Part II

New technologies to improve quality

13

On-line measurement of product quality in dairy processing

G. Ellen and A. J. Tudos, NIZO Food Research, The Netherlands

13.1 Introduction

The dairy industry has to guarantee that the quality and safety of products meets well-defined specifications. This can be implemented by thoroughly checking the quality of each batch of the final product. The problem with this approach is that deviations are signalled at a stage when corrections are usually not possible. Probably, a more attractive approach is a thorough analysis of not only the input and output streams, but also control of all relevant processing parameters in between. This approach yields better product quality because slight deviations of relevant process parameters can be rapidly detected and corrected for. Safety margins can be minimised, yielding increased productivity and profitability. Finally, a faster product release to the market is possible.

For end-product testing, a properly working analytical laboratory is sufficient. The decision of product release will be based on reliable analytical results. From the viewpoint of business efficiency, immediate release of finished products is vital. This can be achieved by chain management of the whole process, i.e. total quality assurance. The tools to achieve this goal include fast measurements, discussed in this chapter, and rapid feedback systems for process control, dealt with elsewhere in this book.

Sampling and analysis can be carried out *on-line*, *in-line*, *at-line* or *off-line*. The distinction between on-line and in-line is not always clear. In this chapter we define these categories as follows. *On-line* analysis means that the data on a process stream segment are available in real time or with only a short delay after the segment has passed the measuring point. The measurement is called *in-line* if the measuring point is in the main process line enabling feedback for process control. Samples taken from the line can be analysed *at-line* with instruments

located in the production area. If none of the aforementioned is applicable, samples have to be sent for *off-line* measurement to a laboratory.

The controllability of a process can be evaluated based on objective parameters such as process controllability (van der Grinten 1968, Leemans 1971). Process controllability (r) ranges from 0 (totally uncontrollable process) to 1 (total control on process). This parameter can be calculated based on results from a process audit and will determine the opportunities to improve product quality through process control. Process controllability can be expressed on the basis of disturbances as follows:

$$r^2 = \frac{\sigma_p^2 - \sigma_\varepsilon^2}{\sigma_p^2}$$

where σ_p is the standard deviation of the process fluctuations before control, a measure for the initial disturbance, and σ_ε is the standard deviation of the process fluctuations after control, a measure for the remaining disturbance after process adjustment.

Table 13.1 demonstrates the effect of the analysis speed and measurement precision on process control. In the table vital parameters are comprised for off-line, at-line and in-line analysis systems. In Table 13.1 the measurement time (the time period between sampling and availability of the analytical result) of the off-line analysis was assumed to be 1 h. In practice this time lag often amounts to several days due to delays at transportation to a central facility, scheduling of analyses and delays with reporting of results. At-line analysis provides a faster turnover, as transportation and scheduling delays are eliminated (0.2 h in Table 13.1). In-line analysis provides results practically instantaneously. For off-line analysis the sampling interval was chosen to be 1 h, for at-line analysis this parameter was set at 0.5 h, whereas in-line analysis was assumed to provide results continuously.

A vital parameter, measurement uncertainty, represents the precision of measurements. In analytical laboratories skilled staff, sophisticated instrumentation, validated and standardised procedures, in combination with frequent calibration and stringent quality control, ensure high precision and accuracy of the measurements. At-line instruments usually compromise accuracy due to time

Table 13.1 Effect of analysis speed and measurement uncertainty on controllability of a process with a response time on corrections of 0.1 h (adapted from Tummers and Wienke 2002)

Parameter	Off-line analysis	At-line analysis	In-line analysis
Measurement time	1 h	0.2 h	0 h
Sampling interval	1 h	0.5 h	0 h
Measurement uncertainty	1%	30%	50%
Process controllability (r)	0.46	0.73	0.87
Remaining disturbance (σ_ε)	90%	70%	50%

and cost limitations. In- and on-line apparatus mostly provides even less accuracy. In the example of Table 13.1 this parameter was chosen to be 1% for off-line analysis, 30% for at-line and 50% for in-line measurement.

The process controllability in case of in-line and at-line analysis appears quite high, whereas off-line analysis provides poor controllability. In practice, controllability values below 0.5 indicate uncontrollable processes, because only 10% of the disturbance is compensated. Based on the parameter of remaining disturbance, in-line analysis is clearly advantageous over at-line analysis. A striking conclusion of the above example is how vital the time lag between sampling and analytical results can be for process control. A central laboratory can guarantee process control only for relatively slow processes.

Dairy processes are usually complete within a time frame of hours, sometimes minutes or even seconds. Process control requires fast measurement, with less stringent demand on accuracy. Often, in- and on-line analysis is the method of preference with restrictions posed by the optically dense, inhomogeneous and fouling matrix. In-line analysis eliminates the need for batch sampling and can minimise sampling error by averaging of virtually instantaneous, continuous measurements. A prerequisite is that the instrument is placed at the correct analysis spot and timely changes can be made to the process. A restriction is that any component of the probes in contact with the product needs to comply with HACCP requirements. The advantages of effective process control are better compliance with product specification, hence narrower margins; faster release of products to the market, therefore less storage needed at the production site; less wasted product or products sold under the regular market price; and a decrease in the number of customer recalls.

In this chapter the existing technology for fast measurement is discussed for the determination of physical parameters, chemical concentration and micro-organisms. Examples are given for in-line measurements for process control in fermentation of yoghurt, renneting of milk, preparation of milk powder and pasteurisation. Applications for monitoring (bio)fouling and cleaning are also included. The chapter ends with a short review of exciting technologies suited to solve outstanding issues and an outlook on future trends.

13.2 On-line measurement of physical parameters

Measurement systems used in a food production environment must comply with stringent regulations. First, the choice of material in contact with the product is limited to food-grade materials. Secondly, in the design dead-zones must be avoided, and the surfaces must be smooth. Finally, the system must fulfil the requirements for cleaning and sterilisation in place, enduring the often harsh environment used for the various cleaning and disinfecting steps ($pH < 1$ and $pH > 11$). These requirements are common for all instruments applied in-line. In this section an overview is given of the available principles and measurement systems for the determination of physical parameters, concentration of

Table 13.2 Sensors for physical parameters, their principle of operation and relevant examples in dairy processing

Sensor	Principle of operation	Relevant processes
Temperature	Pt resistance wire	thermisation, pasteurisation, sterilisation, cooling, renneting
Pressure	(piezo)resistance, capacitance	filtration, pasteurisation, homogenisation
Flow	electromagnetism, displacement, turbine, ultrasonic, differential pressure, thermal mass	standardisation of fat content, mixing, heating, filtration
Level	conductivity, hydrostatic, vibration, ultrasonic, optical	storage tanks, mixing, packaging, CIP
Density	vibrating tubes, microwave	standardisation of fat content, powder production, mixing
Conductance	electrodes, microwave	cleaning in place (CIP)
Heat flux	thermopile (array of thermocouples)	fouling
Particle size, shape and distribution	focused beam reflectance, light scattering, microwave, video	cheese, yoghurt and powder production
Turbidity	IR and visible light scattering	CIP, filtration
Viscosity	diffusing wave spectroscopy, oscillation, vibration, NIR, hot wire, laser doppler anemometry, magnetic resonance imaging (MRI), NMR	cheese and yoghurt production, fermentation
Colour, optical density	optical reflection and absorbance	fermentation, powder production

compounds, and micro-organisms. Each section ends with relevant examples of application of the technology for process control in the dairy industry.

Various measurement systems have been successfully developed for the in-line determination of physical parameters. Table 13.2 is a compilation of the most commonly applied sensors in the dairy industry. The table contains the basic principles of operation together with relevant examples for use in dairy processing. For a comprehensive review on the measurement principles for pressure, temperature, flow and level, the reader is referred to Chapters 10 and 11 in *Instrumentation and Sensors for the Food Industry* (Berrie 2001a, 2001b). Up-to-date information on commercially available systems can be found at the websites of manufacturers.

Two examples of widespread application of sensors for physical parameters in the dairy industry are control of heat load and fat standardisation. Heat load is a quality parameter determined by the combination of temperature and residence time (i.e. flow). The organoleptic and storage quality of dairy products are largely determined by the heat load. The classification of pasteurised, sterilised

and UHT milk, and of milk powders, is based on the heat load. In order to meet stringent specifications the temperature needs to be controlled within ± 0.1ºC and at a time scale of <1 second, imposing high demands on the response time and sensitivity of the sensors.

The second example of in-line process control in the dairy industry is fat standardisation. Narrowly defined by legal regulations and product specifications, the fat content of liquid dairy products is adjusted in-line using fat standardisation units. This process is based on the fact that differences in the density of milk are determined by variations in fat content. Therefore, systems available on the market for fully automatic in-line fat standardisation rely on measuring the density of the skimmed milk and whole milk or cream phases in combination with controlling the flow of each component to standardise the milk to the required fat content. Using current technology, fat content can be regulated within $\pm 0.02\%$ (m/m) of the target level in the final product.

A powerful new tool for in-line monitoring of texture changes is based on diffusing wave spectroscopy (DWS). DWS is an optical measuring technique based on multiple scattering of laser light by colloids and polymers in turbid systems (Pine *et al.* 1990). It is a non-destructive method applicable in a broad temperature range suited to determine the mobility of the colloidal particles (oil droplets, protein particles) even in concentrated systems such as emulsions and protein gels (Ten Grotenhuis *et al.* 1999). Physical contact of the probe with the product can be avoided by measuring through a window.

Incident laser light is multiply scattered due to the turbidity of the system. Scattered light can be detected at the opposite side of the incidence (transmission) or at the same side using a light fibre probe (back-scattering). The detected light intensity is a stochastic signal due to the mobility of the particles. Via determination of the intensity correlation curve, a numeric value for the mobility of the scattering particle can be obtained. The mobility of particles is determined by their surroundings and therefore reflects the visco-elastic properties of the system.

DWS-based systems have been used for monitoring acid-induced gelation of milk (Arikainen 2000, Vasbinder *et al.* 2001). A DWS-based measuring instrument called NIZO RheoLight (NIZO Food Research, Ede, The Netherlands) was developed to monitor curd formation in-line during cheese manufacturing (Ten Grotenhuis 1999). During standard and test production of more than 80 batches of cheese, the renneting process was followed for a period of 3 months with NIZO RheoLight. The fat content and amount of curd fines in the whey were determined (Fig. 13.1).

For the test batches the cutting programme started at gel strengths below or above the usual value. The critical gel strength was determined to be approximately 30 DWS units. When the curd was too soft at cutting, dramatic losses of fat and curd fines were seen: a renneting time approximately 2 minutes shorter (20 DWS units instead of 30) increased the losses in curd fines sixfold and increased fat loss by 50%. At this stage, the gel is not yet strong enough to be cut without damage. Longer cutting times result in slightly higher cheese

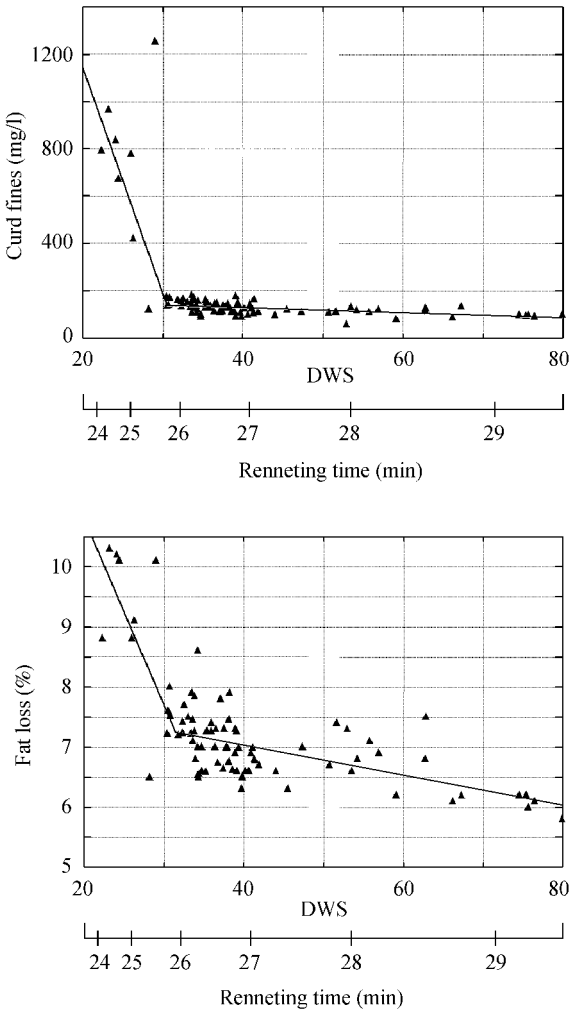

Fig. 13.1 Curd fines and fat content in whey depending on the gel strength and renneting time in cheese manufacturing.

yield, but can be disadvantageous for the production throughput (Table 13.3). The in-line sensor has been successfully installed in cheese factories where it contributes to cheese yield and process control (Straatsma *et al.* 2001, 2002).

The NIZO RheoLight system provides distinct advantages for the cheese-making process. For example, the complete process of cheese-making can be automated, and the renneting process can be continuously monitored with improved control over the water content of the product. Additionally, the final product shows less variation in shape. Finally, the product composition is less prone to seasonal effects. The applications have been extended to follow

Table 13.3 Effect of cutting time and gel strength on fat and protein yield in cheese processing, at an annual production of 25 000 000 kg cheese

Gel strength (DWS)	Renneting time (min)	Yield increase (kg/year) Fat	Protein
20	23.5	−27 300	−142 590
30 (ref)	25.7	–	–
50	27.8	4195	3205
70	28.9	8345	6406

changes in the rheology characteristics of turbid systems such as desserts, drinks, sauces and the production of yoghurt (Ten Grotenhuis *et al.* 2000). An advantage of this in-line system is that dosing errors of ingredients are immediately detected. Deviations from normal process trend can be traced at an early stage.

An alternative optical technique for cutting time control in cheese-making is represented by the CoAguLite (REFLECTronics Inc., Lexington, KY, USA). The CoAguLite sensor measures changes in light back-scattering during coagulation of milk. From the reflectance profile, a prediction is made for the optimal cutting time. The two systems, CoAguLite and NIZO RheoLight, show a major difference in determining the optimal cutting time. The RheoLight measures real-time gel strength throughout the process, whereas the CoAguLite extrapolates the optimal cutting time from measurement data obtained during the first stages of flocculation. Extrapolation can be hampered by unexpected effects during the process, resulting in incorrect prediction of the optimal cutting time.

Further systems for viscosity determination are based on induced mechanical effects (shear, torsion, ultrasound) which by themselves can disrupt the structure to be measured (Bourne 2002). Additionally, a heated thermistor was used for monitoring curd formation, based on decrease of thermal conductivity on flocculation of milk. The error of prediction was 1.9 min in 16 experiments (Passos *et al.* 1999). As seen in Table 13.3, this precision is not sufficient.

13.3 Measuring product composition

The use of process analytical equipment grew by more than 5% annually during the 1990s (McMahon and Robertson 1995, McIvor 1997). As a consequence, the number of laboratory-based analyses has been shrinking and the work has been shifting away from chemists and chemical technicians to plant operators trained to make analytical determinations. Various measurement systems have been successfully developed; Table 13.4 is a compilation of the most commonly applied systems for concentration measurement in dairy processes. The table contains the basic principles of operation together with relevant examples for use in dairy processing. For information on the operating principles behind the

Table 13.4 Chemical parameters, the principle of their determination and relevant examples for application in dairy processing

Parameter	Principle	Relevant applications
pH	ion selective electrode (ISE), field effect transistor (FET)	fermentation, cleaning-in-place
Water content	(near) infrared spectrometry, sensors	powder and cheese production
Fat content	(near) infrared spectrometry	standardisation, quality control of dairy products
Protein content	(near) infrared spectrometry	standardisation, quality control of dairy products
Lactose/ carbohydrates	flow injection analysis, (near) infrared spectrometry, sensors	fermentation process control, quality control
Lactic acid	flow injection analysis, sensors	fermentation process control
Flavour components	fast mass spectrometry, electronic nose, electronic tongue, sensors, spectroscopic techniques, dedicated mass spectrometry	process control, quality control, cleaning
Residues/ contaminants	fast mass spectrometry, electronic nose, electronic tongue, sensors	process control, quality control, cleaning
(Bio)fouling	heat transfer resistance, pressure drop	production processes
Byproducts	sensors, optical measurements	smouldering of milk powder
Cleaning/ disinfecting	conductivity, electronic nose, electronic tongue, sensors, spectroscopic techniques, dedicated mass spectrometry, ISE	cleaning-in-place

analytical techniques, the reader is referred to basic literature on sensors (Taylor and Schultz 1996, Kress-Rogers 1997, Kress-Rogers and Brimelow 2001) and spectrometry (Skoog and Holler 1996).

One of the most established techniques, infrared (IR) spectrometry, provides a rapid and direct method for process analysis. Based on the wavelength of irradiation, infrared techniques can be divided into mid- and near-infrared, often called MIR ($\lambda = 2$–$14\,\mu$m) and NIR ($\lambda = 0.75$–$2.6\,\mu$m) (Scotter 1997). IR is a non-destructive and non-invasive technique suited for at-, on- or in-line application in food processing plants. Determination of more than one component is possible within one spectral acquisition time, i.e. within minutes, seconds or less. MIR is mostly applied for analysis in gas and liquid phase, whereas NIR is applicable for the analysis of solid or liquid products.

Few analytical methods are capable of direct measurements in complex food matrices. Infrared techniques are suited for such matrices but lack the potential

of 'seeing through' thick layers of inhomogeneous samples such as an intact cheese. Nevertheless, the technologies represent probably the most successful analytical tools in food analysis, because they are fast, versatile and non-invasive. IR measurements can be carried out in solid, liquid and gas samples and are not hampered by viscosity or turbidity of the sample. Analysis can be implemented in the transmission, reflection or attenuated total reflection (ATR) mode. Even immersion probes are commercially available. Various manufacturers provide dedicated systems suited for process analysis in the food industry. An overview of the companies, the measuring principle and applications is provided in Table 13.5.

Originally used for the identification of organic compounds, mid-infrared spectrometry has gained widespread application for quantitative measurements and recently for process control of high moisture content dairy products. A typical example is an FT-MIR-based on-line analyser and dedicated process controller developed by FOSS for standardisation of milk used in the manufacture of dairy products. The standardisation is carried out on multiple components, such as fat, protein, lactose and total solids, to within $<0.01\%$ of the target value. The idea of on-line standardisation is to decrease the spread in distribution of, for example, the fat content in the processed dairy product. With manual standardisation, the distribution is very broad as indicated by curve 1 in Fig. 13.2. By using the standardisation control system of FOSS, the fat distribution curve was considerably narrowed around the old target value (curve 2), but as long as the target is not changed, the average of the production will be the same. The improved fat distribution figures make it possible to move the average of the production down from 3.07 to 3.02 and at the same time get

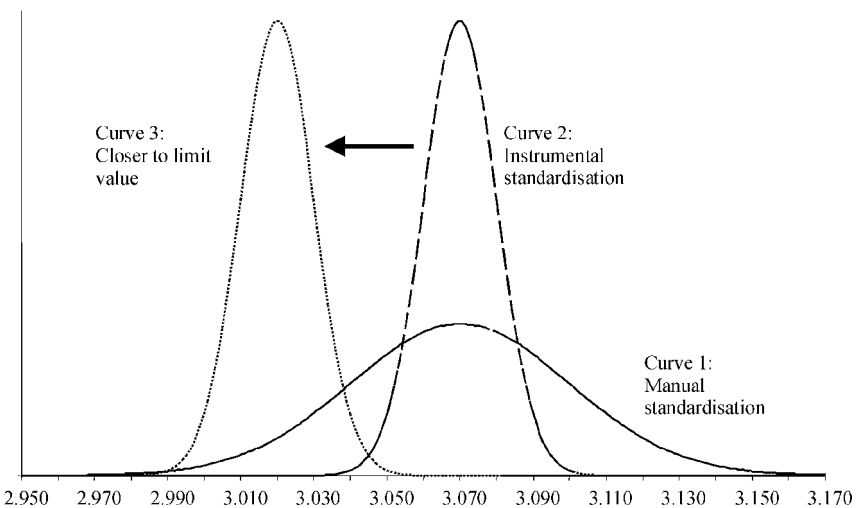

Fig. 13.2 Effect of improving standardisation accuracy on the economy of production (courtesy of FOSS).

Table 13.5 Producers of dedicated IR instruments

Company	URL	Measurement principle	Applications	Remarks
ABB Bomem Inc., Quebec, Canada	www.bomem.com	FT-NIR	fat, salt, protein moisture in butter; standardisation of fat, protein and moisture in liquid dairy products	at-line, 2 min/sample in-line and on-line 1-5 samples/min
AIS-Tech	www.adnex.de	NIR	moisture in solid food products	on-line probe
Analyticon Instruments Corp., Springfield, NJ	www.analyticon.com	NIR	moisture in solid food products	on-line probe
Analytical Spectral Devices Inc., Boulder, CO	www.asdi.com	NIR	fat and moisture in cheese	at-line fibre optic probe
Axiom Analytical Inc., Irvine, CA	www.goaxiom.com	NIR FT-MIR	food and other applications	in-line ATR probe, immersion probe, non-contact analyser and on-line sampling system
ChemQuip Ltd, Stockport, UK	www.chemquip.co.uk	NIR	gas, liquid and solid samples including food	in-line ATR probe, single and double path cell
FOSS, Hillerød, Denmark	www.foss.dk	NIT	fat, moisture, protein, TS[a] in cheese, butter, quark, yoghurt	at-line, approx. 1 min per sample
		NIR	solids, liquids, powders	at-line, approx. 1 min per sample
		FT-MIR	in-line fat, protein, lactose, SNF[b] in milk	in-line milk standardisation
Kett Electric Laboratory, Tokyo, Japan	www.kett.co.jp	NIR	moisture, protein, fat, lactose content in milk powder	at-line

Leco Corp., St Joseph, MI	www.leco.com	NIR	moisture and fat in cheese; moisture, salt, fat, ash and protein in whey powder	at-line at-line
Thermo Electron Corporation, Chelmsford, MA	www.thermo.com	NIR	fat, protein, moisture in foods including dairy products	at-line
NDC Infrared Engineering, Maldon, Essex, UK	www.ndcinfrared.com	NIR	moisture, fat, protein in dairy powders	on-line
Perten Instruments, Huddinge, Sweden	www.perten.com	NIR	fat, protein, salt and moisture in foods including dairy products	at-line, <1 min per sample
Polytec GmbH, Waldbronn, Germany	www.analytic-web.com	NIR	fat, protein, moisture in foods including dairy products moisture in powder	at-line on-line
Process Sensors Corp., Milford, MA	www.processsensors.com	NIR	moisture in dairy powders	at-line
Wilks Enterprise Inc., South Norwalk, CT	www.wilksir.com	MIR	fluids	in-line ATR plug sensor
Zeltex Inc., Hagerstown, MD	www.zeltex.com	NIR	fat, protein, moisture in cheese and other foods	at-line, <1 min per sample

[a] TS = total solids.
[b] SNF = solids-non-fat.

batches within the legal limit (curve 3). In this way expensive milk components are saved, and both production economy and product quality are improved.

An example of *in situ* fermentation monitoring of glucose, fructose, lactose, galactose, lactic acid and ethanol was demonstrated using an attenuated total reflection (ATR) sensor connected to a remote dispersive mid-IR spectrometer with an optical fibre (Fayolle *et al.* 2000). A well-established application proven in daily practice is the early warning system for fire in drying installations, based on IR detection of carbon monoxide in the drying air (Steenbergen *et al.* 1991; see also Chapter 20 in this book). The system, called NICOSYS, is currently marketed by Hobré Instruments (Purmerend, the Netherlands). Another system, called STUVEXCOPS by StuvEx Sicherheitssysteme GmbH (Hamm, Germany), is also on the market.

Near infrared (NIR) plays a key role in the analysis and process control of dairy products. The technique offers flexibility in the determination of protein moisture, fat and lactose contents in a wide range of dairy products, e.g. liquid milk, dairy powders, cream, cheese and processed cheese. Many of these products are emulsions, whose sampling for classical chemical analysis is cumbersome. Fundamental literature on NIR is available (Burns and Ciurczak 1992, Osborne *et al.* 1993) as well as a review on food analysis (Osborne 2000). NIR instruments are generally very fast and easy to operate, providing results similar in accuracy to the reference methods to which they are calibrated. NIR requires little or no sample preparation and no chemicals, and is ideal for complex matrices, e.g. food. For some in-line applications, fibre optic probes are used. The applications span the range from purely quantitative measurements such as protein, moisture and fat content to qualitative measurements and product identification.

It is profitable to make products which narrowly match the required specifications. Milk powders are analysed on-line, enabling the moisture content to be narrowly controlled as demonstrated by Holroyd (2002). A FOSS 5500 scanning NIR apparatus was placed after the fluid bed drier. Via a sample grab arm operated with compressed air, 100 g of sample is presented to the instrument. The sample is either returned to the flow or retained for later reference. In Fig. 13.3 the results of the on-line NIR and an off-line reference method (IDF 26A:1993) are compared. An overall match of the two methods is easily seen, though at the indicated time region serious deviation from the target value occurred, unseen by the reference method due to low sampling frequency. An additional disadvantage of the reference measurement is that the analysis data do not become available until after more than 3 hours, whereas the NIR measurement provides data instantaneously. The economic benefits for process control are obvious.

Sometimes at-line measurements provide sufficient benefits and are cheaper than in-line options (Holroyd 2002). The example shown in Fig. 13.4, the determination of moisture, salt and fat in butter, takes less than 1 min. Other examples for application of NIR for dairy process control include the continuous in-line determination of moisture, protein and fat in cottage cheese and

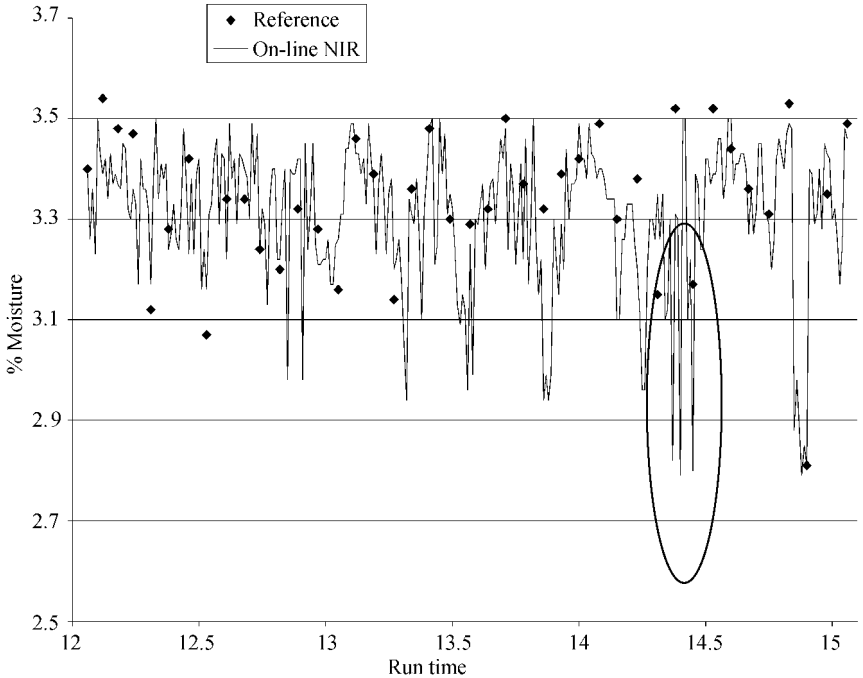

Fig. 13.3 Comparison of on-line and reference (IDF 26A:1993) measurements of moisture in milk powder (Holroyd 2002).

processed cheese (Hoyer 1997). Correlation coefficients between 0.988 and 0.999 were found between the NIR and reference methods in 35 samples of processed cheese and 49 of cottage cheese. The standard errors of prediction varied from 0.06% to 0.38%. No information on the reference methods is provided in the publication.

A specific example for in-line measurements is represented by testing of return PET milk bottles for abuse. Before refilling, glass bottles undergo steam cleaning, whereas plastic bottles do not endure this treatment. Therefore, the air inside each bottle is tested for the presence of organic compounds, mainly hydrocarbons and remnants of household chemicals, using a dedicated mass spectrometry system. These systems are commercially available, but the sampling device usually needs to be tailor-made.

Flow injection analysis (FIA), first described by Růžička and Hansen (1975), is a well-established analytical technique, known for its high sample throughput combined with good precision, reproducibility and accuracy. The basis for the technology is a continuous flow of liquid into which reagents are injected as small liquid segments that are transported, mixed, diluted and reacted under well-controlled conditions. The technique allows chemists to easily automate and optimise well-developed wet chemical methods for routine laboratory use, and even for at-line or on-line process analysis. Reagents can also be

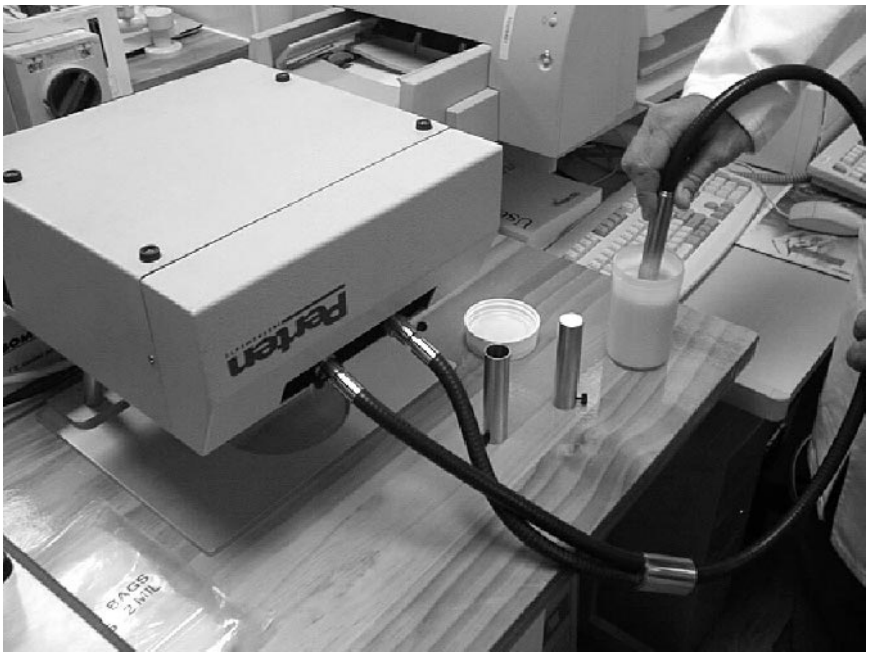

Fig. 13.4 At-line NIR determination of moisture, salt and fat in butter (Holroyd 2002).

immobilised in small reactors, limiting the cost per sample. This technology is especially useful when biochemical reactions are required in FIA systems, e.g. by using enzymes (Mattiasson 1994). Present commercially available FIA systems and producers are listed in Table 13.6. The table also contains system characteristics such as sample volume and throughput, detection systems and areas of application. The table is based on a recent publication (Smith and Hinson-Smith 2002). As the field is developing rapidly, the reader is advised to check product reviews of periodicals for updated information.

An example of the at-line application of FIA in dairy processes is the determination of D- and L-lactate in butter, yoghurt and buttermilk production (Becker *et al.* 1995). The FIA system contained a microreactor with immobilised D- and L-lactate dehydrogenase enzymes for the production of pyruvate in the presence of nicotinamide adenine dinucleotide (NAD^+). The produced NADH was detected photometrically. The analysis could be performed within 5 minutes. The only sample preparation required was dilution. The analysis cost 10% of the reference method. The FIA analysis results of 15 different dairy products were within 3% of those obtained with the reference method (DIN 10335).

A similar on-line application in an accelerated, fed-batch yoghurt fermentation process was developed at NIZO Food Research by de Jong (1994) using in-line dialysis and fluorometric detection (Fig. 13.5). The sample throughput was 20 per hour and the results were in agreement with HPLC. The

Table 13.6 Overview of commercially available FIA systems (adpated from Smith and Hinson-Smith 2002)

Company	AMKO Systems, Richmond Hill, Ontario, Canada	FIAlab instruments, Bellevue, WA	FOSS, Hillerød, Denmark	Global FIA, Fox Island, WA	Lachat Instruments, Milwaukee, WI	OI Analytical, College Station, TX	Skalar Inc., Breda, The Netherlands
URL	www.amkosystems.com	www.flowinjection.com	www.foss.dk	www.globalfia.com	www.lachatinstruments.com	www.oico.com	www.skalar.com
Detection principles	colorimeters, ISE[a] conductivity	light absorbance, fluorescence, bioluminescence	dual-wavelength photometer	UV-vis absorbance, chemiluminescence amperometric	photometric, ISE, conductivity, flame, photometric, amperometric, pH, fluorimetric	photometrics, ISE, amperometric	photometric, UV, IR, fluorimetric, flame, conductivity, pH, ISE
Applications	chemical, environmental, biotechnology, pharmaceutical, food and beverage	water quality, environmental, proteomics, food sample handling for FTIR, ICP-MS, chemical sensors, immunoassays	food, environmental and industrial	organic and inorganic analytes on-line, lab and field analysis	high throughput, environmental, industrial QC, bioreactor monitoring, food and beverage, in-line digestions	water and waste, industrial QC, agricultural, food and beverage	water and waste, industrial QC, agricultural, food and beverage, detergent and pharmaceuticals
Sample volume and throughput	2–100 μl 20 samples/h		20–400 μl 60–120 samples/h	variable, 1–3 min/sample	1 μl to 2 μl 60–120 samples/h	20–75 samples/h	20–140 samples/h/manifold 16 manifolds simultaneously

[a] ISE = ion selective electrode.

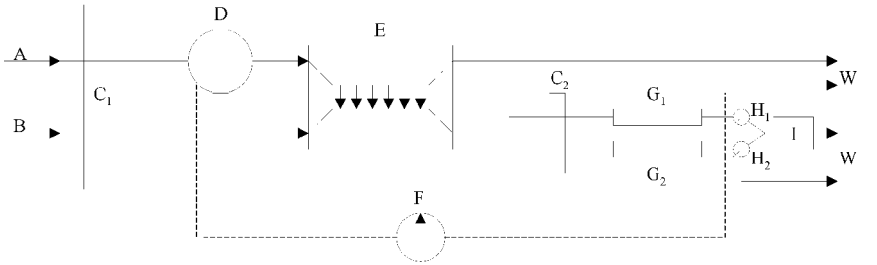

Fig. 13.5 Scheme of the FIA setup for simultaneous determination of *D*- and *L*-lactate. (A) 5% Na-citrate carrier solution; (B) 2.5 mM NAD in hydrazine–glycine–EDTA buffer at pH 9.0; (C) pumps, flow $C_1 = 1.2$ ml/min, $C_2 = 0.6$ ml/min; (D) injection valve 200 μl; (E) dialyser unit; (F) timer/controller; (G_1) reactor column width with immobilised *D*-lactate dehydrogenase; (G_2) reactor column with immobilised *L*-lactate dehydrogenase; (H) valves; (I) fluorescence detector (340/460 nm); (W) waste.

system provides a useful tool for on-line control of product claims in the production of novel and functional foods.

Well-known devices for in-line concentration measurement are sensors. The most common example is the glass electrode for pH sensing. A chemical sensor or a biosensor can be defined as an analytical device comprised of a chemical or biological recognition element directly interfaced to a signal transducer, which together relate the concentration of an analyte or group of analytes to a measurable response. Hence, a sensor can provide continuous information about its environment, and in principle is ideal for in-line measurements. In recognition of this promise, several journals are specialising in sensors, large professional societies have sensor divisions and frequent international conferences are organised. At the turn of the millennium, more than 2000 sensor-related articles were published per year (Janata 2001). Yet, all these efforts have so far yielded few examples in process analysis, most sensors having been developed for the determination of sugars (mainly glucose) and ethanol in fermentation processes.

The main hurdles for the application of chemical and biosensors in a process environment are the price vs. lifetime ratio, mismatch between analytical characteristics (reproducibility, robustness, drift, sensitivity, etc.) and requirements, and deterioration of analytical characteristics on cleaning-in-place. Further limitations, practical problems and future demands are outlined in reviews by Mehrvar *et al.* (2000) and O'Connell and Guilbault (2001).

A process example of the application of (bio)sensors in fermented milk and yoghurt was provided by Mannino *et al.* (1999). Two parallel amperometric biosensors were applied to the simultaneous detection of glucose and galactose. The two rhodium-on-carbon paste sensors were constructed using glucose oxidase and galactose oxidase enzymes, respectively. The sample throughput was 70 per hour. All results were within 10% agreement with the HPLC results. The advantage of fast data acquisition is manifested in better controllability of the process (see Table 13.1). If extended with a microdialysis system, the

method will be suited for on-line monitoring. Further examples include the use of pH sensors for monitoring cleaning-in-place.

Validation of chemical sensors and concentration measurement systems can be a costly adventure. A useful workaround is to measure physical parameters (pressure, temperature, conductivity) which are correlated to the compound to be measured. If the correlation is sufficiently robust, the determination of the chemical parameter(s) can be replaced by monitoring the physical parameters.

13.4 On-line microbiological testing

Microbiological testing in the dairy plant is critical to ensure the quality of raw milk and finished products. The presently available methods include standard plate count (SPC), direct microscopic count (DMC), preliminary incubation (PI)-SPC, direct microscopic somatic cell count (DMSCC), and fast detection methods such as Bactoscan (FOSS, Denmark), Bactoscope (Delta Instruments, the Netherlands) and ATP-based measurements. Finally, indirect methods, such as the determination of conductivity, titratable acidity and gas formation, are also available.

The traditional methods usually require several hours or days of culturing, but provide relatively low limits of detection (in the range of 1 cfu/ml or lower). Fast methods can provide results within approximately 10 minutes; however, the limits of detection are in the range 10^4–10^5 cfu/ml. With the majority of indirect methods the effects of the growth of micro-organisms are only traceable at a stage when the product is already spoiled.

Micro-organisms presenting problems in dairy production are divided into two categories, pathogens and spoilage microbes. Production steps such as pasteurisation, (ultra) high temperature (UHT) treatment and sterilisation inactivate all pathogens. UHT and sterilisation also inactivate spoilage micro-organisms. The major problem for UHT and sterilised products is post-sterilisation contamination: spoilage micro-organisms can reach high levels during the long shelf-life of the products. Early detection of contamination is essential and requires determination at very low levels.

Despite extensive efforts to develop reliable and rapid analysis technology, no commercial methods are available as yet. Promising developments include a plastic food wrap suited for indicating bacterial contamination (Kleiner 2000). The food wrap, presently at the verge of market introduction by Toxin Alert (Mississauga, Ontario, Canada), will signal bacterial contamination without the need to open the package. Magnetic resonance imaging (MRI) has also been used to detect spoilage in closed packages (Schenz *et al.* 1999). Conductance and impedance techniques offer yet another non-destructive approach to detect bacterial growth in closed packages (Raaska and Mattila-Sandholm 2000). Extensive description of the technology and the practice can be found in Gibson (2001). Also ultrasonic imaging can be used for testing closed packages as well as calorimetric and volumetric methods (Raaska and Mattila-Sandholm 2000).

The detection limits of these techniques do not allow in-line measurements during production. The closed packages need to be incubated, sometimes for as long as several days. Additionally, the reliability of these techniques is not yet fully established.

The running times of continuous-flow process equipment such as pasteurisers are limited mainly by thermoresistant Streptococci (TRS). Raw milk may contain 10^2–10^4 TRS/ml. These micro-organisms attach to surfaces up to 10^7 TRS/cm^2. TRS are not completely inactivated by pasteurisation and proliferate at temperatures between 30º and 50ºC, i.e. in the regenerative section of heat exchangers. In the course of a running period the TRS are released into the product flow. Depending on the initial level in the raw milk, running times of approximately 4 to over 11 hours can be realised before the critical level of 10^5 TRS/ml is reached and the pasteuriser must be cleaned. Bactoscan and ATP measurements were tested for indication of reaching the critical level (Te Giffel *et al.* 2001). The results revealed that, owing to the detection limits (10^4–10^5 cfu/ml), both systems are suited only as an 'emergency break', but not as a timely indicator that cleaning is necessary. If equipped with a suited filtration–concentration unit (e.g. Aquamarijn Microfiltration B.V., Zutphen, the Netherlands), the technology can reach the target detection limits.

13.5 Monitoring fouling and cleaning-in-place

The formation of fouling deposits within processing equipment has a significant economic impact in the dairy industry. Monitoring of fouling can provide useful information on when cleaning is necessary, and ensure effective operation of pasteurisers, sterilisers and drying equipment. When the tolerance level is reached, production has to be stopped and the equipment is cleaned in place (CIP). Monitoring of (bio)fouling and of CIP provides examples of the concerted application of physical sensors and devices for microbial growth detection and for concentration measurement.

An established technique for the monitoring of fouling in dairy processing lines is based on heat transfer measurements (Otten and Van Boxtel 1989, Truong and Anema 2002). An early example of monitoring the build-up of a fouling layer was provided by Otten and Van Boxtel (1989) by on-line measurement of the level of deposit based on the disturbance of hydrodynamic characteristics and on disturbance of heat transfer. The build-up of deposits on the inner wall of a pipe creates an additional thermal resistance and reduces the heat transport through the wall. Heat flux sensors consist of an array of thermocouples in which the elements are separated by a thin layer of thermal resistance material. Under a temperature gradient the thermocouple junctions are at different temperatures and therefore generate a voltage difference, proportional to the heat flux. These sensors provide more accurate information than simple temperature measurements, improving the accuracy of temperature-based control systems.

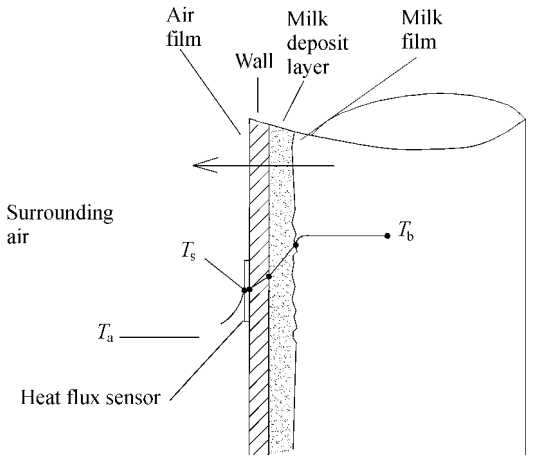

Fig. 13.6 Sectional view of a fouled pipe showing heat flux and temperature profile across the pipe wall. Temperature profile: bulk milk (T_b), sensor (T_s) and ambient air (T_a).

Truong and Anema (2002) measured fouling using a heat-flux sensor attached to the outer surface of a pipe of a direct steam injection milk heater (Fig. 13.6). The figure shows the temperature profile from the bulk milk (T_b) through the deposit layer and the pipe wall to the ambient air (T_a). The thicker the deposit layer on the wall, the smaller the temperature difference between the sensor (T_s) and the ambient temperature (T_a), resulting in a decreased heat flux.

The heat flux in relation to the average deposit thickness was measured in a pilot plant and in a commercial plant with the heat-flux-based system shown in Fig. 13.7. The method is suited for mapping critical points most sensitive to

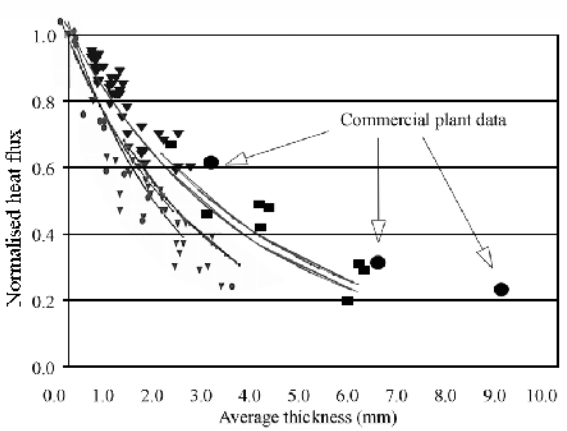

Fig. 13.7 Relation between the normalised heat flux and the average desposit layer thickness, both measured at the end of runs of heating whole milk to 85ºC (■ top line), 95ºC (▼ middle line) and 100ºC (• bottom line).

fouling in the production line. Sensors placed at these critical points provide on-line information on when cleaning is necessary.

Cleaning and disinfection are essential for ensuring and maintaining quality and safety in the food industry. In liquid food processing frequent cleaning is a prerequisite. Dairy processes require even daily cleaning. These procedures are often based on experience. Large margins are chosen regarding the intensity and length of the cleaning steps to ensure food safety. With production batches getting smaller and product diversity increasing, flexibility in CIP processes gains in relevance. Strategies based on in-line and on-line monitoring of cleaning steps can save energy and time, and decrease consumption of water and

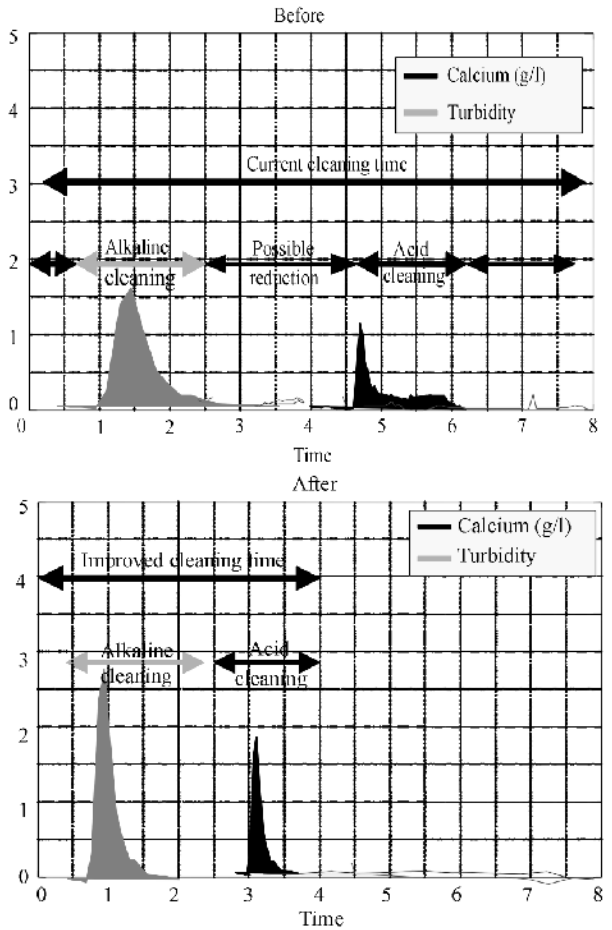

Fig. 13.8 Optimisation of CIP based on in- and at-line measurements. Turbidity corresponds with the amount of undissolved organic and inorganic material removed by alkaline cleaning. Calcium ion measurements: removal of inorganic deposition during acidic cleaning.

raw materials. Cleaning and disinfecting protocols include pumping an alkaline solution through the system to remove organic material (mainly proteins) and an acidic cleaning step to remove inorganic deposits, mainly calcium phosphate. Each step is preceded by aqueous rinsing, and the procedure ends with a thorough rinsing with water to ensure complete removal of the cleaning agents.

NIZO Food Research has developed a monitoring system, called OPTI-CIP, based on in- and at-line measurements of removal of deposits and cleaning agents (van Asselt *et al.* 2002). With OPTI-CIP, processes can be continuously analysed and optimised. Figure 13.8 demonstrates how optimisation of CIP can be accomplished by monitoring organic and inorganic material in the effluent. In a plant a two-step cleaning process was followed using a turbidity sensor (Type AF 56-N, OPTEK, Essen, Germany) and monitoring calcium. The efficiency of cleaning was improved by reducing the cleaning time by 50%.

13.6 Future trends

As shown in the previous sections, the challenge of in-line determination of most *physical parameters* relevant in dairy processing has been successfully tackled. In the near future, existing in-line methods can be used to acquire data on processes for predictive modelling and feed-forward process control (see Chapter 20 in this book). This approach will result in products narrowly matching the required specifications and depending less on fluctuations in the composition of raw materials.

Further outstanding issues are still to be solved in the area of on-line determination of *chemical compounds*. A challenging area is early detection of veterinary drug residues and contaminants in raw milk. The solution for this issue is urgently awaited owing to problems in fermentation processes, as well as to guarantee the safety and quality of final products. With proper 'farm to fork' chain management, abnormalities in composition will be detected very early in the chain, preferably during milking. Other outstanding issues include detecting abnormal milk in automatic milking systems, monitoring of the development of flavour compounds during fermentation, and the determination of the water content of intact cheeses before brining.

The technology of on-line analysis of *microbial contamination* at the required level is presently not available at all. In-line methods are urgently needed to trace microbes and spores.

There is light at the end of the tunnel in the guise of novel analytical techniques. In the following paragraphs a few innovative techniques that promise a breakthrough are discussed. Most of the illustrations of applications for these techniques are outside the dairy area.

Innovative *sensing systems* are currently under development to detect 'abnormal milk'. Abnormal milk, i.e. milk with clots, blood or a watery consistency, is not suited for human consumption and according to European Council Directive 92/46/EEC shall not reach the farm milk tank. Automatic

detection of abnormal milk has gained importance due to the introduction of automatic milking systems where visual inspection is not possible (Rasmussen 2001). Present systems are based on conductivity sensors, yielding significant numbers of false positive as well as false negative results (de Mol 2000). Novel systems under development for the detection of abnormal milk are based on colour analysis (Espada and Vijverberg 2002), enzyme detection (Pemberton *et al.* 2001) and the electronic tongue (Rudniskaya 2002, Vlasov *et al.* 2002). If further developed, these sensor systems could also be used in the production line: the colour determination of products (custards, chocolate drinks, fermented dairy drinks), deviations in the composition of fermented products, authenticity and product control (e.g. sweeteners and flavours).

Another commercially available sensor suited for in-line process applications is based on surface plasmon resonance. The Spreeta™ sensor (Texas Instruments, Austin, TX, USA) can be used to control the mixing ratio of fluid ingredients. If suited selective coatings are developed, Spreeta technology can in future also provide contamination monitoring.

The *electronic nose* (e-nose) is another example of an innovative sensor. An e-nose uses an array of chemical sensors to detect volatile analytes, and pattern recognition software to check the resulting chemical fingerprint. Most commercially available e-noses are built of metal oxides, conductive polymers or polymer composites as sensing surfaces. An overview of commercially available instruments can be found in a recent product review (Zubritsky 2000). All e-noses are subject to drift of two categories: sensor drift, which is due to the ageing or degradation of the individual sensors, and system drift, which encompasses all sensors. Volatile sulphur-containing compounds in food matrices cause additional problems as they can poison the sensing materials. The above effects cause the most common problem with e-noses, their poor reproducibility (Van Ysacker and Ellen 1998). An illustration of the application of e-noses in the dairy area was presented by classifying cheddar cheeses (Kress-Rogers 1997). In 80% of the tested samples the e-nose could distinguish among mild, medium and mature cheeses.

Several of the commercially available e-noses are based on gas-phase *quartz crystal microbalance* (QCM) sensors. QCM is a technology to measure the mass of a material deposited on an oscillating quartz crystal surface. The mass difference is a linear function of the observed change in the crystal's resonant frequency. QCMs can measure masses ranging from micrograms to fractions of a nanogram, the mass of a layer or even a partial layer of atoms. However, a practical disadvantage lies in the high sensitivity: not all that is measured is an interpretable signal. The selectivity of the sensor can sometimes be regulated by varying the surface layer. QCM is suited for applications where the sample matrix is very well defined (Henry 1996). The versatility of QCM is demonstrated by its ability to be used in liquid environments as well as gas or vacuum. Its fast response and versatility make it a promising candidate for process analysis. Early examples of applications in the liquid and gas phase of QCM-based devices are listed in D'Amico *et al.* (1997).

Contrary to the vast number of applications, the use of *biosensors* is often hampered by practical problems. Some of the most common are poor reproducibility, short lifetime, lengthy cycle times due to sluggish reaction, and the need for regeneration. In general, spectroscopic techniques are more established, and although not always matching biosensors in terms of selectivity and sensitivity, they are considerably more robust. Spectroscopic techniques can often be applied non-contacting, through a suited window.

In addition to MIR and NIR, *Raman spectrometry* is a third molecular spectroscopic technique for qualitative and quantitative analysis (Doyle 2001). Raman spectrometry is based on inelastic light scattering to measure the vibrational frequencies in components of the sample. Raman spectrometry can provide a very attractive alternative to both MIR and NIR, as it combines the functional group-specificity of MIR with the optical convenience of NIR, with considerable potential for on-line analysis. In addition, Raman spectrometry provides the advantage of no interference by water nor by extensive scattering by emulsion particles. Flexible waveguides and probes for FT-Raman spectrometers allow in-line monitoring directly in the reaction vessel or process line. Backscattering detection permits the evaluation of coatings and thin films. The widespread application of the technique has been hampered by slow instrumental development. Recently, NIR/FT-Raman has been successfully applied to the monitoring of an emulsion polymerisation reaction: qualitative and quantitative results were obtained in lab and pilot-scale systems (Charmot *et al.* 1999). Raman spectroscopy provided valuable insight at the molecular level for process development. As the instrumental and sampling equipment for on-line analysis has only recently become available, examples in food processing are expected to follow.

Nuclear magnetic resonance (NMR) spectroscopy provides quantitative information on the chemical composition of a sample. NMR is an extremely versatile, non-invasive, non-destructive technique. It can be used to gain static and dynamic information from intact, highly complex, heterogeneous materials such as foods (Belton *et al.* 1999). Contrary to many other techniques, the NMR signal is directly proportional to the amount of analyte in the sample, without the need for determining response factors. With high-resolution NMR, within a few seconds the contents of water, fat, protein, lactose and additives can be determined in a dairy product. The technique has been extended to determine the structure of food matrices. One of the widest applications of bench-top NMR spectrometers is the determination of the solid/liquid ratio of fats. Currently, NMR is considered to be a relatively slow analytical technique, and therefore high-throughput applications are scarce. A practical limitation of the throughput in NMR is the filling of the special, expensive sample tubes, which is a time-consuming operation. With a newly introduced concept, BEST-NMR (Bruker Efficient Sample Transfer, Bruker Analytik, Karlsruhe, Germany), this step can be automated using a FIA system, enabling a sample throughput up to 720 per day (Spraul *et al.* 1999). So far, the system has applications mainly in the pharmaceutical industry.

Table 13.7 Novel techniques suited for on-line analysis in the dairy process industry

Technique	Applications	Predicted year of application on-line
NMR and MRI	composition, texture, spoilage	before 2005
Raman spectrometry	composition, standardisation	before 2005
ISFETS, CHEMFETS	composition, CIP	before 2005
Colour sensor	quality control of composite products	2005 to 2010
Dedicated mass spectrometer	fermentation, flavour compounds, authenticity, off-flavours, contaminants	2005 to 2010
Ion mobility spectrometry	composition, authenticity, off-flavours, contaminants	2005 to 2010
Ion selective electrodes	composition, CIP	2005 to 2010
Electronic nose	fermentation, flavour compounds, authenticity, off-flavours, contaminants	2005 to 2010
Quartz crystal microbalance	fermentation, flavour compounds, authenticity, off-flavours, contaminants	2005 to 2010
Fast gas chromatography	fermentation, flavour compounds, authenticity, off-flavours, contaminants	2005 to 2010
(Photo)acoustic techniques	micro-organisms, flavour compounds, authenticity, off-flavours, contaminants	2005 to 2010
Biosensors	various	after 2010
Electronic tongue	fingerprint of compounds, authenticity, off-flavours, enzyme detection	after 2010
Capillary electrophoresis	composition, CIP, micro-organisms, contaminants	after 2010
Fibre optic biosensors	micro-organisms	after 2010
FT-MIR and FT-NIR	micro-organisms	after 2010
Micro total analysis concepts (μTAS)	composition, various	after 2010

Ion mobility spectrometry (IMS) offers attractive features for in-line analysis. IMS is a technique based on the analyte molecules being ionised by ion–molecule interactions in a radioactive ion source. The ions are subsequently separated according to differences in their mobility in a weak electric field at atmospheric pressure (Eiceman and Karpas 1994). The main advantage of the technique is that no vacuum is needed for its operation. This instrumental simplicity and facile operation has allowed it to be widely implemented in airports to detect narcotics and explosives. Although application examples in

process analysis are limited, the system is ideal for this purpose owing to its high sensitivity, small size and low energy consumption together with high throughput (<30 seconds per sample) and reliable operation. Applications of IMS include measurements in fermentation processes (Kotiaho *et al.* 1995), and verification of cleaning between production batches of pharmaceuticals (Walia *et al.* 2002).

Undoubtedly, many more promising examples can be found. However, it is beyond the scope of this chapter to provide an exhaustive list of possible techniques. The authors are convinced that methods using mass spectrometry, fast gas chromatography, capillary electrophoresis (maybe on-a-chip), micro total analysis concepts (TAS), ion selective electrodes, ISFETs and CHEMFETs, fibre optic biosensors, (photo)acoustic techniques and more will be used for on-line process monitoring sometime in the future.

In- and on-line techniques are essential for improving quality in production processes. The tools are available, and as shown in this chapter several of them have found application in the dairy industry. There is a distinct need for more. Table 13.7 gives an overview of promising techniques, their possible applications in the dairy field and the expected time required for fully-fledged introduction in the dairy process industry.

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