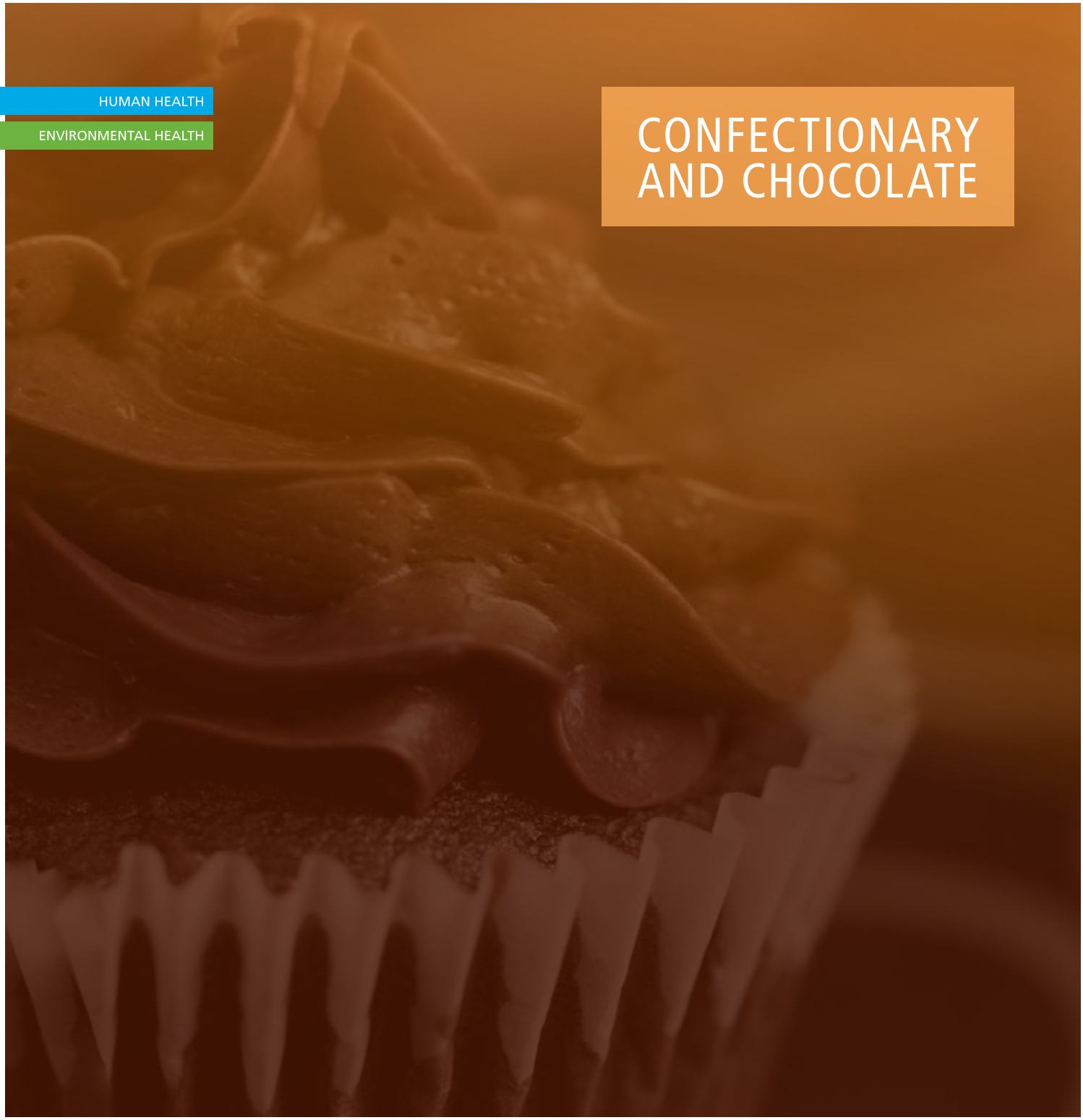
HUMAN HEALTH

ENVIRONMENTAL HEALTH

# CONFECTIONARY AND CHOCOLATE



Confectionary and Chocolate Compendium

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# CONFECTIONARY AND CHOCOLATE

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APPLICATION BRIEF

FT-NIR Spectrometry

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# Rapid Testing for Adulteration of Yogurt Candy using Near-infrared Spectroscopy and Adulterant Screen

## Introduction

Melamine is an adulterant commonly found in milk, as it can increase the nitrogen content. Therefore, its apparent protein content, resulting in a better market price. Melamine adulteration can be fatal, as was highlighted in 2008 when six infants died due to melamine adulteration in milk powder and thousands were sickened in China. Consequently, there have been stricter regulations globally and improved testing methods including the use of the PerkinElmer DairyGuard™ instrument for powdered milk testing.

However, cases of melamine adulteration are still appearing in other products. This year in Guangdong Province, China, 25 tons of yogurt candy tablets were seized as they were found to contain melamine. What follows is a description of a near-infrared (NIR) testing method of yogurt candy for melamine adulteration.

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## Experiment

Four different flavors of commercially-available yogurt candy were purchased (peach, cherry, blueberry, and tropical). The samples of yogurt candy for testing were ground into a powder and placed in a Petri dish. Spectra were collected on a PerkinElmer Frontier™ NIR spectrometer in reflectance using the sample cup spinner on the NIRA II sampling accessory at a spectral resolution of 16 $cm^{-1}$ using 32 scans. Several replicate samples of the yogurt candies and the spectrum of pure melamine were added into Adulterant Screen™ as "Material" and "Adulterant" spectra, respectively. A sample of a mixture of the different yogurt candies was prepared using equal amounts of each flavor. The NIR spectra of melamine and the mixture of yogurt candies are shown in Figure 1.

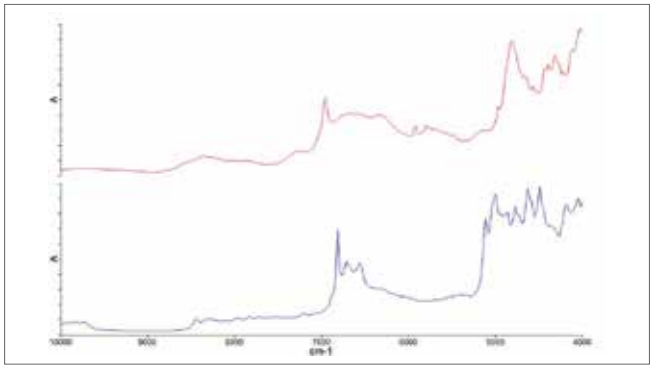

*Figure 1.* NIR spectra of melamine (blue) and mixture of yogurt candies (red).

The mixture of yogurt candies was spiked with melamine at 9.8%, 1% and 0.2% w/w levels and the spectra measured.

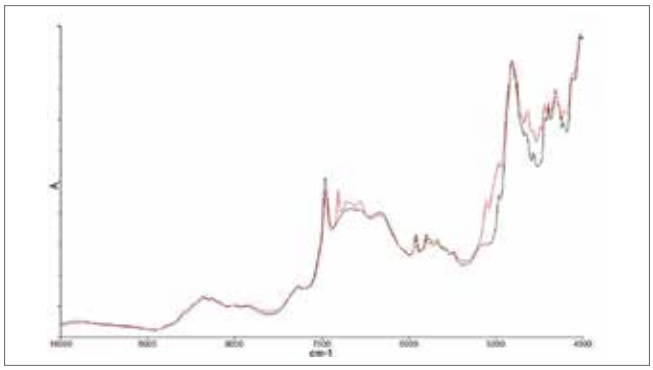

*Figure 2.* Spectra of yogurt sample with 9.8% melamine (red) and yogurt (black).

Figure 2 shows spectral features related to melamine present in the yogurt sample containing 9.8% melamine. The Adulterant Screen method was used to predict the presence and level of melamine in the samples, shown in Table 1. The close correlation between the measured amount and the predicted amount of melamine in the yogurt candy indicates that this Adulterant Screen method can be used to accurately predict the level of adulterant contamination.

*Table 1.* Adulterant Screen results for spiked samples.

| Sample Name | Adulterant | Estimated Level (%) | Confidence |
|---|---|---|---|
| 0.2% Melamine | Melamine | 0.275 | Likely |
| 1% Melamine | Melamine | 1.358 | Likely |
| 9.8% Melamine | Melamine | 10.004 | Likely |

The Adulterant Screen method generates residual spectra from the analysis; showing the residual spectrum before adding in the adulterant spectrum, and the residual spectrum after adding in the adulterant spectrum. The spectral bands in the residual spectrum should decrease with the addition of the adulterant. Any remaining residual features are not accounted for by the method. Adulterant Screen allows for multiple adulterants to be detected and their concentrations estimated. The residual spectra from the analysis of the 0.2% melamine sample are shown in Figure 3.

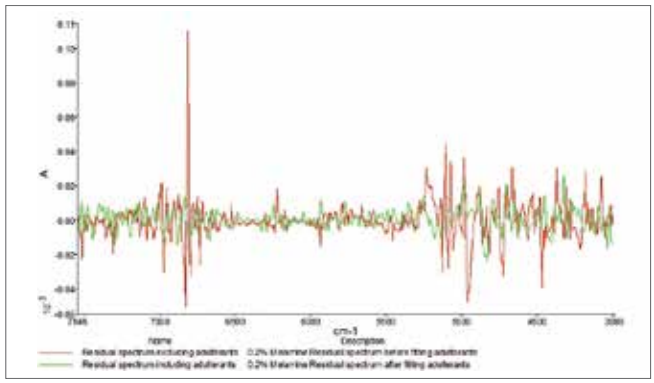

*Figure 3.* Residual spectra from Adulterant Screen for the 0.2% Melamine sample. Excluding adulterants (red), Including adulterants (green).

The addition of melamine into the Adulterant Screen model significantly reduces the residual spectrum, indicating the presence of melamine as an adulterant.

## Conclusion

NIR spectroscopy with Adulterant Screen is a quick and simple method for detecting melamine adulteration in yogurt candy. The software is able to accurately predict the concentration level of melamine and identify any new adulterants. Rapid deployment of the method can be achieved for yogurt candy and similar products.

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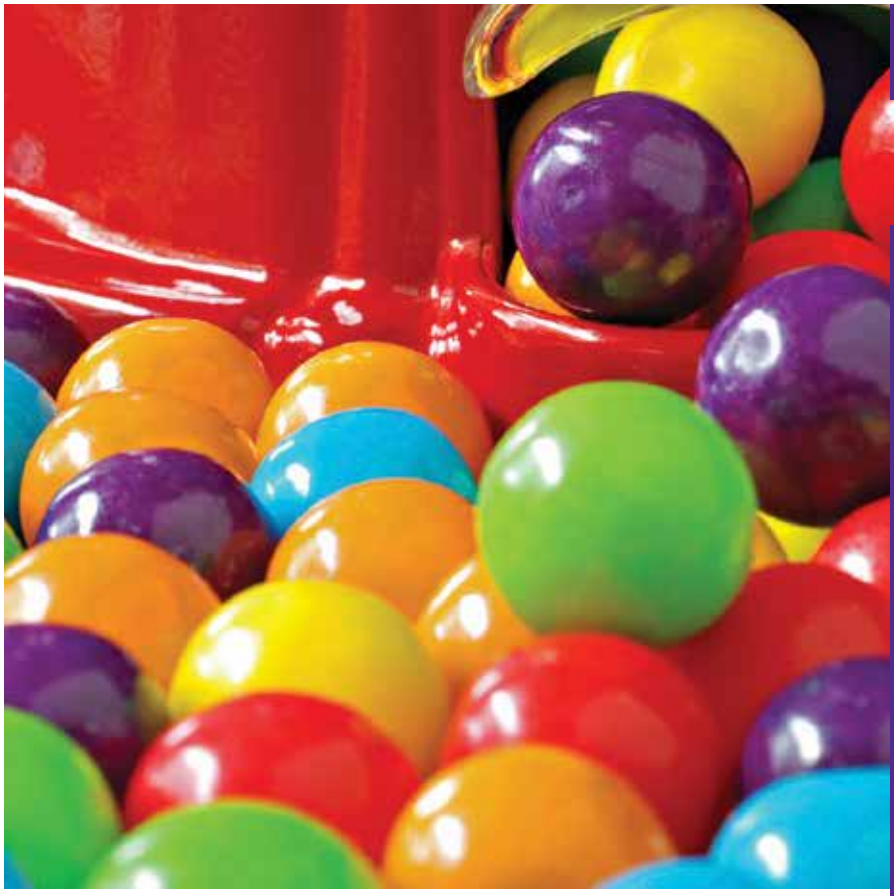

APPLICATION NOTE

Thermal Analysis

*PerkinElmer Pyris 1 TGA*

# Better Quantitative Analysis of Chewing Gum with AutoStepwise TGA

## Introduction

The gum base of chewing gums is a complex mixture of a number of components, including: PVAC (poly vinyl acetate), natural elastomers, glycerin, softening agents, and carbonates. In addition, chewing gum contains flavoring agents, sucrose or other sweeteners and colorants. These various components provide the desired textural and viscoelastic properties to the chewing gum. The correct combination of the gum formulation provides the end characteristics to the chewing gum, including: stickiness, softness and chewability.

It is desired to have a means of characterizing the composition of chewing gum for quality assurance purposes. One of the best means of detecting components in a complex formulation, such as chewing gum and other foods, is with thermogravimetric analysis (TGA).

TGA is a well-established method for the characterization of materials. The technique measures sample mass as a function of temperature or time and provides useful decomposition temperature information.

However, for complex formulations or multi-component materials, standard (constant heating) TGA may not possess the necessary resolution for separating out the weight losses associated with the various components. What is required is a TGA, which can provide enhanced resolution or separation using AutoStepwise isothermal methods.

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## AutoStepwise TGA

With AutoStepwise TGA, the instrument heats a sample at a constant rate until a significant weight loss event is encountered. Using a feedback approach, the TGA automatically holds the sample under isothermal conditions until the rate of weight loss (dm/dt) becomes small, meaning that the given component has essentially completed its given degradation. The TGA instrument will then automatically resume heating, at a constant rate, until the next significant weight loss event. By this process, the AutoStepwise TGA method is able to nicely resolve closely occurring decomposition events and provide better quantitative analysis of a sample.

For the best possible sample characterization for complex materials or formulations, it is recommended to have a TGA instrument with AutoStepwise capability, such as the PerkinElmer® Pyris™ 1 TGA.

## Pyris 1 TGA

The high performance Pyris 1 TGA offers many important features, including:

- Low mass, ultra-light balance for ultra-low noise and outstanding sensitivity
- Iris shutter assembly to isolate balance chamber from sample/furnace
- Automated ion stream to eliminate troublesome static effects
- High performance heat/sensor furnace technology
- Reduced furnace volume for more efficient switching of purge gases and elimination of oxygen during pyrolysis
- 20 position, autosampler accessory for reliable, unattended operation
- Accupik accessory for better handling of volatile samples without uncontrolled and unmeasured weight loss while waiting to run
- Ability to operate under vacuum conditions
- AutoStepwise isothermal analysis for the best possible separation of overlapping decomposition events.

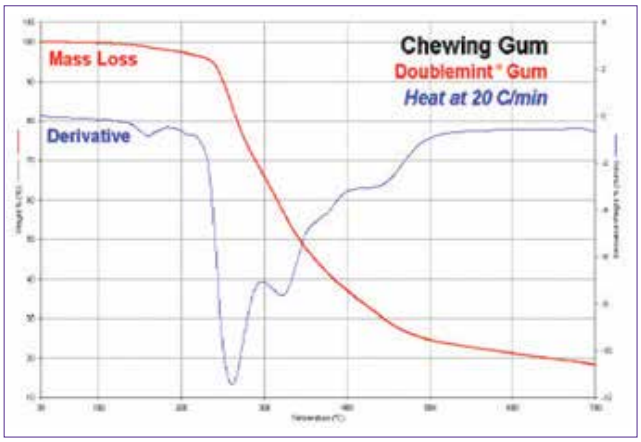


*Figure 1.* Standard TGA results for Doublemint® chewing gum sample.

## Experimental

In this study, the decomposition properties of two chewing gums (Doublemint® and Dentyne®) were studied using the TGA AutoStepwise approach. The following experimental conditions were used to analyze the chewing gums.

| Experimental Conditions | |
|---|---|
| Instrument | Pyris 1 TGA |
| Mode of operation | AutoStepwise isothermal |
| Heating rate | 50 °C/min |
| Entrance threshold value | 4%/min |
| Exit threshold value | 0.5%/min |
| Sample mass | 15 mg |
| Purge gas | Nitrogen |
| Temperature range | 25 to 900 °C |

The TGA instrument was calibrated for temperature response using the Curie points of nickel and iron.

## Results

Displayed in Figure 1 are the TGA results obtained on the Doublemint® chewing gum sample using the standard TGA approach of constant heating (i.e., non-AutoStepwise). The gum was heated, as received, at a rate of 20 °C/min between room temperature and 900 °C.

The plot shows the percent mass as a function of sample temperature along with the rate of mass loss or derivative signal (d%/dt).

The sample yields about 75% of its original mass between 200 and 500 °C. Although the weight loss curve appears to yield a single continuous mass loss event, there are actual several overlapping transitions. This is most clearly seen in the derivative signal and the various peaks reflect the decomposition of the different components in the chewing gum sample. With standard TGA, it is difficult to resolve or quantify the amounts of each of the components due to the severe overlapping of the transitions.

The Doublemint® gum was analyzed using the AutoStepwise approach and these results are presented in Figure 2. The AutoStepwise method provides much better resolution as these results demonstrate. Five distinct mass loss events are obtained and can be quantitatively analyzed, as is shown in Figure 2.

The following results were obtained for the Doublemint® sample using the AutoStepwise approach with the Pyris 1 TGA:

| Temperature | % Mass Loss |
|---|---|
| 154 °C | 2.1% |
| 268 °C | 38.5% |
| 336 °C | 18.7 % |
| 418 °C | 12.5% |
| 470 °C | 5.6% |

The AutoStepwise approach yields very good reproducibility and this may be seen in Figure 3, which shows a direct overlay of duplicate experiments performed on the Doublemint® gum sample.

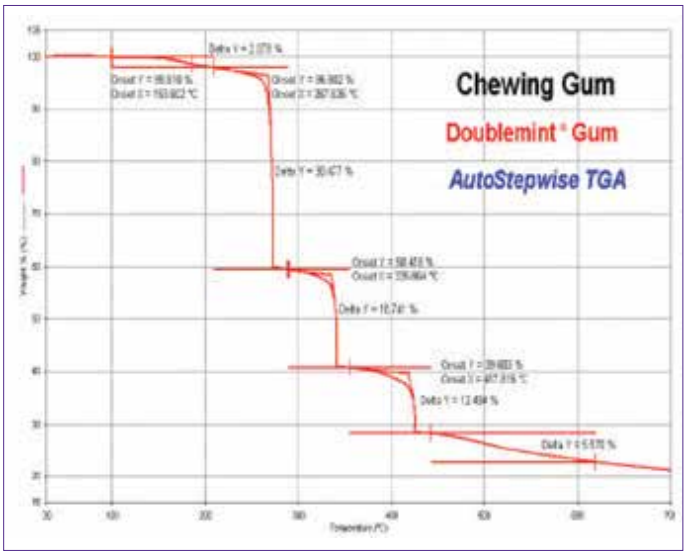


*Figure 2.* TGA AutoStepwise results obtained for Doublemint® gum sample.

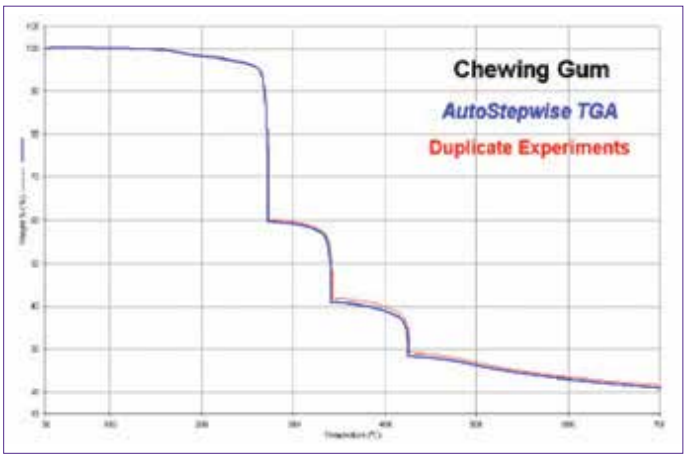


*Figure 3.* Duplicate results generated using the AutoStepwise approach for the Doublemint® gum sample.

A sample of a different chewing gum, Dentyne®, was analyzed using the AutoStepwise TGA method and these results are presented in Figure 4. The following quantitative results were obtained for the Dentyne® gum:

| Temperature | % Mass Loss |
|---|---|
| 151 °C | 1.2% |
| 270 °C | 35.8% |
| 341 °C | 17.5% |
| 419 °C | 15.4% |
| 451 °C | 5.7% |

Although the plotted results from the Dentyne® gum sample appear similar to those obtained for the Doublemint® gum, there are distinct and significant differences. These are more evident in a direct overlay plot, which is shown in Figure 5. The overlay results show that there are distinct formulation differences between the Dentyne® and Doublemint® gums.

## Summary

The PerkinElmer high performance Pyris 1 TGA instrument provides the AutoStepwise isothermal mode of analysis which yields the highest possible resolution between successive decomposition events. Complex, multi-component materials (foods, polymers, elastomers, and pharmaceuticals) are best characterized using the AutoStepwise TGA mode.

The AutoStepwise approach is time efficient as a very fast heating rate (50 °C/min) can be used in the regions between the isothermal steps. This allows samples to be analyzed relatively quickly with the highest possible resolution and the best possible quantitative analyses of results.

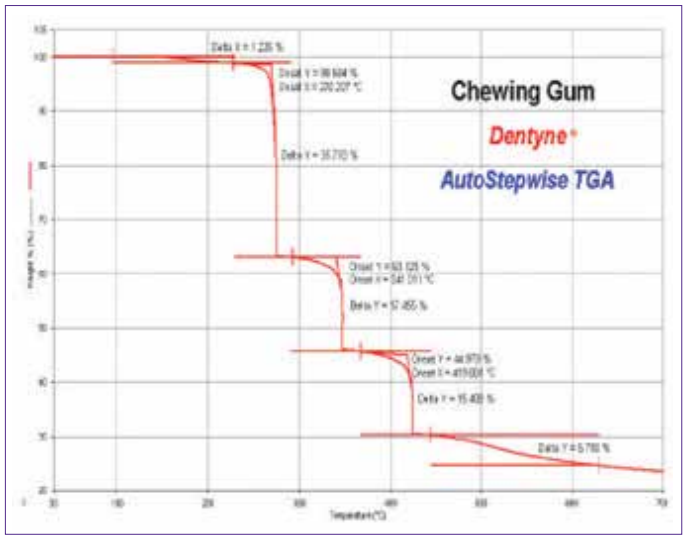


*Figure 4.* AutoStepwise TGA results obtained on Dentyne® chewing gum.

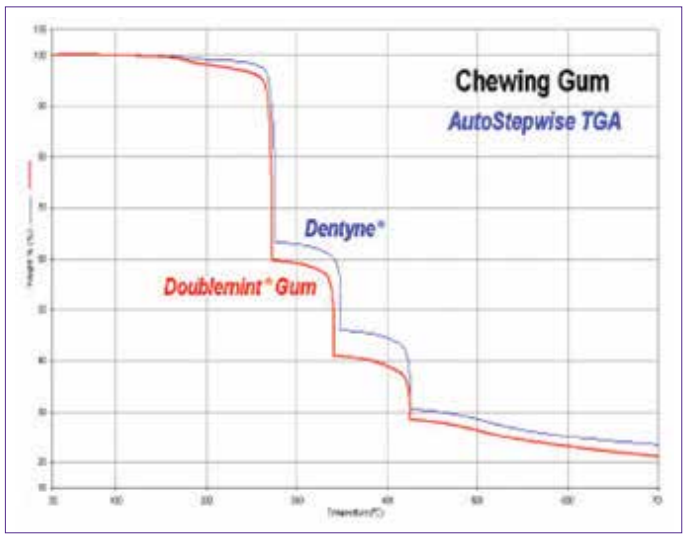


*Figure 5.* Direct comparison of AutoStepwise TGA results for Dentyne® and Doublemint® gum samples.

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APPLICATION NOTE

Thermal Analysis

# Characterization of Fats in Cookies Using Power Compensation DSC

## Introduction

Differential scanning calorimetry (DSC) is a useful technique for the characterization of food products, including:

- The gelatinization and staling (retrogradation) behavior of starches
- Polymorphism of fats such as cocoa butters and chocolate
- Effects of moisture content or absorbed moisture
- Aging effects
- Protein denaturation
- Determination of fat content or solid fat index (SFI)

The processing and handling behavior of food fats has been found to depend upon the solid-to-liquid fat ratio in the food sample. Many rheological or flow properties, and their resultant effect on the texture of the final product, stem from this fat ratio index.

The study of the fat content and the nature of the fats of foods is becoming increasingly more important due to health considerations, especially with regards to the level of solid fats, saturated fats and trans fats in food products. There is a variety of fats with different levels of solid fats available in food products. An example of this is the Oreo® Cookie where there is the regular Oreo® and the reduced fat version. There are also Oreo®-like cookies with no solid, hydrogenated fats present.

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With the current customer concerns with low fat and no-trans fat foods, an opportunity for fraud has been created by mislabeling foods that contain cheaper and less healthy fats. Fats are very complex materials and the analysis can be difficult for many reasons. Part of this complexity is fats can exist in both crystalline and amorphous forms. This can be further complicated by the presence of polymorphic melting forms of the given fat. A polymorph is an unstable melting form and this can be controlled by processing. Different polymorphic forms are sometimes desired in order to obtain a certain desired texture for the fat. For example, the fat used in chocolates, cocoa butter, has six polymorphic forms and only one of them gives the "melting in your mouth" feel to foods.

The successful analysis of fats in foods requires a DSC with high sensitivity and high resolution. The resolution performance aspect is important to be able to separate out the glass transition (Tg) and the different melting events associated with fats and possible polymorphic forms. The DSC with the best resolution and sensitivity performance available is the Power Compensation DSC from PerkinElmer.

## Power Compensation DSC

The ideal DSC for the characterization of foods and fats is the Power Compensation or double furnace DSC. The very low mass furnaces provide low thermal inertia and the fastest response time of any DSC instrument on the market. This allows for the best peak definition and separation of over-lapping peaks of any commercially available DSC. The Power Compensation DSC uses two independently controlled, ultra low mass furnaces (mass of 1 g) in the design of the DSC cell. The very low mass provides low thermal inertia and a very fast DSC response time, which is critical for high resolution.

In contrast, heat flux DSCs or Boersma DTAs, with their more massive furnace or those using a large silver block, have a more sluggish responsiveness. This translates to a higher inherent thermal inertia and a much slower DSC response time. The resolution from DSC instruments with a large mass furnace is much poorer than with the Power Compensation DSC. Some instrument companies attempt to correct for the problems caused by using a large silver block with algorithms. These algorithms try to adjust the data to account for the slower response time of that kind of DSC cell. However, there are concerns with such treatments since this alters the actual heat flow results. The Double Furnace or Power Compensation DSC provides the true sample response based on actual DSC hardware rather than mathematical manipulation of results.

In this study, the fats associated with three different fillings of cookies were assessed:

- Regular Oreo®
- Reduced fat Oreo®
- Oreo®-like cookie with no hydrogenated (solid) fats

## Experimental

The following experimental conditions were used to analyze the fillings of the three different cookies.

| Experimental Conditions | |
|---|---|
| Instrument | Pyris™ Power Compensation DSC |
| Cooling | Intracooler II |
| Sample Pan | Open aluminum pan |
| Sample Mass | Approximately 11 mg |
| Temperature Range | -60 °C to 100 °C |
| Heating Rate | 20 °C/min |
| Purge Gas | Nitrogen |

The DSC was calibrated for temperature and enthalpic responses using high purity indium metal.

## Results

Displayed in Figure 1 are the DSC results generated for the filling of the regular Oreo® cookie. The plot shows the DSC heat flow as a function of sample temperature. The sample yields a complex DSC thermograph due to the nature of the fats and polymorphic forms associated with the as-received Oreo® cookie filling. The fat undergoes melting beginning at –18.8 °C. A series of melting peaks are observed at –2.6 °C, 16.1, 28.0, 35.1 and 44.5 °C for the fats in the filling. The complex melting spectrum reflects the occurrence of poly-morphic forms due to the particular processing conditions used to produce the Oreo® filling. The total heat of melting of the cookie filling is found to be 28.2 J/g. The DSC results show that a significant amount of the fat in the Oreo® cookie filling melts above room temperature and this behavior is due to the hydrogenated fats in the filling.

The high resolution response of the Pyris™ Power

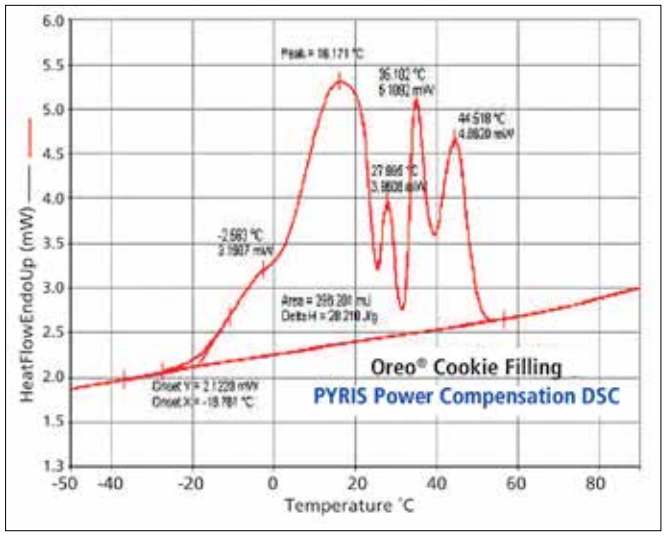


*Figure 1.* DSC results for regular Oreo® cookie filling.

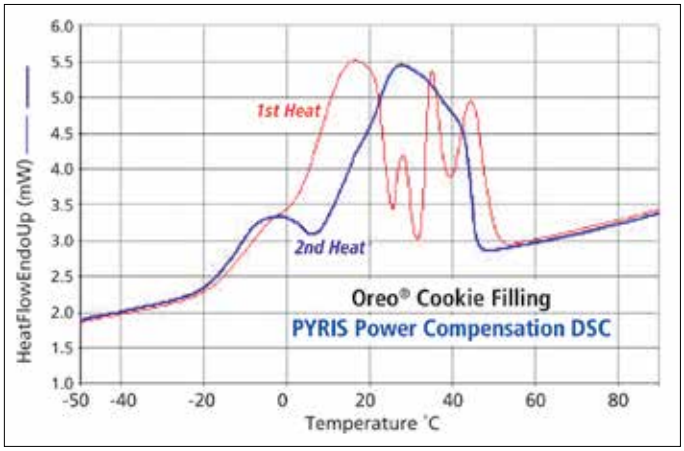


*Figure 2.* Comparison of first and second DSC heats for filling.

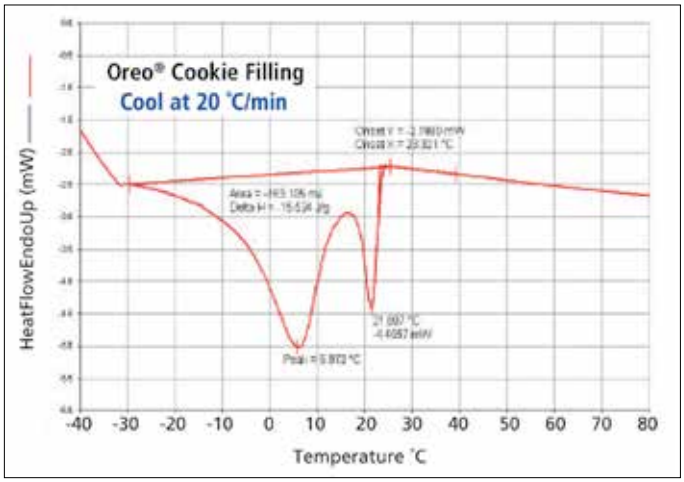


*Figure 3.* DSC cooling results for Oreo® cookie filling.

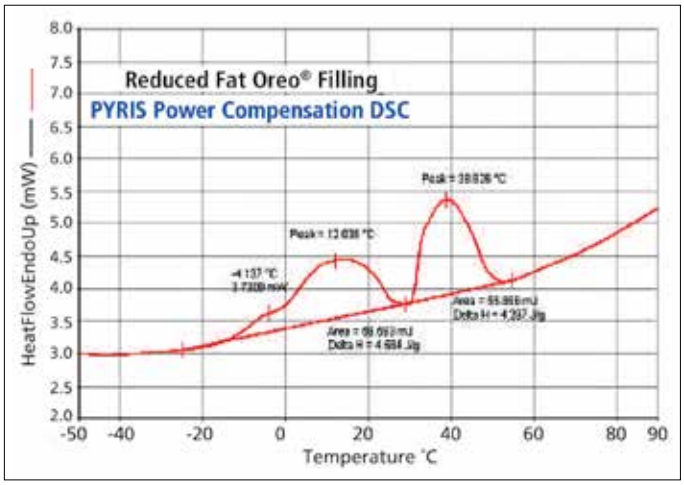


*Figure 4.* DSC results for reduced fat Oreo® cookie filling.

Compensation DSC is necessary to be able to detect the various peaks associated with the polymorphic forms of the cookie filling, even at the fast heating rate of 20 °C/min.

Heat flux DSC instruments, especially those using a massive silver block, would tend to smear out the various transitions associated with the fats and polymorphic forms in the filling making the characterization less definitive and incomplete. With the Pyris™ Power Compensation DSC, all of the important transitions, both large and small, are observed.

The regular Oreo® cookie filling was cooled back to –60 °C and then reheated at 20 °C/min and the results of the reheat experiment are displayed in Figure 2. The filling now exhibits a very different thermal response and this reflects the differences due to thermal history. Melting, cooling and reheating produces a new morphology or structure in the fat. DSC is a valuable technique for studying the effects of thermal history on fats and their polymorphic forms.

The Power Compensation DSC also provides excellent results during cooling experiments. Fats yield well-defined crystallization events during cooling and this information is valuable for characterization and process control purposes. Displayed in Figure 3 are the DSC results generated for the Oreo® cookie filling by cooling from 100 to –60 °C at a rate of 20 °C/min. The crystallization of a fat component occurs sharply at 23 °C. The cooling data reflects two different crystallizable fats in the cookie filling.

The DSC results obtained for the reduced fat Oreo® cookie filling are displayed in Figure 4. This filling undergoes multiple melting transitions at –4.1 °C, 12.0 and 38.8 °C. Although the reduced fat filling contains solid or hydrogenated fats, the amount of fat is reduced as is demonstrated by the lower values of the heats of melting. The first and second melting transition yield heats of melting of 4.6 and 4.3 J/g, respectively, for a total heat of 8.9 J/g. This is much lower than the value obtained for the regular Oreo® cookie filling (28.2 J/g).

The Oreo®-like cookie contains a filling with no hydrogenated or solid fats and the DSC results for this sample are shown in Figure 5. The melting of the fat in this filling completely takes place below 0 °C with melting peaks occurring at –26.0 and –17.3 °C. The total heat of melting for the non-hydrogenated fat filling is 16.1 J/g.

Displayed in Figure 6 is a direct overlay of the DSC results obtained for the three different cookie fillings. The differences in the melting responses of the fats comprising the fillings are very evident from these results.

## Summary

The Power Compensation or double furnace DSC yields excellent results for foods including the fat nature and content. The fast responsiveness of the Power Compensation DSC provides the highest possible resolution and this is critical for characterizing the various polymorphic melting forms associated with fats in foods. Even at the fast heating rate of 20 ˚C/min, the Power Compensation DSC is able to provide high resolution to be able to detect the multiple melting peaks of the polymorphic forms for the as-received Oreo® cookie filling. This data is important for the full characterization of the food fats, quality assurance, product uniformity and process control purposes.

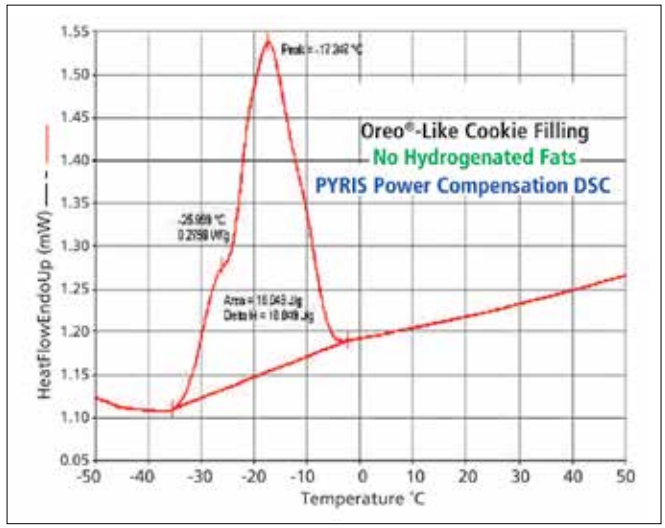


*Figure 5.* DSC results for Oreo®-like cookie filling (no hydrogenated fats).

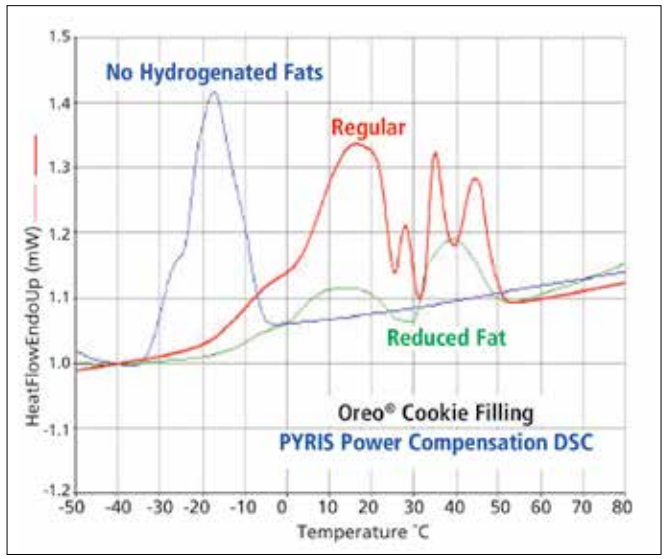


*Figure 6.* Overlay of DSC results for regular Oreo®, reduced fat and non-hydrogenated fillings.

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APPLICATION NOTE

FT-IR Spectroscopy

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# Investigating Phase Transitions with Variable Temperature ATR

## Introduction

Heating and cooling cause phase changes in many materials with consequent effects on their physical properties. IR spectroscopy is a powerful tool for studying these changes since the spectra are sensitive to variations in both intermolecular and intramolecular interactions. Changes in the IR spectra due to temperature variations can be correlated with structural changes and the spectra can be associated with specific crystalline forms. For example, any transition from a crystalline to an amorphous phase results in a broadening of bands as the molecules are in more varied environments. In crystalline materials, a change from one polymorph to another generally causes band shifts and splitting. For many materials transmission and external reflection measurements are not practicable without some sample preparation but ATR can often be used directly. In this note we illustrate the use of heated ATR to follow thermal changes in chocolate, which is largely a suspension of sucrose and cocoa solids in a matrix of cocoa butter. Chocolate and cocoa butter both have several polymorphs with melting points between 17 and 37 °C.[1] The polymorphic form has to be carefully controlled in manufacture because of its importance for storage and its major contribution to the sensory experience when eating chocolate.

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## Experimental

Spectra were measured with a Frontier FT-IR spectrometer using a single bounce PIKE ATR accessory with a ZnSe crystal that could be heated at a controlled rate up to 135 ˚C. The heating rate was usually 1 degree C/minute with 4 $cm^{-1}$ spectra collected at 15 second intervals using PerkinElmer® TimeBase™ software (Figure 1). The materials used were cocoa butter and a commercial dark chocolate product containing 85% cocoa and about 15% sucrose with other minor constituents.[2]

## Results

Caution is needed in interpreting ATR spectra because they come from the first few microns depth of material in contact with the crystal. Because of this, ATR spectra may differ from those of the bulk material. The penetration depth is proportional to wavelength which means that relative band intensities in different regions may change if the degree of contact with the crystal changes. In this case the bands used to generate band ratios were separated by less than 20 $cm^{-1}$ so the difference in penetration depth is insignificant.

Typical ATR spectra of chocolate and cocoa butter are shown in Figure 2. The chocolate spectrum is dominated by the cocoa butter which is largely a mixture of di and triglycerides of stearic, palmitic and oleic acids, and by sucrose. As the sample is heated (Figure 3) the features associated with cocoa butter broaden and shift while the sucrose bands are unchanged. Melting causes an overall increase in band intensities because of improved contact with the ATR crystal. At the same time there is a reduction in the intensities of all the sucrose bands relative to those of the cocoa butter. This is attributed to the liquid cocoa butter flowing around the sucrose crystals on to the surface of the crystal.

Although there are changes occurring in many regions of the spectra they are seen most clearly in the complex C=O absorption around 1740 $cm^{-1}$. The C=O feature of three samples of the same chocolate with different thermal histories at about 20 ˚C are seen in Figure 4. Three peaks are seen in the original material but their relative intensities are affected by heating and cooling. After melting and cooling there is a broad unresolved band. The changes with temperature can be followed by monitoring appropriate band intensities within this region or, in more detail by using principal components analysis (PCA).

TimeBase software provides several different ways of presenting the data, as individual spectra or a stacked plot. The changes with temperature can be examined as the intensities at specific frequencies or as ratios of pairs of peak heights or band areas that can be chosen interactively. The use of band intensity ratios is especially appropriate for ATR data as the overall intensities can be affected by changes in the contact with the ATR crystal. Figure 5 shows typical TimeBase screen displays.

In Figure 6 the ratio of intensities at different frequencies within the C=O band for chocolate is compared with the same ratio for a cocoa butter as each is heated to above its melting point. There appears to be a single smooth transition for cocoa butter while the chocolate melting appears more complex. PCA of the chocolate spectra identifies several significant principal components. Combinations of the scores for the first two PC's separate one process that appears complete at 25 ˚C from a second that occurs between 25 and 30 ˚C (Figure 7). Identifying the specific polymorph changes associated with these transitions would require reference spectra of the individual polymorphs which were not available at the time of this study.

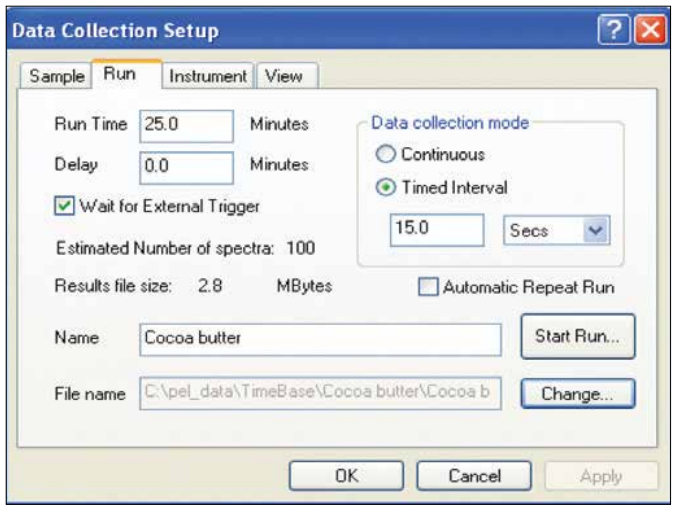


*Figure 1.* Set-up screen for TimeBase.

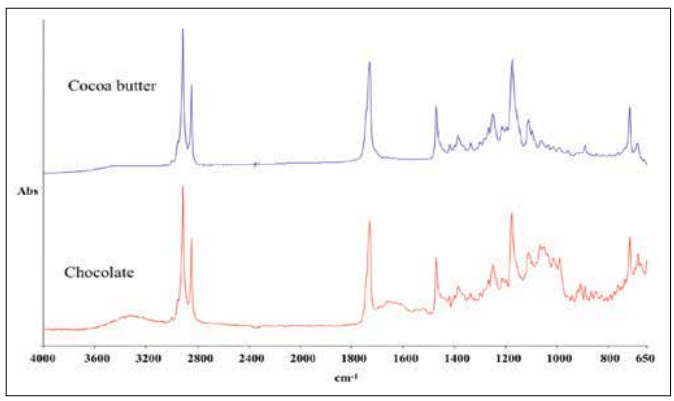


*Figure 2.* Spectra of chocolate and cocoa butter.

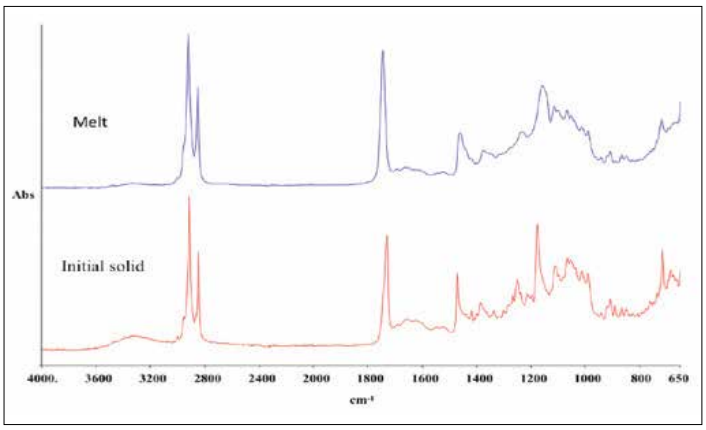


*Figure 3.* Chocolate solid and melt.

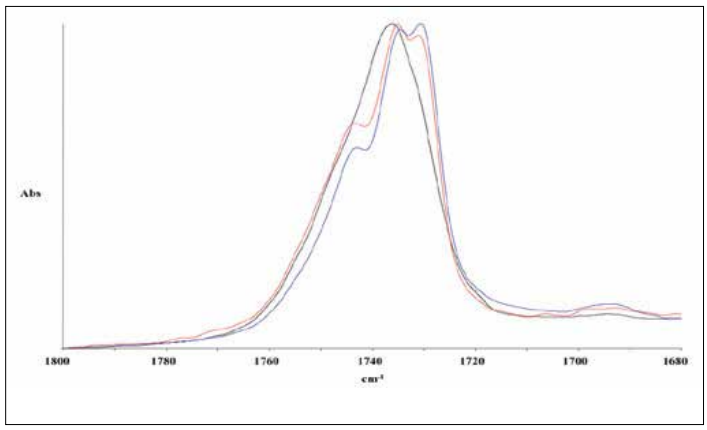


*Figure 4.* C=O region for chocolate with different thermal histories.

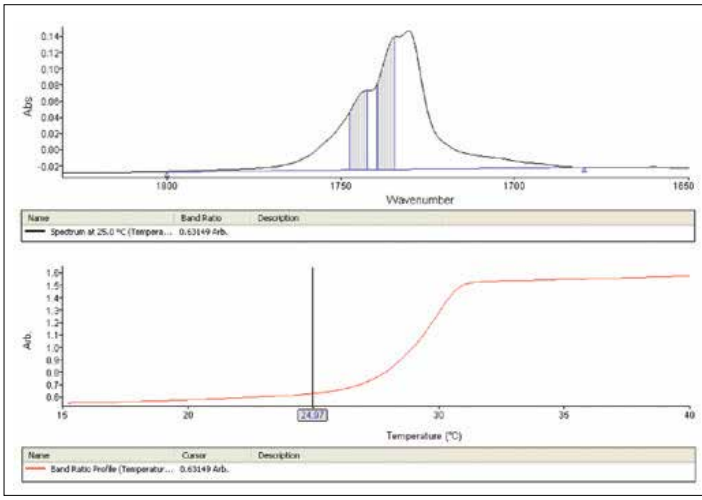


*Figure 5a.* TimeBase spectral display and band ratio profile for cocoa butter.

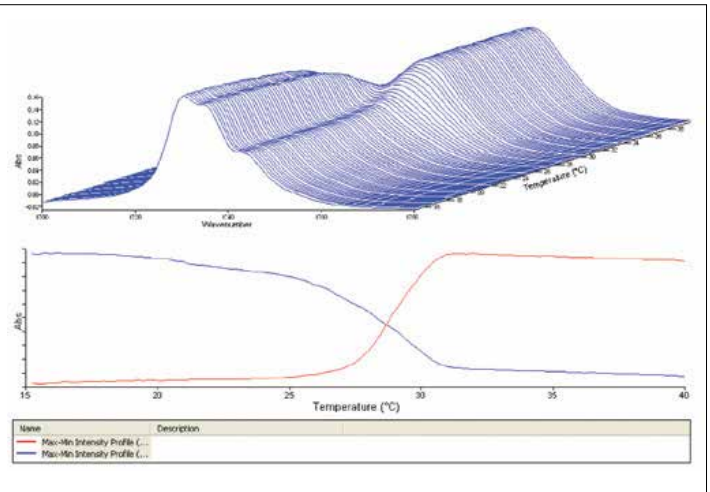


*Figure 5b.* TimeBase stacked plot and specific band intensity profiles for cocoa butter.

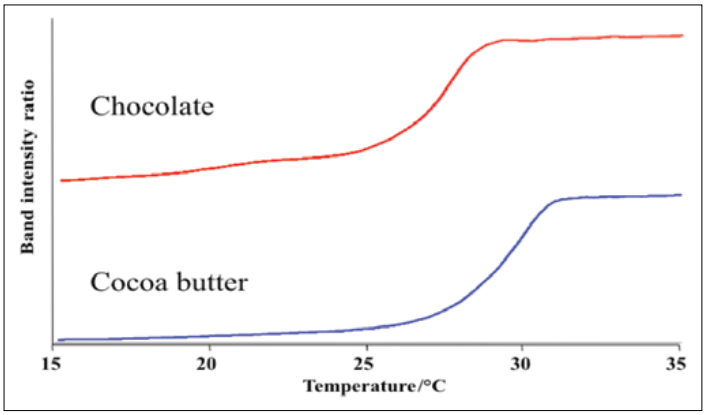


*Figure 6.* Band intensity ratios for chocolate and cocoa butter.

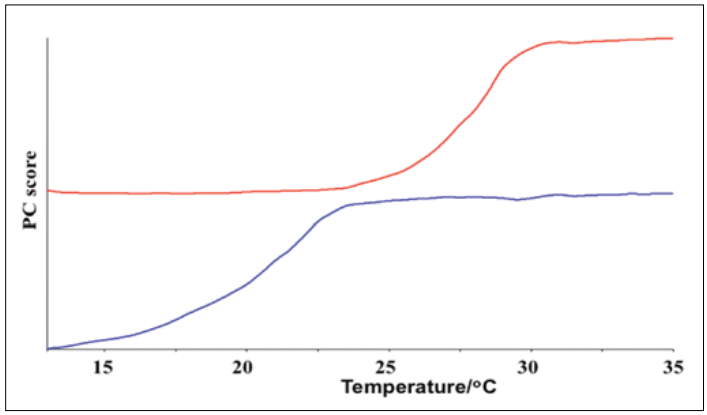


*Figure 7.* PCA scores for chocolate showing successive transitions.

## Summary

These data show how variable temperature IR measurements can be used to monitor complex phase transitions. The transitions in chocolate are more complex than that seen in cocoa butter. Because the transitions have different spectral signatures they can be separated by choosing to look at different band intensity ratios, or more systematically by using PCA. The spectra at 20 ˚C show how the thermal history affects the spectra observed at ambient temperatures. Any systematic study to identify the polymorphic changes would require materials with well characterized thermal histories, for example by using Differential Scanning Calorimetry.[1]

As the temperature is raised there is an observable reduction in the intensity of bands due to sucrose compared to those from the cocoa butter. This implies that the cocoa butter concentration at the crystal surface increases, displacing sucrose.

## References

1. 'Characterization of Chocolate Using Power Compensated DSC' PerkinElmer Thermal Analysis Application Note. PETech-43.

2. Lindt & Sprüngli AG, Kulrich, Switzerland, courtesy of W. Böttcher.

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APPLICATION BRIEF

FT-IR NIR Spectrometry

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# Single NIR Measurement for the Detection of Adulteration and Measurement of Important Parameters in Cocoa Powders

## Introduction

Cocoa powder is a product regularly used within the personal care, food, and beverages sectors. There have been reports indicating several health benefits of cocoa, from lowering blood pressure antioxidants to containing essential fatty acids, fiber, and minerals.

There have been cases of cocoa adulteration reported in Eastern Europe and across the world. In a recent case, samples contained 20% less cocoa compared to values listed on the labels, which was found to be fraudulent activity by the supplier.[1]

The initial method used to assess the quality of cocoa beans is the cut-and-taste test, although this is a subjective technique. Liquid chromatography methods are also often used for testing cocoa powder, but they are time consuming and can be complicated. A much faster and easier technique to verify the authenticity of cocoa is Near-Infrared (NIR) spectroscopy.

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## NIR Methodology

Spectra of six cocoa brands and two adulterants (arrowroot and dark rye flour) were collected on a PerkinElmer Frontier™ NIR spectrometer in reflectance using the NIRA II sampling accessory at a spectral resolution of 16 $cm^{-1}$ using 32 scans. These spectra were entered into PerkinElmer's Adulterant Screen™ in the Spectrum 10 software as a library of material (good) and adulterant spectra, as shown in Figure 1. Different lots of one of the cocoa samples were then spiked at concentrations of 10% and 20% weight/weight concentration of arrow root and dark rye flour to test the capability of Adulterant Screen™.

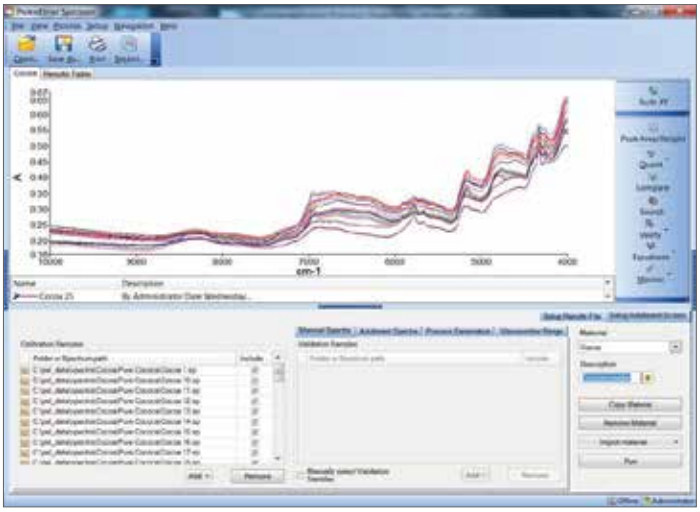

*Figure 1.* Adulterant Screen setup for cocoa powder showing cocoa powder material spectra.

Adulterants are commonly added to products at for financial gain. Adulterant Screen is able to correctly identify the adulterant used and estimate its concentration, as shown in Table 1, and can give an estimated level of detection of the adulterant, in this case <1%.

*Table 1.* Results from Adulterant Screen for spiked samples.

| Sample Name | Adulterant | Level | Confidence | Material Fit |
|---|---|---|---|---|
| 10% Dark Rye | Dark Rye Wholemeal Flour | 0.10111 | Likely | Abnormal |
| 20% Dark Rye | Dark Rye Wholemeal Flour | 0.18440 | Likely | Abnormal |
| 10% Arrow | Arrowroot | 0.10105 | Likely | Abnormal |
| 20% Arrow | Arrowroot | 0.17882 | Likely | Abnormal |

Adulterant Screen can be deployed using Spectrum Touch™ methods. This allows for an easy-to-use software environment for routine operators. A sample spiked with 1% Dark Rye Wholemeal Flour was tested using a Spectrum Touch method and the same Adulterant Screen. The resulting output in Figure 2 shows that the sample failed because adulterants were detected.

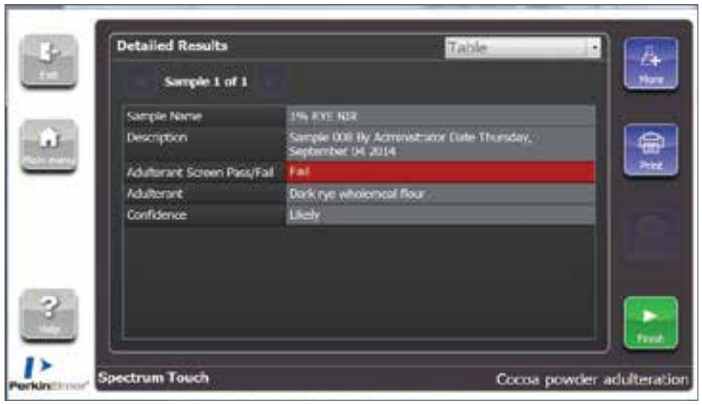


*Figure 2.* Spectrum Touch method deployment for an adulterated cocoa sample.

The NIR spectra of the samples also have the capability of determining the fat and dry-mass contents of cocoa samples. Cocoa 1 and 6 contained 22.6 g and 2.3 g of fat per 100 g of cocoa powder high-fat, respectively. The different fat levels are apparent in the spectra shown in Figure 3, particularly in the first overtone region of the C-H stretch, just below 5,900 $cm^{-1}$ and the combination region at about 4,300 $cm^{-1}$.

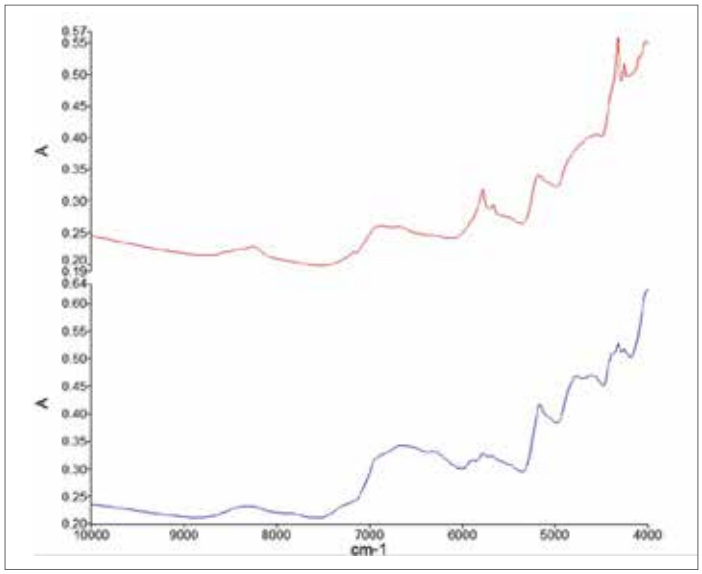


*Figure 3.* NIR spectra of high fat cocoa (top) and low-fat cocoa (bottom).

The spectral differences can be further highlighted by applying the second derivative to the spectra as shown in Figure 4. Applying the second derivative to the spectra will remove any broad baseline slope and offset due to the different scattering properties of the powders. These spectra show clear differences between the low- and high-fat cocoa powders and would form the basis of any quantitative measurement.

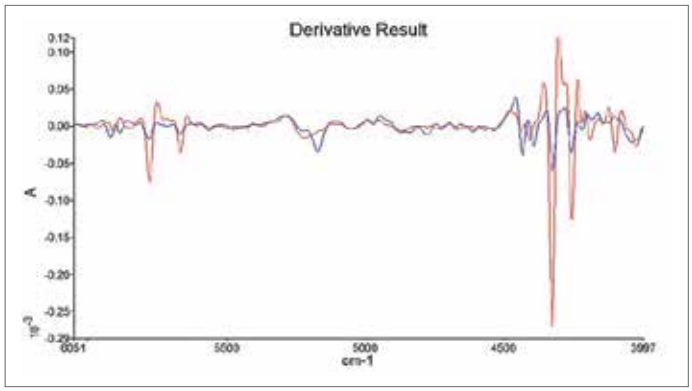


*Figure 4.* 2nd derivative of high-fat cocoa (red) low-fat cocoa (blue).

The dry-mass content of the powders can be measured in the combination region of the spectrum just above 5200 $cm^{-1}$. The second derivative spectra of a series of cocoa powders with very small variation in the dry-mass content are shown in Figure 5.

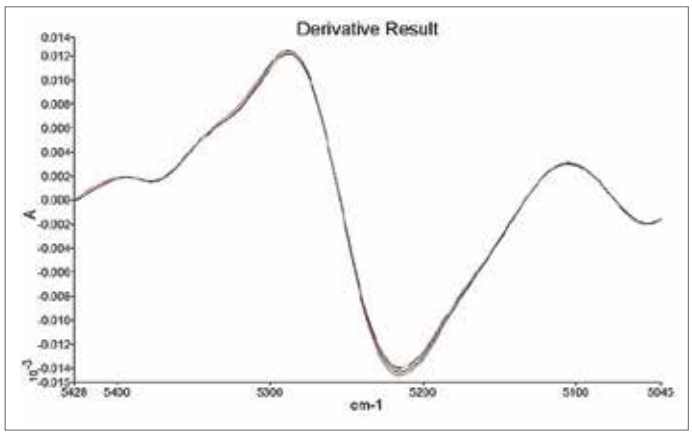


*Figure 5.* Variation in dry-mass content of cocoa powders.

This spectral region would form the basis for a quantitative measurement of the dry-mass content of the cocoa powders.

## Conclusion

A single NIR measurement of cocoa powders can allow easy measurements for adulteration of the material and, with calibrations, also allow for determination of fat and dry-mass content within cocoa powder. Adulterant Screen allows for a fast, easy, and low-cost method for screening adulterants within cocoa powder. New adulterants can be added into the method simply by measuring the spectrum of the pure adulterant. This results in an easier method for the detection of adulteration in cocoa powder.

## Reference

1. Czech Agriculture and Food Inspection Authority: Press Release Polish cocoa adulteration classes in Kaufland 04/25/2012

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