fermentation

Review

The Application of State-of-the-Art Analytic Tools (Biosensors and Spectroscopy) in Beverage and Food Fermentation Process Monitoring

Shaneel Chandra, James Chapman, Aoife Power, Jess Roberts and Daniel Cozzolino *

Agri-Chemistry Group, School of Health, Medical and Applied Sciences, Central Queensland University, Central Queensland Innovation and Research Precinct, Bruce Highway, North Rockhampton, Rockhampton, Queensland 4701, Australia; s.chandra@cqu.edu.au (S.C.); j.chapman@cqu.edu.au (J.C.); a.power@cqu.edu.au (A.P.); j.j.roberts@cqu.edu.au (J.R.)

* Correspondence: d.cozzolino@cqu.edu.au

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Abstract: The production of several agricultural products and foods are linked with fermentation. Traditional methods used to control and monitor the quality of the products and processes are based on the use of simple chemical analysis. However, these methods are time-consuming and do not provide sufficient relevant information to guarantee the chemical changes during the process. Commonly used methods applied in the agriculture and food industries to monitor fermentation are those based on simple or single-point sensors, where only one parameter is measured (e.g., temperature or density). These sensors are used several times per day and are often the only source of data available from which the conditions and rate of fermentation are monitored. In the modern food industry, an ideal method to control and monitor the fermentation process should enable a direct, rapid, precise, and accurate determination of several target compounds, with minimal to no sample preparation or reagent consumption. Here, state-of-the-art advancements in both the application of sensors and analytical tools to monitor beverage and food fermentation processes will be discussed.

Keywords: fermentation; beer; wine; food; sensors; chemometrics

1. Introduction

Food quality is one of the major concerns of the food industry [1]. In the modern food industry, prompt low-cost analysis with minimal or no sample preparation and environmentally friendly methods used to assess and monitor quality are of paramount importance among the production requirements [2–5].

The immediate continuous analysis and monitoring of critical and complex parameters such as flavour, taste, texture, spoilage, or changes in chemical composition during storage are not considered as serious options by industry, because of their cost and the slow turnaround time experienced when traditional analytical methods have been used [2–5]. Either the exploitation of novel sensing methods or the combination of state-of-the-art analysis tools with traditional analytical methods has the potential to provide robust, rapid, and inexpensive tools for the assessment of food and beverage composition and quality.

Modern instrumental techniques based on vibrational spectroscopy like visible (Vis), near-infrared (NIR), mid-infrared (MIR) and Raman spectroscopy have been widely used in many applications [6–8]. These methods or techniques present many advantages over chemical, physical, and other classic instrumental methods of analysis currently utilised in the food and beverage industries, particularly the alcoholic beverage industry [2–5]; for instance, all the listed methods are non-destructive. In addition, these techniques boast high specificity and sensitivity; MIR spectroscopy can capture the alcohol's absorption bands originating from fundamental vibration modes while NIR can help observe a variety of overtones and coupled modes, resulting in broad and strong overlapping absorption bands that allow the technique to be tuned/adapted for a wide range of bioprocesses [9].

To date, much of the research using analytical chemistry in fermentation processes has focused on the alcoholic beverage industry (e.g., wine, beer, vodka). The majority of research reported has been conducted in a manner that is best described as univariate in nature, since it has focused only on the examination of the effects (responses) of a single variable on the overall matrix [10–12]. When many of the standard statistical methods used in modern industry were developed around the 1920s, samples were considered cheap and measurements expensive [13]. The evolution of technology—particularly computer-based systems and new instrumentation—means that now the reverse is true [13,14].

These significant technological leaps have led to the development of multivariate analysis (MVA) or chemometrics in the late 1960s by a number of research groups, focused mainly in the fields of analytical, physical, and organic chemistry, with the aim of capitalizing on the introduction of modern instrumental methods capable of performing high-throughput sample analyses and measurements (e.g., HPLC, NMR, GC, MS and IR) [14–23].

Today, many instrumental techniques are multivariate and based on indirect measurements of the chemical and physical properties of the sample [24,25]. Therefore, modern analytical tools can be defined as systems that are integrated, by the combination of instrumental techniques and the chemometric method with the sample that allows a better understanding of the compositional changes occurring within the process that affect the quality of the sample being analysed [14,21–23].

However, current industry standards still employ traditional/classical analytical methods based on a univariate statistical analysis. These techniques fail to consider the contributions of more than one variable, which results in models that can oversimplify the analysis and fail to adequately resolve and ultimately evolve/augment/improve the processes employed. Conversely, chemometric methods provide the means to move beyond the univariate dimension [14,21,23] while still employing traditional analytic instruments. In many cases, the application of chemometrics can reveal constituents that despite their importance to the process as a whole are ignored/unobserved by these traditional methods, as a consequence of the various interferences and interactions of the components of the sample being analysed [26].

Here, state-of-the-art advancements in both the application of sensors and analytical tools to monitor beverage and food fermentation processes will be discussed. We will provide an overview and examples of the application of both individual and novel online sensing methodologies and the combined utilisation of chemometric techniques with instrumental methods as tools to measure and monitor the composition of different fermentation processes. The majority of examples given here focus on the use of spectroscopic (NIR and MIR spectroscopy) techniques and their application in the production of alcoholic beverages.

Background

Considering the scale of the impact of foodborne illness globally (food-associated illnesses in the United States contribute to approximately 9.4 million episodes, 55,961 hospitalisations, and 1351 deaths annually [27]), it is unsurprising that increasing public and regulatory awareness regarding food quality and food safety has driven considerable research into the development of multiple sensors and sensing platforms within the food and beverage industries.

The highly competitive and innovative modern fermentation industry is an excellent illustration of the impact of this research push, exploiting novel technologies for food fermentation to better meet both the industry demand for energy efficient processes and regulatory standards for higher-quality products [28,29]. Multiple novel processing and monitoring technologies including ultrasound and electrochemical (conductive) biosensors [30] have been exploited to enhance the productivity and process efficiency of food fermentation.

2. Data Mining and Analysis

2.1. Univariate Analysis Limitations

Despite the continuous evolution of sensing platforms and analytical devices, in an ongoing effort to perform greater (more sensitive/selective) analysis and simultaneous detection of multiple analytes, the simple evaluation of data in a monocular fashion is not sufficient to adequately monitor the complexity of bioprocesses such as fermentation. This classical approach has led to the development of mathematical protocols for data mining such as partial least squares (PLS) to better equip the industry to ensure that quality standards are maintained.

2.2. Chemometrics

Most of the effort and time dedicated to R&D of the application of rapid instrumental methods and chemometrics in the alcoholic beverage industry was related to calibration development, where the primary objectives of these applications were related to cost reduction and improved turnaround time in the laboratory during routine analysis [3,4,14]. In most of these applications the main issues were—and still are—identified to be associated with calibration development, such as sample selection (e.g., number and type of samples, sampling), presentation to the instrument (e.g., path length, transmission, type of cuvette), reference analysis (accuracy and precision), and algorithm selection including multiple linear regression (MLR) or PLS [16–20].

The selection of samples used during calibration development is incredibly important [31–35] in the development of models that will be used to monitor a process. The development of such models involves the selection of series of samples, which ideally should encompass all possible sources of physical and chemical variability in the samples to be subsequently predicted [31–35]. In this process, the whole data set or population of available samples is split into subsets called the calibration (used to develop the model) and validation sets [31–35].

Calibration has been defined as a process by which the mathematical relationships between the values provided by a measuring instrument or system and those known for the measured material object are established [19,33,36–39]. The mathematical expression relating the response of a procedure for known concentrations of an analyte is known as the calibration curve [40] or calibration model [41]. Calibration curve construction generally involves least square regression (LSR) of absorbance (true or apparent) values for a known standard versus analyte concentrations [42]. Unfortunately, issues can occur in real-world applications, as the data achieved can be subject to noise, which may result in the variables observed not being fully correlated. It is possible that if a reasonable degree of correlation is observed between variables, an unstable inverted matrix is achieved [15,19,33,36–39,43–48].

As instrumental methods are a relative technique, the samples used for calibration must be previously analysed using reference methods with adequate accuracy and precision [49]. Such analysis requires a simple yet sturdy model that is capable of maintaining its predictive capability over a prolonged period, coupled with instrumentation that is similarly robust in terms of operational lifetime. The capability of the calibration model to successfully predict unknown samples (i.e., samples not present in the calibration set used to construct the model) must also be assessed; this is done by applying the model to a small number of samples for which the models target property for prediction is defined [3,33,50–55]. Once the model's results are comparable with those of the reference values, the model can be considered to be accurate and useful for determining that target property in the future analysis of unknown samples. An assessment of the model's accuracy is essential to avoid overfitting; consequently, different validation procedures should be applied, as a calibration model without validation is nonsense. In feasibility studies, cross-validation is a practical method to demonstrate that the instrumental method can predict something; however, the predictive ability of the method needs to be demonstrated using an independent validation set [3,33,50–58].

3. Applications

3.1. Biosensors

Biosensor devices have emerged as one of the first relevant diagnostic techniques for food, clinical, and environmental monitoring due to their rapidity, specificity, ease of mass fabrication, economics, and field applicability. These attributes are particularly attractive, as many scientists consider that while the traditional analytical techniques for in-process fermentation monitoring (spectrophotometric and chromatographic techniques) are widely used, they tend to be expensive, time-consuming, laborious, and often require sample pre-treatment [59]. Here, biosensors bring their powerful attribute of specificity, which is derived from a range of interactions that include antigen/antibody, enzyme/substrate/cofactor, receptor/ligand, chemical interactions, and nucleic acid hybridisation in combination with a range of transducers [60,61].

Malic acid is a C4-dicarboxylic acid and is used predominantly in the food and beverage industries as an acidulant and taste enhancer/modifier—particularly in combination with artificial sweeteners [62]. Malic acid is also found in wines, where monitoring the malolactic fermentation is an essential step to improve the quality of red wines. This refers to the microbial conversion of L-malic acid to L-lactic acid in grape musts or wine by malolactic fermentation bacteria, which reduces the acidity of wines [63,64]. Thus, monitoring the malolactic fermentation process is an important aspect of wine production. A decade ago, biosensors for direct determination of D(−)L (+) lactic acid and of L(−) malic acid in wines were presented by Mazzei et al. [65]. The multi-enzymatic biosensors enabled the selective determination of the three analytes using L(+) lactate oxidase, D(−) lactate dehydrogenase, and horseradish peroxidase together with coupling the enzymes L(−) malic dehydrogenase (L-MDH) and horseradish peroxidase (HRP) [65]. More recently, the potential of a miniaturised amperometric bienzymatic biosensor using thin-film gold electrodes with malate dehydrogenase and diaphorase enzymes together with nicotinamide adenine dinucleotide cofactor as the selective receptor and an adequate redox mediator has been reported by Giménez-Gómez et al. [66]. The authors have described their biosensor as presenting excellent working stability, retaining above 90% of its sensitivity after 37 days, thus enabling the monitoring of the malolactic fermentation of three red wines. The results showed excellent agreement with the standard colourimetric method. Furthermore, a new biosensor for measuring L-malic acid levels, constructed using gold film co-immobilized with the malate dehydrogenase and diaphorase enzymes together with the redox mediator tetrathiafulvalene on a stainless steel disk electrode has been proposed. Its application as a simple, rapid, and field-based tool for routine wine and fruit control has been reported [67]. Other work on malic acid determination using biosensors has relied on screen-printed carbon electrodes modified with gold nanoparticles, tetrathiafulvalene, and malate quinone oxidoreductase enzyme. The biosensor has been applied to the determination of malic acid in white, rose, and red wine samples [68]. Similarly, Molinero-Abad and co-workers exploited nano-modified screen-printed electrodes to achieve the selective and simultaneous detection of malic and gluconic acids in wine [69]. Shkotova et al. have recently proposed a multi-biosensor based on lactate and glucose oxidases developed for the determination of lactate and glucose in wine with high reproducibility and storage stability of the multi-biosensor [70]. Paper-based and screen-printed biosensors for the detection of ethanol in beer samples have been reported [71]. The authors report the quantification of ethanol at 10 mM (0.058 $\%_{vol}$), with a sensitivity of 9.13 μA/mM cm^2 (1574 μA/ $\%_{vol}$ cm^2), and boast a detection limit equal to 0.52 mM (0.003$\%_{vol}$).

The optimisation of a biosensor with surface plasmon resonance detection allows for the added determination of an allergen protein, lysozyme, with high accuracy, good sensitivity, and detection limits of 2.4 nM for spiked red and white wines [64]. Here, quantitative recovery factors higher than 88% for wine lysozyme were achieved. The use of additional surface enhanced chemical techniques expands the ability to detect new or emerging analytes in the fermentation process.

3.2. Ultrasound

The application of high- and low-frequency ultrasound has been exploited for some time in the fermentation industry. Whereas low-frequency ultrasound has been used for various means including pasteurisation of dairy products, the maturation of wines, and ultimately the enhancement of fermentation rates [72–74], our interest will focus on the application of high-frequency ultrasound as a non-destructive method for fermentation process monitoring [75]. The technique works off the premise that the velocity of an ultrasonic wave travelling through a fermentation tank can infer the concentration of alcohol and sugars during a fermentation process as a consequence of the changing density of the solution [76–78].

Several studies, including work by Nakamura [79], Salazar [75], and Resa [77], among others, clearly demonstrate how the application of high-frequency ultrasonic waves can characterise fermentation processes in real-time. Moreover, similar studies have shown that the methodology can be exploited in both homogenous and multi-phase systems. Such an approach is made even more appealing to an industry at large, as it is has been widely demonstrated that acoustic-based measurement systems are non-invasive, hygienic, precise, rapid, low-cost, and suitable for automation [75,80].

3.3. Spectroscopy

The majority of the applications of instrumental methods (e.g., NIR spectroscopy) in the beverage industry have focused on the measurement of ethanol (e.g., see works by Grassi et al. [81], Giovenzana et al. [82], and Iñón et al. [83]). Currently, there are a number of dedicated NIR-based alcohol analysers, and this technique has become a routine analytical method for the determination of alcohol content in wine and other alcoholic beverages [84–88]. The use of NIR spectroscopy has also been reported for the measurement of several chemical parameters in wine and other alcoholic beverages, such as volatile acidity [89,90], organic acids [91–93], glycerol [94,95], reducing sugars [96,97], sulphur dioxide [98], and minerals [99,100]. With more recent developments in instrument design and sample presentation modes such as short path-length transmission cells and attenuated total reflectance modules (ATR), the use of both Fourier transformed mid-infrared (FT-MIR or FTIR) and NIR spectroscopy have been reported by several authors and implemented for the routine analysis of a large number of beer and wine parameters such as alcohol content [101,102], volatile acidity [103], dry extract [104], sugars and acids [105], glycerol [106], anthocyanins [107], polyphenols [108], and amino-nitrogen [109], among others.

Similarly, Kutyla-Olesiuk et al. demonstrated that biosensors coupled with chemometric analysis can be applied to wine fermentation monitoring and maturation processes [110]. The authors combined potentiometric and voltammetric sensors, coupled with a PCA technique. The resulting "hybrid electronic tongue" was used to assess the impact on storage on the fermentation process and also proved useful for the detection of chemical/microbiological contaminants. The chemometric analysis allowed the identification of the various fermentation stages and had the capability to differentiate between aged samples stored under different conditions (standard storage conditions and modified conditions that caused deterioration of the sample quality).

The authors concluded that the hybrid electronic tongue based on multiple electrochemical sensors could be exploited for wine fermentation process monitoring [110]. Examples of the application of state-of-the-art technologies to monitor fermentation are presented in Table 1.

Table 1. Examples of the application of state-of-the-art technologies to monitor fermentation.

Chemicals Monitored	Fermentation Process	Techniques	Authors
Volatile flavour chemicals—acetates, ethyl esters, C_4–C_8 fatty acids	Grapes during yeast fermentation	Gas chromatography	Stashenko et al. [111]
Short chain monocarboxylic and dicarboxylic acids-butyl esters of volatile (C_1–C_7) and nonvolatile (lactic, succinic, and fumaric) acids	Microbial fermentation	Gas chromatography flame ionisation detection.	Salanitro and Muirhead [112]
Proteases and ethanol, ethylene glycol, glucose, isopropanol, and mannitol	Fermented soybean foods	Electrophoresis and ^{1}H NMR methods	Liu et al. [113]
Malolactic fermentation compounds	Wine fermentation	Pulse-echo ultrasound of 1 MHz measurement using sound velocity	Resa et al. [77]
Oligosaccharides, improved fermentation rates, accelerated lactose hydrolysis	Probiotic fermented milk	20 kHz low-frequency ultrasound technique	Nguyen et al. [73]
Total sugar content, alcohol, and pH	Rice Wine	UV-Vis and NIR spectroscopy coupled with multivariate analysis	Ouyang et al. [84]
Tyramine	Cheese	Electrochemical enzyme biosensor based on calcium phosphate	Sanchez-Paniagua Lopez et al. [114]
L-Lactic acid	Wine	Electrochemical bienzymatic	Gimenez-Gomez et al. [115]

4. Conclusions

Considering that quality can be defined as fitness for purpose, the first step in the development of applications to measure composition in a given material is to determine the exact objective of the analysis. A synopsis of these techniques has been shown in Table 1. In addition, the sampling protocol and the sample itself are two of the main factors that will determine the successful development and further application of an instrumental analytical method.

Calibration development can be considered as a complex process that implies the understanding of a system constituted by the participation of the sample, the instrumental method, the multivariate data method (algorithm, pre-processing), and the requirements imposed by the final user. In this way, one of the main challenges in the application of these approaches is still related to the interpretation of the complex models/calibrations obtained.

The advent of biosensors, aided by the cheaper construction of the working electrode and several customization possibilities has also featured in recent monitoring of fermentation processes of wine. Considerable successes have been attained to this end for routine screening of typical wine constituents such as anthocyanins, phenolics, and antioxidants. The challenges of isolating matrix interference remain, but biosensing's reliance on the highly-specific binding of analyte to the working electrode may yield further development and perhaps lead to the future of alcoholic beverage characterization and quality control.

Finally, the lack of formal education (academia, universities) in the use or application of instrumental techniques combined with chemometrics to quantitatively measure composition is still one of the main obstacles in the development and adoption of these methods and techniques by the industry.

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