the original β-modification is now present and melts above 30 °C.

Evaluation

Peak integration gives the results needed to estimate the relative stability of the fat modification:

	Heat of fusion	Peak temperature
Original chocolate	31.2 J/g	33.1 °C
After rapid crystallization	20.8 J/g	18.4 °C
After slow cooling	24.5 J/g	33.9 °C

Conclusion

The raw material quality, the process parameters and the composition of the chocolate have an influence on the shape of the DSC melting curve.

Publishing Note:
This application has been published in the METTLER TOLEDO Thermal Analysis Application Handbook Food.
See **www.mt.com/ta-handbooks**

7.2 Thermal Characterization of Cocoa Butter

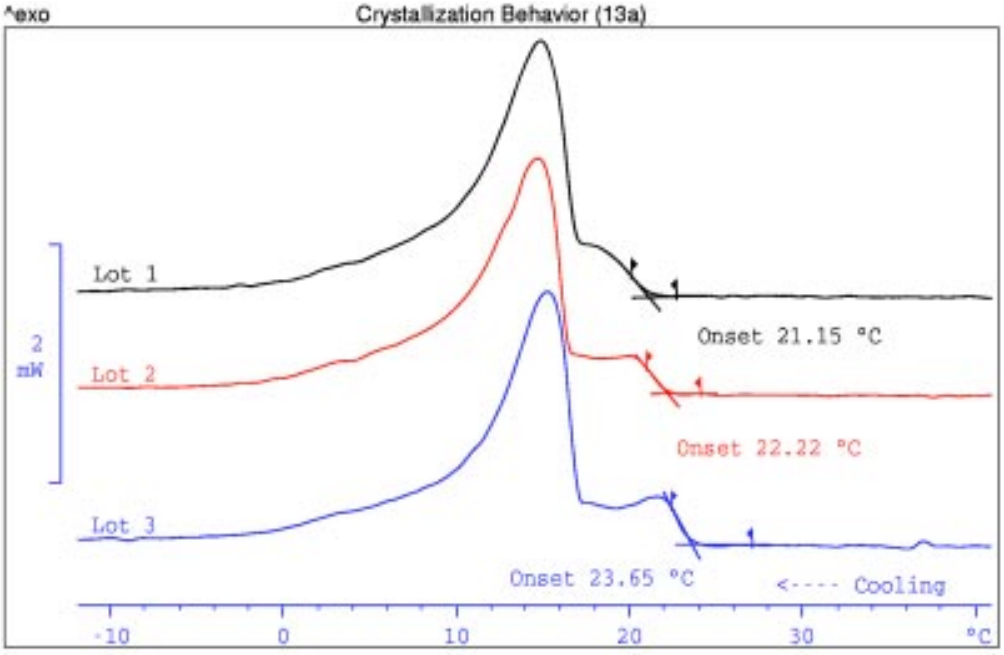
(Thermal Analysis Application No. HB 1017, METTLER TOLEDO TA Application Handbook Food [14])

Samples

Three different lots of cocoa butter obtained from Swiss chocolate manufacturers

Conditions (a)

Measuring cell:	DSC20 (placed in a deep freezer at -20 °C)
Pan:	Aluminum standard 40 µl, hermetically sealed
Sample preparation:	The samples are melted at 60 °C in 20 ml beakers for homogenization. Approximately 10 mg of each are weighed in
DSC measurement:	Cooling from 60 °C to -10 °C at 1 K/min



Interpretation

The shape of the DSC curves indicates a two step crystallization process with reproducible onsets of 21.2 °C, 22.2 °C and 23.6 °C for the butter samples 1, 2 and 3 respectively.

When the crystals formed are heated in the DSC, the peak temperatures are in the region around 23 °C, which indicates the presence of metastable products. It is known that crystallization of a few milligrams requires lower temperatures than gram or kilogram quantities. In other words, the supercooling is greater with small samples. Therefore the use of small samples (crystallizing at a very low temperature) gives rise to extremely metastable products.

Evaluation

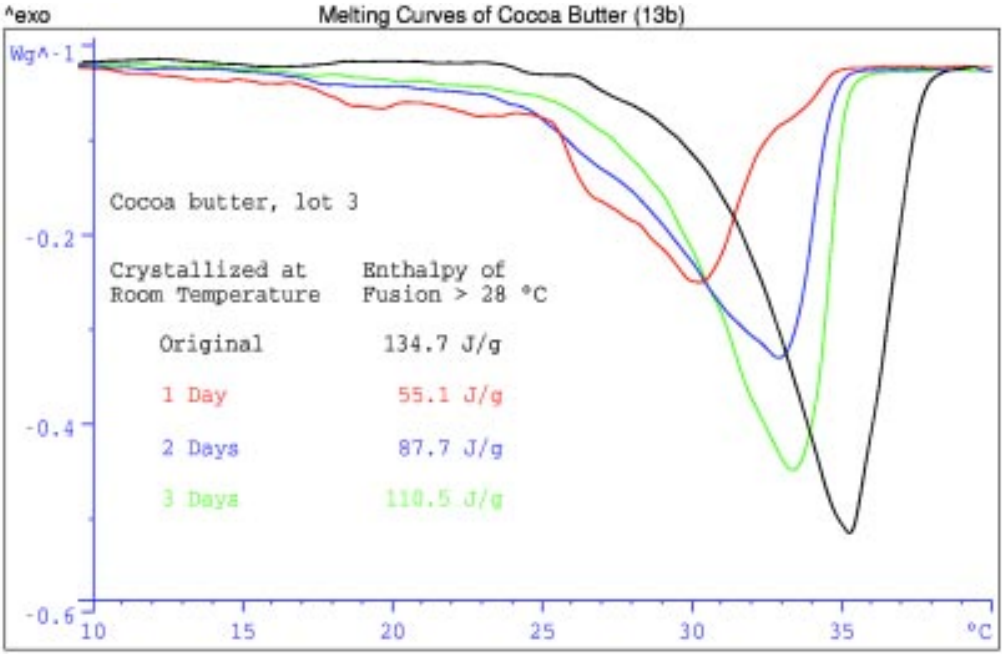
In this case only the onset temperature of crystallization is evaluated.

Lot	Sample weight, mg	Onset, °C
1	10.82	21.2
2	10.32	22.2
3	10.87	23.6

Conditions (b, c)

Sample preparation: To overcome the problems of severe unrealistic supercooling, the course of crystallization is studied using approximately 10 g each of melted cocoa butter in glass beakers. After complete fusion at 60 °C the beakers are kept at room temperature for crystallization and samples are taken (10.5 ±0.5) during the first 3 days of recrystallization.

DSC measurements: Heating from 0 °C to 45 °C at 1 K/min

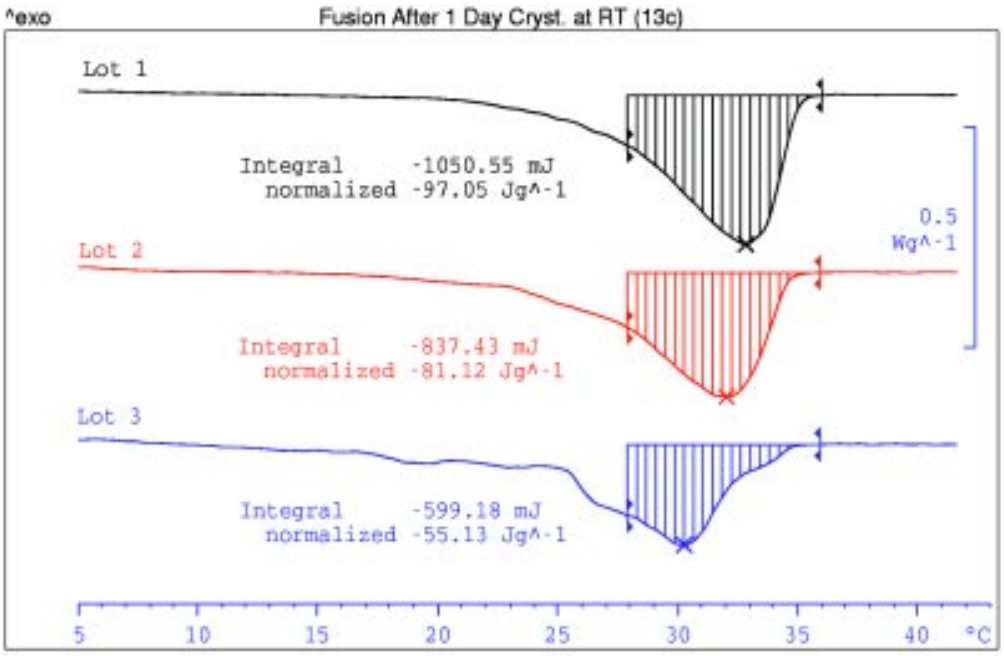


Interpretation

The DSC melting curves show the course of crystal formation in samples of lot 3 in comparison with the unheated original product. The integral above 28 °C represents the fractional amount of the stable modification. Both the heat of fusion and the peak temperature increase towards the values of the unmelted original sample.

Evaluation

Crystallization time at room temperature	Peak temperature, °C	Heat of fusion > 28 °C, J/g	$\Delta H/\Delta H_{ori}$ %
1 day	29.9	55.1	40.9
2 days	32.5	87.7	65.1
3 days	32.8	110.5	82.0
Original	34.6	134.7	100.0



Interpretation

The diagram shows the DSC melting curves of the 3 different lots of cocoa butter measured after they were allowed to crystallize for one day in beakers kept at room temperature (RT). Each lot shows a different course of crystallization. Lot 1 after one day of crystallization is almost completely in the stable modification, whereas lot 3 shows a much slower transformation. As previously explained, the integral above 28 °C represents the fractional amount of the stable modifications.

Evaluation

After 1 day of crystallization at RT	Peak temperature, °C	Heat of fusion > 28 °C, J/g	$\Delta H/\Delta H_{ori}$ %
Lot 1	32.3	97.0	72.0
Lot 2	31.6	81.1	60.2
Lot 3	29.9	55.1	40.9
Original (lot 3)	34.6	134.7	100.0

Conclusion

Depending on the conditions of crystallization, a variety of melting points (the temperature of the DSC peak maximum) between 17 °C and 37 °C can be observed, which indicates that no distinct polymorph is obtained. The respective heats of fusion range from 50 J/g (possibly containing an amorphous fraction) to approximately 140 J/g.
The stable modification that is obtained after long term storage under optimum conditioning melts between 28 °C and 37 °C. The heat of fusion measured in this region is therefore proportional to the content of the stable modification.

The undesired blooming of chocolate is due to the migration of liquid fat which then crystallizes as a separate phase at the surface. Such a liquid phase exists before complete crystallization or it can be formed during the transformation of metastable polymorphs.

Publishing Note:
This application has been published in the METTLER TOLEDO Thermal Analysis Application Handbook Food.
See **www.mt.com/ta-handbooks**

7.3 Chloride Content in Ketchup

(Titrimetric determination using the silver chloride method, METTLER-TOLEDO Method M404-2009 from Application Brochure 34 [21])

The chloride content in ketchup is determined by precipitation titration with silver nitrate. The content is given as sodium chloride, NaCl (salt).

Sample	Ketchup, 1.4-1.6 g
Compound	Sodium chloride, NaCl, M = 58.44 g/mol, z = 1
Chemicals	50 mL sulphuric acid, H_2SO_4 $c(H_2SO_4)$ = 0.02 mol/L
Titrant	Silver nitrate, $AgNO_3$ $c(AgNO_3)$ = 0.1 mol/L
Standard	Natrium chloride, NaCl c(NaCl) = 0.1 mol/L , 5 mL
Indication	DM141-SC
Chemistry	$NaCl + AgNO_3 \rightarrow$ $AgCl + NaNO_3$
Calculation	R1: Content (%), expressed as w/w R1 = Q*C/m, C = M/(10*z)
Waste disposal	Filtration. The precipitate (AgCl) has to be classified as special waste. The liquid phase has to be neutralized to pH 7 before final disposal.
Author, Version	Claudia Schreiner, April 2009, Thomas Hitz, July 2006, Market Support Group Anachem

Preparation and Procedures

1) The titer determination of silver nitrate is performed using sodium chloride (NaCl) as a primary standard.
   Since small amounts of salt cannot be weighed in exactly, it is recommended to prepare an aqueous solution of NaCl, and then to add the standard with a pipette.
2) Approximately 1.5 g ketchup is added in a titration beaker. Ketchup is dissolved by adding 50 mL 0.02 mol/L H_2SO_4.
3) After each sample the DM141-SC electrode, the stirrer and the titration dispensing tube are cleaned using a paper tissue soaked with deionized water to completely remove any AgCl residue.

Remarks

1) The method parameters have been developed and optimized for the above mentioned sample.
2) Since there are different ketchup producers, it may be necessary to slightly adapt the method to your specific sample.
3) The method can be easily modified for automated operation. Select the appropriate sample changer in the method function "Titration stand".

Instruments	- T50/T70/T90 Titration Excellence, G20 Compact Titrator (with small changes). - XS205 Balance
Accessories	- DV1010 burette - Titration beaker ME-101974 - Olivetti Printer JobJet 210

Results T50/T70/T90

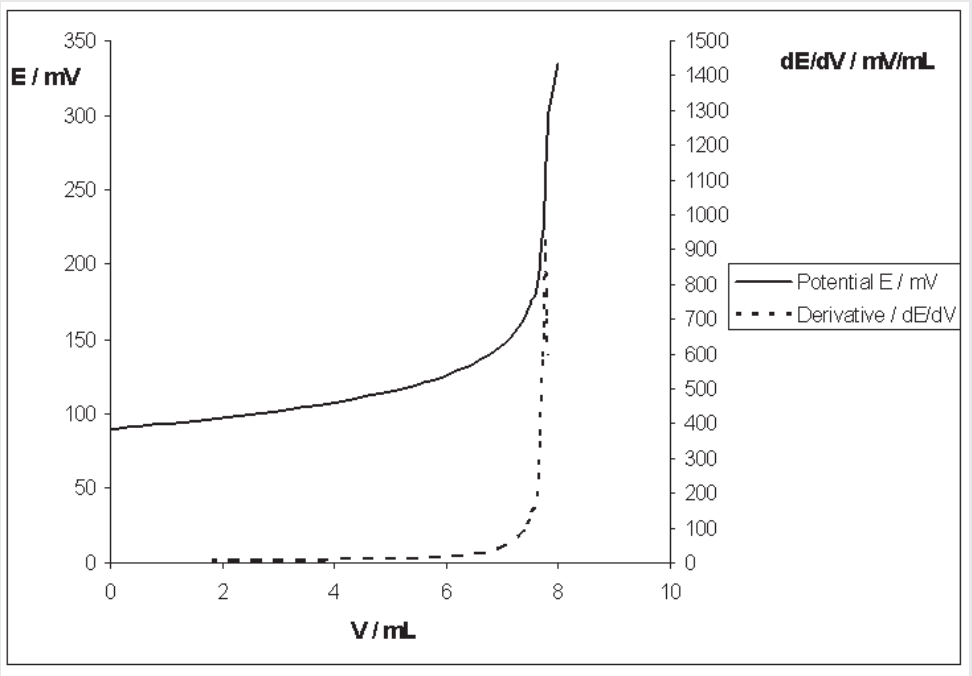
All results

	Method-ID	M404
	Sample	Ketchup (1/1)
	R1 (Content)	3.287 %
	Sample	Ketchup (1/2)
	R1 (Content)	3.274 %
	Sample	Ketchup (1/3)
	R1 (Content)	3.287 %
	Sample	Ketchup (1/4)
	R1 (Content)	3.290 %
	Sample	Ketchup (1/5)
	R1 (Content)	3.273 %
	Sample	Ketchup (1/6)
	R1 (Content)	3.284 %

Statistics

	Method-ID	M404
	R1	Content
	Samples	6
	Mean	3.282 %
	s	0.007 %
	srel	0.220 %

Titration curve T50/T70/T90



Please note, that the samples of Application M404-2009 and AP202 are different and cannot be compared.

7.4 Sodium Content in Ketchup

(METTLER-TOLEDO Method AP202 Determination with Sodium Analyzer based on standard addition method [22])

Sodium Content in Ketchup	
The sodium content of ketchup was determined by multiple standard addition technique using direct sampling.	
Sample	Ketchup, 0.6 – 0.9 g
Preparation procedures	**Preparation - CAUTION** • Use safety goggles, a lab coat and wear gloves. If possible, work under a fume hood. • Ensure sufficient cleaning of the sensors using deion. H_2O after each measurement. **Sample Preparation** • Accurately weigh 0.6 – 0.9 g ketchup directly into a sample beaker. Use plastic lab ware (glass contains sodium & unknown interactions may happen) • Add 20 mL ambient deionized water • Add 20 mL 1M ISA solution (See chemicals) **ISA solution containing 1 M Diisopropylamine, 0.36 M HCl** • Find preparation instructions on page 9 of this brochure • The ratio of standard or sample to ISA should be 1:1. **2000 mg/L sodium in 0.5 M ISA solution** • Weigh between 5.05 – 5.10 g NaCl for a 1 Liter solution • Dissolve in a volumetric flask using 400 mL deion. H_2O • Add 500 mL 1 M ISA • Fill up with deion. H_2O up to the 1000 mL volumetric mark • Enter the actual concentration in mg/L of your final sodium solution (depending on the corresponding weight of NaCl) as Standard S1 Na^+, e.g 2001.61 mg/L for 5.088 g NaCl
Compound	Sodium, M=22.98977 g/mol
Chemicals	ISA solution: containing 1 M Diisopropylamine, 0.36 M HCl
Na^+-Standard	2000 mg/L sodium in 0.5 M ISA solution
Instruments	Easy Na
Indication	• ISE DX222-Na • Reference DX205-SC • Temperature sensor NTC 30K
Accessories	Balance MS/ML (NewClassic) with USB A/B cable USB-P25 compact printer with USB A/B cable EasyDirect™ software
Principle	Aqueous Na^+ standard solution is added to the sample solution in multiple steps.

Method

Na measure

Standard	S1: Na^+
2001.61	mg/L
No. of additions	5
Potential diff. dE	10 mV
Analysis type	direct
Control	fast
Sample ID	ketchup
Stir speed	medium
Prestir duration	60 sec

Sample type	solid
Sample size entry	variable weight
Sample size	0.8112 g
Sampling	Direct
Water volume	20 mL
ISA volume	20 mL
Multiple determination	Yes
Calculation 1	Content [g/100g]
Calculation 2	Content [ppm]
Report	long

Sample Series Result Summary

Na^+-content in the sample

R1: 0.903 g/100g
R2: 0.895 g/100g
R3: 0.863 g/100g
R4: 0.921 g/100g
R5: 0.895 g/100g

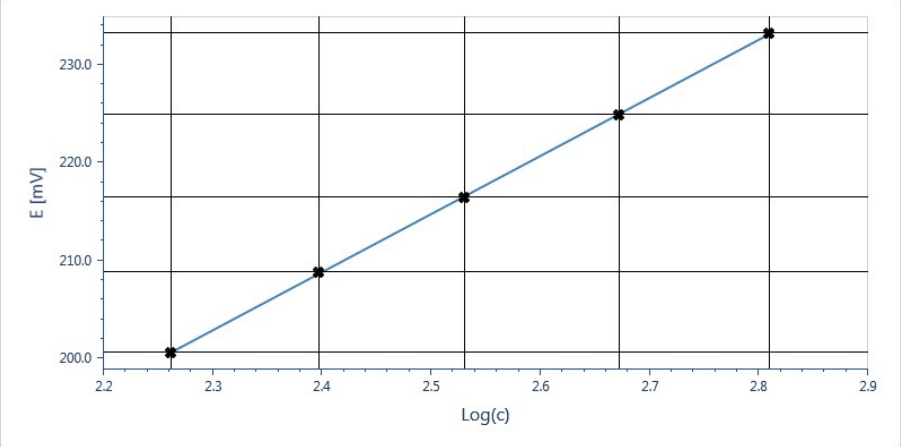
Statistics **Mean 0.895 ± 0.021 g/100g**
Srel = 2.3 % (n = 5)

Single Result

Results

Sample ID	Ketchup
Content (R1)	0.903 g/100g
Content (R2)	9025.51 ppm
Sample size	0.8112 g
Volume	13.650 mL
No. of additions	4
Termination	Fixed
Slope	59.4 mV/log(c)
Coefficient of determination (R^2)	0.99996148

Graph



Please note, that the samples of Application M404-2009 and AP202 are different and cannot be compared.

8. Information

8.1 Literature

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8.2 Webinars

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Mettler-Toledo International Inc
Laboratory Division
Im Langacher
CH-8606 Greifensee, Switzerland
Tel. +41 44 944 22 11
Fax +41 44 944 30 60