



## TA Instruments – Application Note

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### **Food Spoilage and Heat Generation**

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Food quality is affected by a number of factors such as physiological ageing of biological tissue, loss of nutritional value as vitamins degrade, and microbial growth. Microbial growth is recognized as a common cause for spoilage of food with consequences such as bad taste and food poisoning. The types of organisms involved are typically mould, yeast, and bacteria. While yeast and mould may appear in foods such as fruits and vegetables, bacterial infection is a problem in processing and storage of less acidic food stuffs like meat and fish as well as some vegetables that have been minimally processed, e.g. fresh carrot juice. As will be shown in the examples collected for this application note, calorimetric techniques can be used as a general monitor to quickly assess the processes responsible for food degradation.

Processes causing changes in matter, including the above mentioned are generally accompanied by an exchange of heat with its surroundings. The faster the rate of a process, the higher the heat generation rate. Hence, heat measurements have been proposed as a way of gaining insight into the processes responsible for food spoilage. Heat measurements can be performed using calorimetric instruments that measure the heat generation rate of a sample. Typically, these types of events are monitored continuously as a function of time while the measured specimen is kept at a constant temperature. Since heat generation is non-specific, all processes causing changes in a sample are measured, e.g. growth of microbes, or metabolic changes, such as enzymatic browning of tissue.

The origin of heat production in biological systems has been discussed extensively in the literature; see for instance Gustafsson (1991) or Battley (1987) for a review. It is interesting to note that one of the first ever calorimetric measurements was conducted on a living organism. Lavoisier and Laplace (1780) measured the heat production of a whole living animal which led to the conclusion that respiration is merely a combustion process: “*La respiration est donc une combustion, à la vérité fort lente*” as they stated in their famous paper. In these experiments calorimetry was used as an analytical tool to gain insight into the respiration processes. Their calorimeter was as simple as it was ingenious. The specie to be measured was kept in an enclosure surrounded by a jacket filled with ice and the calorimeter was kept just below the freezing point of water, therefore measurements could only be made in the winter. The heat



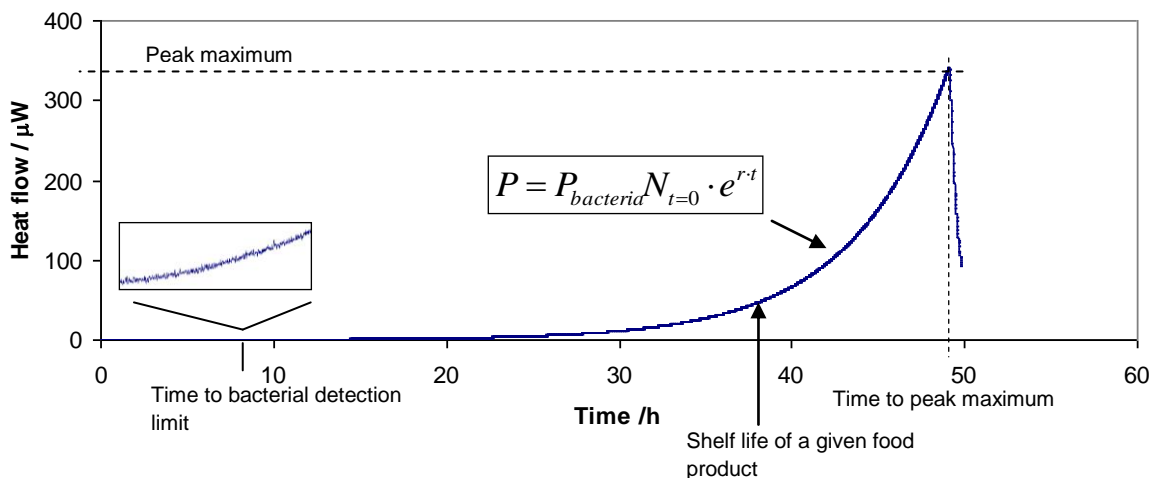
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given off by the animal melted part of the ice and the liquid water was collected and weighed. The amount of water produced from the melting ice gave a direct measure of the heat produced by the animal.

With the development of highly flexible, ultrasensitive calorimetric instruments and the refinement of calorimetric techniques over the last few decades, increased attention has been focused toward the use of this technique as a process monitor to get kinetic as well as analytical information from specimens. Today, accurate, reproducible studies can be conducted at different (constant) temperatures, with the possibility of modified atmospheres surrounding the sample and no restriction as to whether the sample is a liquid, semi-solid or solid.

### Characterization of a calorimetric bacterial growth curve

A number of characteristics of a growing bacterial culture can be identified in the heat flow profile, figure 1. In addition to a quantitative characterization of the bacterial culture, the exponentially increasing heat flow curve gives a qualitative yes or no answer as to whether the measured sample is infected or not.



**Figure 1. Characterization of a bacterial growth curve as measured in terms of heat flow. In this simulated example the growth rate constant was set to  $0.18 \text{ h}^{-1}$  and the total initial number of bacteria was  $10^4$ .**

The time required to detect bacterial presence in an unknown sample is another parameter of interest as it determines how fast a bacterial infection can be assessed. This time is dependent on a number of factors including the time of lag phase, the detection limit of the calorimeter, the initial number of bacteria present and, naturally, the growth rate.



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Bacterial growth can be modeled by a first order growth rate equation (equation 1).

$$\frac{dN}{dt} = r \cdot N \quad (1)$$

Where  $r$  is the growth rate constant and  $N$  is the population density either in terms of biomass or in terms of the number of viable units. Integrating equation 1 between the limits  $t=0$  and an arbitrary time  $t$  leads us to equation 2.

$$N = N_{t=0}e^{r \cdot t} \quad (2)$$

Averaged over the time of a reproductive cycle, a single bacterium has been said to produce heat in the range 1-3 picojoule per second (pWatt), depending of the bacterial specie and the growth medium, James (1987). If we designate this constant the subscript,  $P_{bacterium}$ , the heat flow of a growing population of bacteria is given by equation 3.

$$P = P_{bacterium} N_{t=0} e^{r \cdot t} \quad (3)$$

Thus, the experimental growth curve can easily be identified with equation 3 to give the bacterial growth constant and the mean generation time,  $mgt$ , or the “doubling time”. In addition to these growth parameters, one can obtain a rough estimate of the number of bacteria in the sample at time zero.

Equations 1 through 3 normally model bacterial growth well as long as there are no external factors limiting the exponential growth phase. Naturally, this model does not take into account the various growth limiting factors that may appear at some point during growth, for instance as the oxygen or energy sources are depleted. In such cases, more complex growth models need to be considered.

The shelf life of a given food product at the relevant storage conditions can be characterized with respect to a specific point in time when the product has given of a certain amount of heat relative when compared to a defined initial state of the product. Such an estimation of shelf life, in terms of evolved heat, is most accurately determined on an empirical basis.

### **Meat and Fish**

The potential of using calorimetry as a way of getting an assessment of spoilage of fish and meat was investigated by Gram and Sögaard (1985). Suspensions for calorimetric measurements were made by homogenizing meat or fish samples together with a nutrient broth.



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The time taken to reach the maximum peak in the heat flow–time curve from the start of the measurement was defined as the calorimetric measurable, see Figure 1. In the case of these fish samples, this measurable was compared with the results from the classical culture plate count method and also sensory quality assessment.

A significant linear correlation was found between the calorimetric measurable and the bacterial plate counting method, as well as with the sensory quality assessment of the food samples.

### **Minimally processed vegetables and fruits**

Minimally processed fruits and vegetables are products with, as much as possible, maintained taste and nutritional contents compared to the fresh product. Gómez Galinda et. al. (2005) proposed isothermal calorimetry as a way to get fast predictions of quality during the production and storage of such products.

More specifically, the metabolic processes related to the tissue wounding after cutting was found to be separated in time from the subsequent bacterial spoilage, giving the opportunity to study both these processes in one and the same measurement.

In another study, Gómez et al (2004) used calorimetry to study the effect of blanching of carrots in the frozen vegetable industry. The heat rate measurements were used to quantify the decrease in cell viability in carrot tissue during processing, in order to evaluate tissue damage at different stages of the blanching process.

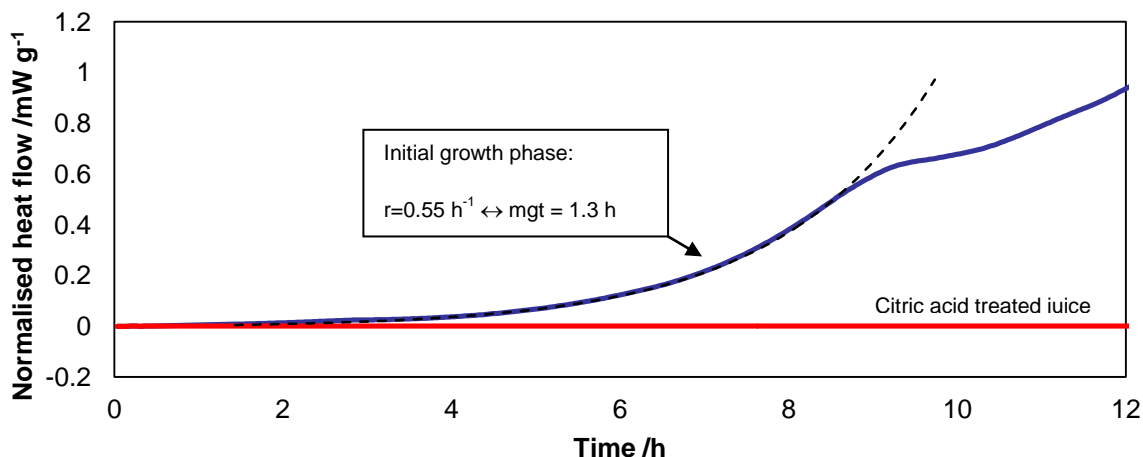
### **Fruit Juices**

Alklint et al (2003) proposed the use of heat conduction calorimetry for shelf life studies of fruit juices and studied the effect of pH, acids and different juice mixtures on the shelf life of carrot juice. They defined the shelf life of the juice as the time taken to reach 0.1 mW/g of juice in the bacterial growth phase.

Figure 2 below shows the heat production rate of a commercial carrot juice (Bråmhult, Sweden) collected on a TAM III calorimeter available from TA Instruments. According to the manufacturer, the juice had been mildly heated as a way of prolonging shelf life with as much preserved original taste as possible. The blue curve represents the heat production rate of the pure juice and the red curve is the same juice spiked with a small amount of citric acid. All samples were evaluated for heat flow at 25°C.



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**Figure 2. Heat flow - time curve of a commercial carrot juice measured in hermetically sealed 4-ml glass vials. Blue curve: Untreated carrot juice. Red curve: Carrot juice spiked with citric acid. Measurements were performed on a TAM III at the TA Instruments Application laboratory in Sollentuna, Sweden.**

As expected and as the results suggest, small amounts of citric acid function as a preservative. No significant change in the heat flow of the juice was observed during the time of the measurement when the citric acid was added.

Other studies employing isothermal calorimetry for studies related to shelf life in food stuffs include those of Riva et al (2001), who correlated detected heat flow with the shelf life of fresh milk and with carrot convenient salads, Iversen et al (1989) correlating heat flow in sliced pineapple and Berridge et al (1974) studying bacterial growth in milk.

## Conclusions

As implied in this short note, heat production in food stuffs is generally a result of processes that degrade the quality of the food. Hence, the potential uses of calorimetric techniques as evaluation tools in food production and development and in general problems associated with food shelf life are well established and growing. The studies cited in this application note have all shown a significant correlation between shelf life of food stuffs and the heat flow associated with degradation processes.

Only within the last decade has calorimetry made the necessary technical improvements to increase sample throughput and lower the price per measuring unit for this universal heat detection technique to be regarded as a realistic analysis tool for food quality control and/or shelf



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life studies. The development of very sensitive and accurate calorimetry instruments such as the TAM III isothermal calorimetry instrument with its high heat flow sensitivity and wide variety of calorimeters available, has allowed the unique power of calorimetry data to become decision making criteria in a wide range of different industrial activities. With calorimetric sensitivity routinely available at the high nanowatt to low microwatt levels and the sample throughput capabilities available up to 48 samples simultaneously, calorimetry has become a realistic option for fast assessments of the often complex biological processes responsible for the degradation of food.

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