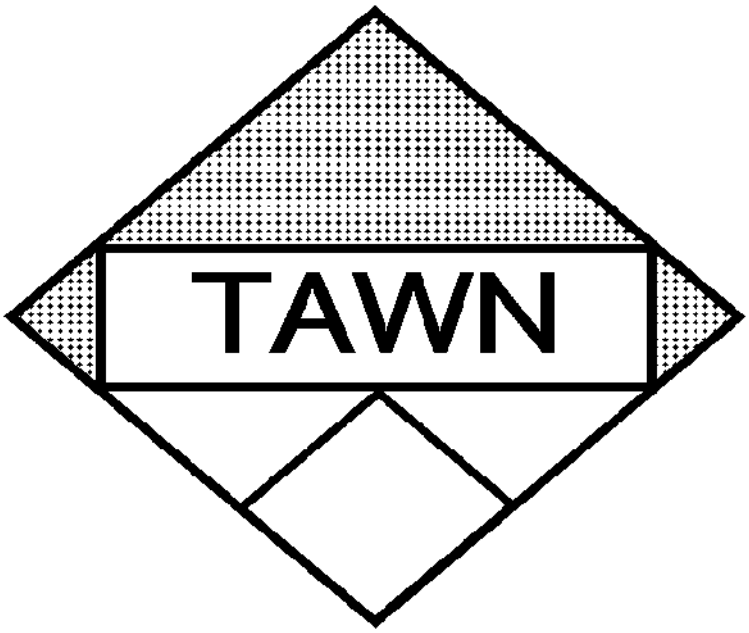
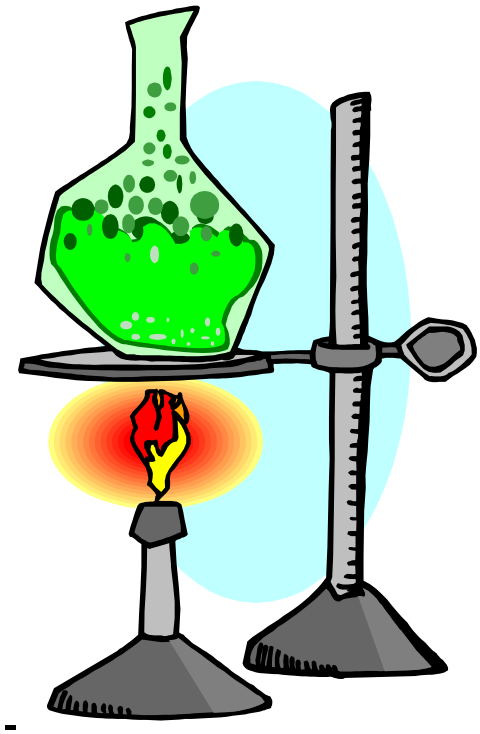
Thermische Analyse Bulletin

Het officiële orgaan van de Thermische Analyse Werkgroep Nederland juli 2011



Conferentie data,
Cursussen , Apparatuur , Din Normen ,
Wetenschappelijke Bijdragen, Etc

Zie voor de oproep sponsor TAD 2011 en de nieuwe resolutie test bladzijde 10 van dit Bulletin



COLOFON

Het Thermische Analyse Bulletin is het officiële orgaan van de Thermische Analyse Werkgroep Nederland (TAWN).
Het bulletin wordt gratis aan de leden gestuurd.

In het bulletin worden opgenomen:
- **nieuws van het bestuur van de werkgroep;**
- **gegevens over congressen, symposia en cursussen;**
- **internationaal nieuws;**
- **boekbesprekingen;**
- **gegevens over nieuwe apparatuur en de toepassing ervan.**

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REDACTIONEEL

We zoeken nog steeds een sponsor voor de TAD 2011. Misschien iets voor bedrijven die tot nu toe afzijdig waren? De kosten zijn alleen een zaal en een eenvoudige lunch.
Jammer dat nog steeds weinig firma's gebruikmaken van de mogelijkheid om nieuwe apparatuur en mogelijkheden in dit blad te presenteren.
Verder moet ik inzenders verzoeken om alleen advertenties in PDF in te zenden. Bijdragen liefst in een text formaat omdat bij omzetten van een PDF file de opmaak vaak verloren gaat.

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Inhoudsopgave

THERMISCHE ANALYSE WERKGROEP NEDERLAND

Sinds 1965 bestaat er in Nederland een werkgroep (vanaf 1990 een officiële vereniging) genaamd Thermische Analyse Werkgroep Nederland, afgekort TAWN. Deze werkgroep heeft thans bijna 300 leden, die zich vanuit zeer verschillende onderzoeksgebieden bedienen van thermische analyse (DTA, DSC, TG, TMA, DMA, etc.) en calorimetrische technieken. De TAWN is lid van de internationale organisatie op het gebied van thermische analyse en calorimetrie, de ICTAC (International Confederation for Thermal Analysis and Calorimetry).

Doel van de TAWN
Het doel van de werkgroep is het bevorderen en verspreiden van kennis en kunde op het gebied van thermische analyse en calorimetrie. Om dit doel te bereiken worden er activiteiten georganiseerd, waar de leden onderling informatie kunnen uitwisselen met betrekking tot de mogelijkheden van thermische analyse en calorimetrie bij fundamenteel en toegepast onderzoek alsmede bij kwaliteitscontrole van producten.

Activiteiten
Jaarlijks wordt een thermische analysedag (TAD) georganiseerd. Daarnaast zijn er thema(mid)dagen over speciale onderwerpen. Tijdens deze bijeenkomsten houden leden of uitgenodigde sprekers voordrachten over hun werk. De toegang is voor leden gratis. Deze bijeenkomsten bieden uitstekende mogelijkheden om contacten op te bouwen met andere onderzoekers in hetzelfde vakgebied.
Daarnaast werkt de TAWN intensief mee aan cursussen op het gebied van de thermische analyse en calorimetrie.
Een aantal maal per jaar geeft de werkgroep een blad uit, het Thermische Analyse Bulletin. Dit blad wordt gratis naar de leden gestuurd.

LIDMAATSCHAP
Het lidmaatschap van de TAWN is slechts mogelijk voor natuurlijke personen; de contributie bedraagt
€ 10,-- per jaar. Opgave is mogelijk door de ingevulde aanmeldingsstrook te zenden naar de secretaris van de vereniging.
Sponsoring
Voor bedrijven en instellingen bestaat de mogelijkheid de werkgroep te sponsoren. Ook kunnen advertenties worden geplaatst in het TA-bulletin. Informatie hierover is verkrijgbaar bij de secretaris van de werkgroep of de redacteur van het TA-bulletin.

Aanmelding als lid van de TAWN

Ondergetekende geeft zich op als lid van de TAWN.

Naam: _____Hr./Mw. Titel(s):_____ Voorletters: _____

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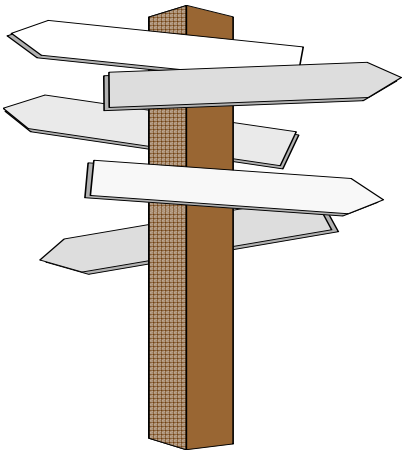
CONGRESSEN, SYMPOSIA, CURSUSSEN



Thermodynamics 2011

Athene, GR, 01.09. - 03.09.2011
http://www.thermodynamics2011.org
info@thermodynamics2011.org

Thermosets 2011 - International Conference on Thermosetting Resins

Berlin, D, 21.09.-23.09.2011
http://www.thermosets.de
info@thermosets.de

European Conference on Thermophysical Properties: 28.8-1.9 2011

ECTP 19, 2011, Thessaloniki, Griekenland

10 th Seminar to the memory of Prof. St. Bretsznajder

We would like to inform that the 10th Seminar to the memory of Prof. St. Bretsznajder will be held in Plock (Poland), September 28-30, 2011.
The Seminar can give a view of general problems of the thermochemistry and kinetics of thermal decomposition reactions as well as ways of control of these processes. The scientific programme will comprise plenary lectures, oral communications and poster presentations on the thermal analysis and calorimetry methods and their various applications, e.g. to study of organic and inorganic compounds, polymers, plastics, petrochemical products, complexes, products of cement hydration, ceramic materials, sorbents etc. Abstracts will be published in the Seminar Materials. Selected oral and poster contributions will be published in a special number of Journal of Thermal Analysis and Calorimetry at Springer, but only after the standard reviewing procedure.

More details about the Seminar and Registration Card you can find on the website www.ich.pw.plock.pl/bretsznajder

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1st Central and Eastern European Conference on Thermal Analysis and Calorimetry, 7-10 September 2011, Craiova, Romania

Dear Colleague,

The ever growing community of Thermal Analysis and Calorimetry scientists working in the Central and Eastern European countries makes the organization of a conference and gathering all those interested in the development of the field a desirable event.

Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC) is wished to become a forum where researchers can meet, present their work, explain their results and discuss the encountered scientific and technical problems of thermal analysis and calorimetry.

Every two years, CEEC-TAC aims to gather scientists from Central and Eastern Europe, from Germany and Austria to Russia and Kazakhstan, and from the Baltic countries to the Balkans, Turkey and the Caucasians. Researchers in the field of Thermal Analysis and Calorimetry from all over the world are welcomed to share experience and knowledge with those working in complementary fields or just using thermo-analytical techniques. Besides the regular conference, we wish organizing working sessions, where in a relaxed and informal environment the participants can talk about plans and their needs, thus fostering new contacts and further collaborations.

Fort the 1st CEEC-TAC (www.ceec-tac.org) to be held in Craiova – Romania between 7-10 September 2011, we take this opportunity and it is our great pleasure to invite joining us.
With best regards,
Andrei Rotaru and Crisan Popescu
Co-chairmen of the CEEC-TAC1 Conference

PS: Please visit the conference website at: www.ceec-tac.org and do not hesitate to contact us at: office@ceec-tac.org

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popescu@dwi.rwth-aachen.de
http://www.dwi.rwth-aachen.de

38th International Pyrotechnics Seminar

Denver, USA, 10.06. - 12.06.2012
http://ipsus.org/index2.htm
linda.crouse@ntscorp.com

18. Symposium On Thermophysical Properties

Boulder, USA, 24.06. - 29.06.2012
http://thermosymposium.boulder.nist.gov/contacts.html
symp18@boulder.nist.gov

15th ICTAC Conference

Osaka, J, 02.08. - 08.08.2012

Herhaalde oproep voor bijdragen TAD 2011 in November 2011

BELANGRIJKE MEDEDELINGEN.

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Er wordt weer een sponsor gezocht voor de organisatie van de TAD 2011. Deze zal bij voorkeur plaatsvinden op een vrijdag in de tweede helft van november 2011 (24 of 25 november) . Hier kan echter in overleg van worden afgeweken.
Gevraagd wordt een zaal geschikt voor ongeveer 50 á 60 deelnemers maximaal en gelegenheid voor een lunch. Willen gegadigden zo spoedig mogelijk contact opnemen met een van de bestuursleden.

@@@

Het bestuur wil een nieuwe aangepaste resolutietest introduceren, welke beter aansluit bij de huidige mogelijkheden van de verkrijgbare TA apparatuur.
Ook hiervoor kunnen belangstellenden zich opgeven bij de bestuursleden van de TAWN.
@@@

Cursus Thermische Analyse met nadruk op praktische handelingen

Wij zijn voornemens bij voldoende deelneming om op 13 en 14 oktober 2011 (bij DSM Resolve in Geleen) een nieuwe cursus Thermische Analyse met nadruk op praktische handelingen te organiseren.

In 2005 werd voor het laatst de uiterst succesvolle cursus "DSC-cursus met nadruk op praktische handelingen" georganiseerd. Geregeld krijgen wij vragen hierover. Echter vorig jaar waren er onvoldoende deelnemers om deze door te laten gaan. Het lijkt dat er weer voldoende belangstelling is om in oktober 2011 een cursus te organiseren.
(zie flyer)

Het is waarschijnlijk dat de opzet van de cursus iets zal wijzigen ten opzichte van de eerder gegeven cursussen. Mogelijk zal naast DSC ook TGA worden behandeld. Wat in ieder geval blijft is dat het een onafhankelijke cursus is
waarbij korte theoretische inleidingen worden gevolgd door het in groepjes uitvoeren van thermische analyse experimenten en het interpreteren van de meetcurven.

Belangstellenden worden verzocht om contact op te nemen met Paul van Ekeren, voorzitter TAWN (e-mail: Paul.vanEkeren@tno.nl) of met andere bestuursleden.

Course program

Thermal Analysis seminar

" Metastability in polymers"

October 4-5, 2011 in Belgium
October 5-6, 2011 in The Netherlands

Free of charge

	Morning Session
09.00 – 09.30	Welcome
09.30 – 10.00	Introduction to meta-stable matter
10.00 – 11.00	Introduction to ultra fast scanning DSC with FDSC1
11.00 – 11.15	Coffee Break
11.15 – 12.15	Last applications - Dynamic up to -2000k/s and isothermal crystallization down to 30°C of iPP - More applications. - New applications.
12.30 – 14.00	Lunch Break
	Afternoon session : demonstration
14.00 – 15.00	Demonstration of FDSC1
15.15 – 16.30	Open discussions : questions & answers

Speakers :

Dr. R.Riesen Mettler Toledo AG Schwerzenbach. CH.
Dr. G. VandenPoel DSM Resolve Geleen. NL.
Dr. D. Auhl UCL Louvain la Neuve. B.

Advertentie Mettler Toledo

Persbericht Mettler-Toledo B.V.

Mettler-Toledo Analytical in Schwerzenbach Zwitserland heeft de firma Triton Technology overgenomen, hierdoor wordt onze positie in de DMA markt duidelijk versterkt.
De TT DMA is een gemakkelijke en eenvoudige DMA, die naast de TMA mode ook Stess-strain en Creep kan meten.
Het is een zeer toegankelijke DMA, waarbij deze kan worden uitgevoerd met een waterdamp generator en metingen door onderdompeling in een waterbad.
Ook metingen m.b.v. UV zijn mogelijk.
Het temperatuurgebied is van -190 – 600 ‘C.

Heeft U vragen of wensen in deze neemt contact op Mettler-Toledo.
Of kijk op de site van: www.mt.com of www.triton–technology.co.uk

TT DMA

Het Mettler-Toledo Benelux team:

Phillippe Larbanois N.V.Mettler-Toledo S.A.Belgie.
Hay Berden Mettler-Toledo B.V. Nederland.

DIN SPEC 91127

Recommendation for Temperature Calibration of Fast Scanning Calorimeters (FSCs) for Sample Mass and Scan Rate

Contents

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Foreword

This DIN Specification on differential scanning calorimetry, which has been developed by a standardization group using the PAS procedure, deals with high to very high scan rates and low to very low sample masses respectively, and is complementary to the International Standard ISO 11357 which is dealing with low scan rates.
It was elaborated by the following authors, members of the Standardization group

- **Dr Geert Vanden Poel, DSM Resolve, Geleen, The Netherlands;**
- **Dr Albert Sargsyan, DSM Resolve, Geleen, The Netherlands;**
- **Prof. Vincent Mathot, SciTe, the Netherlands and Katholieke Universiteit Leuven, Belgium, Chairman;**
- **Prof. Guy Van Assche, Vrije Universiteit Brussel, Belgium;**
- **Dr Andreas Wurm, Universität Rostock, Germany;**
- **Prof. Christoph Schick, Universität Rostock, Germany;**
- **Prof. Andres Krumme, Tallinn University of Technology, Estonia**
- **Prof. Dongshan Zhou, Nanjing University, People's Republic of China.**

The following persons also contributed to the document:

- **Dr Sander van Herwaarden, Xensor Integration, Delfgauw, The Netherlands;**
- **Elina Iervolino, Xensor Integration, Delfgauw, The Netherlands;**
- **Gunnar Schulz, Universität Rostock, Germany;**
- **Davit Zohrabyan, Universität Rostock, Germany;**
- **Evgeny Zhuravlev, Universität Rostock, Germany.**

The work is an outcome of the NaPolyNet project of the 7th Framework Programme of the European Commission and was partially financed by NaPolyNet funds (EU-FP7 CSA NMP-2007-2.1-3).
DIN Deutsches Institut für Normung e.V., Berlin
February 25th, 2011

Introduction

Thermal history – especially cooling and heating in combination with isothermal stays – and sample/product treatment can change the behavior of materials drastically, influencing end properties. Experimentally it has been a challenging and very demanding job to realize fast, controlled cooling and heating at constant rates higher than the typical rates of Standard DSC, which are centred on approximately 10 °C/min. In the past decade this challenge has been met through instrumental breakthroughs resulting in various Fast Scanning Calorimeters (FSCs), including commercial ones. This progress necessitates a dedicated protocol for temperature calibration of FSCs.
To address this need for extending existing temperature calibration protocols, the present Recommendation is firstly intended to inform the user about various types of FSCs and to compare their performances. To the opinion of the authors, FSC opens a new world with respect to the analysis of substances, materials and products thereof. Undoubtedly it will lead to new

concepts in domains like metastability, kinetics, reorganization, crystallization, melting, real-life conditions, and processing conditions.
Secondly, one should be aware that instrumentation facilitating different scan rates has consequences with respect to the way of performing measurements, especially because of the influence of scan rate and sample mass on sensitivity, resolution, thermal lag etc.
Thirdly, because the impact is different for different FSC's, a need arises of a general applicable temperature calibration protocol, covering the issues mentioned and supporting measurements of good quality resulting in trustable and comparable results.
In order to meet the abovementioned requirements an international standardization group has been formed with the aim to provide the users of FSCs with a recommendation covering: *Temperature Calibration of FSCs for Sample Mass and Scan Rate.*

Scope

This specification describes a protocol of temperature calibration procedures for Fast Scanning Calorimeters for *high to very high scan rates* and *low to very low sample masses*, respectively, thus complementing ISO 11357.
Procedures are given for both an extensive temperature calibration as well as a rather quick temperature calibration of FSCs in the heating and the cooling modes for various scan rates and concomitant adjusted sample masses.
Thus, the specification also facilitates making the right choices to minimize the thermal lag arising at increasing scan rates before performing a measurement.

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Reglement Reisbeurzen voor Jonge Onderzoekers

1. **Om het oordeelkundig gebruik van Thermische Analyse en/of Calorimetrie in Nederland en Vlaanderen te stimuleren kan het bestuur van de TAWN een beurs toekennen aan jonge onderzoekers die op een (inter)nationaal congres of symposium resultaten van hun werk willen presenteren door middel van een lezing of een poster.**
2. **Het bestuur van de TAWN zal zich inzetten om deze mogelijkheid bekend te maken.**
3. **Het te presenteren werk moet voor een significant deel bestaan uit het correct toepassen van Thermische Analyse, zoals DSC, DTA, TG, TMA, DMA en DEA, of calorimetrie.**

4. **Het budget dat voor de beurzen beschikbaar is wordt door het bestuur van de TAWN vastgesteld. Het bestuur zal trachten om het budget via één of meer sponsors bijeen te brengen.**
5. **De frequentie van toekenning van beurzen is budgetgebonden, en daardoor mede afhankelijk van de sponsormiddelen. In principe wordt gestreefd naar een jaarlijkse toekenning van een beurs.**
6. **Een beurs kan op ieder gewenst tijdstip worden toegekend aan een kandidaat die een aanvraag indient bij het bestuur. De aanvraag dient te zijn voorzien van een 'abstract' van de presentatie, aangevuld met relevante informatie om de aanvraag te kunnen beoordelen. Tevens dient een begroting van de kosten te worden overlegd.**
7. **De kandidaat voor een beurs dient de leeftijd van 35 jaar nog niet te hebben bereikt.**
8. **Over toekenning van een beurs wordt beslist door het bestuur van de TAWN op basis van de kwaliteit van de voorgestelde presentatie.**
9. **Wanneer een bestuurslid zelf is betrokken bij het werk van een kandidaat, dan zal hij wel mee kunnen overleggen en adviseren, maar niet deelnemen aan een eventuele stemming over toekenning van een beurs.**
10. **De beurs bestaat uit een geldbedrag. De hoogte van dit bedrag wordt bepaald door het bestuur, maar zal nimmer meer bedragen dan het totaal van de inschrijvings-, reis- en verblijfskosten.**
11. **In geval van sponsoring worden de sponsors vermeld bij de uitreiking van de beurs en bij de presentatie.**
12. **Van degene die een beurs krijgt toegewezen wordt verwacht dat hij/zij een voordracht zal houden over zijn/haar werk tijdens een door de TAWN georganiseerde Thermische Analyse bijeenkomst in Nederland of Vlaanderen.**
13. **Een persoon kan slechts eenmalig een beurs ontvangen.**
14. **Het TAWN-bestuur is niet gebonden opening van zaken te geven over de besluitvorming.**
15. **In gevallen waarin dit reglement niet voorziet beslist het TAWN-bestuur.**

Vastgesteld te Utrecht,
in de TAWN-bestuursvergadering op 21 september 2006.

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Practical food applications of Differential scanning calorimetry (DSC)

Patricia Heussen

Unilever Research&Development, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands

Introduction

Food is often a complex system including various compositions and structures. The characterization of food can therefore be challenging. Many analytical methods have been used to study food, including differential scanning calorimetry (DSC) [i]. DSC is a thermal analysis technique to measure the temperature and heat flows associated with phase transitions in materials, as a function of time and temperature. Such measurements can provide both quantitative and qualitative information concerning physical and chemical changes that involve endothermic (energy consuming) and exothermic (energy producing) processes, or changes in heat capacity.
DSC is particularly suitable for analysis of food systems because they are often subject to heating or cooling during processing. The calorimetric information from DSC can be directly used to understand the thermal transitions that the food system may undergo during processing or storage. DSC is easy to operate and in most cases no special sample preparation is required. With a wide range of DSC sample pans available, both liquid and solid food samples can be studied. Typical food samples and the type of information that can be obtained by DSC are listed in Table 1. These tests can be used for both QC and R&D purposes. DSC applications are used from troubleshooting up to new product developments.

Table 1. Typical food samples and their application by DSC

TYPE OF SAMPLES	TYPE OF INFORMATION
Oils, fats and spreads	onset temp of melt / crystallisation/ polymorphic behaviour/oxidation stability
Flour and rice starch	retrogradation / gelatinization / glass transition Tg
Vegetable powders	glass transition Tg
Pastes and gels containing polysaccharides or gums	specific heat Cp, onset temp of melt and crystallisation
Protein	denaturation/aggregation

In this note, several samples of food material systems are given to illustrate the versatility of DSC.

DSC of oils and fats

Using a heat-cool-heat DSC program, the onset temperature, the heat of fusion (ΔH), the identification of polymorphic behaviour and crystallisation of oils and fats can be determined. An isothermal method or scanning method with an oxygen atmosphere can also be used to determine the oxidation induction time (OIT), in which case a heat-cool-heat method is applied to hydrogenated vegetable oils. Sometimes additional information about the sample is necessary for data interpretation, as for example in combination with XRD analysis which provides information on the specific polymorphic transitions. Most triglycerides [ii] exist at least in three crystalline forms, α (alpha), β' (beta-prime), and β (beta) that can be identified according to their X-ray diffraction patterns [iii].

In Figure 1 it can be observed that a α-modification is formed after a heat-cool treatment. This will be transformed into a β'-modification and after a certain time at room temperature partially to the β-modification. In Figure 2 the influence of storage time at room temperature is shown. The first heating of day 8 shows a better resolved peaks due to the transition of the less stable β' to a more stable polymorphic fraction, as it was also confirmed by XRD.

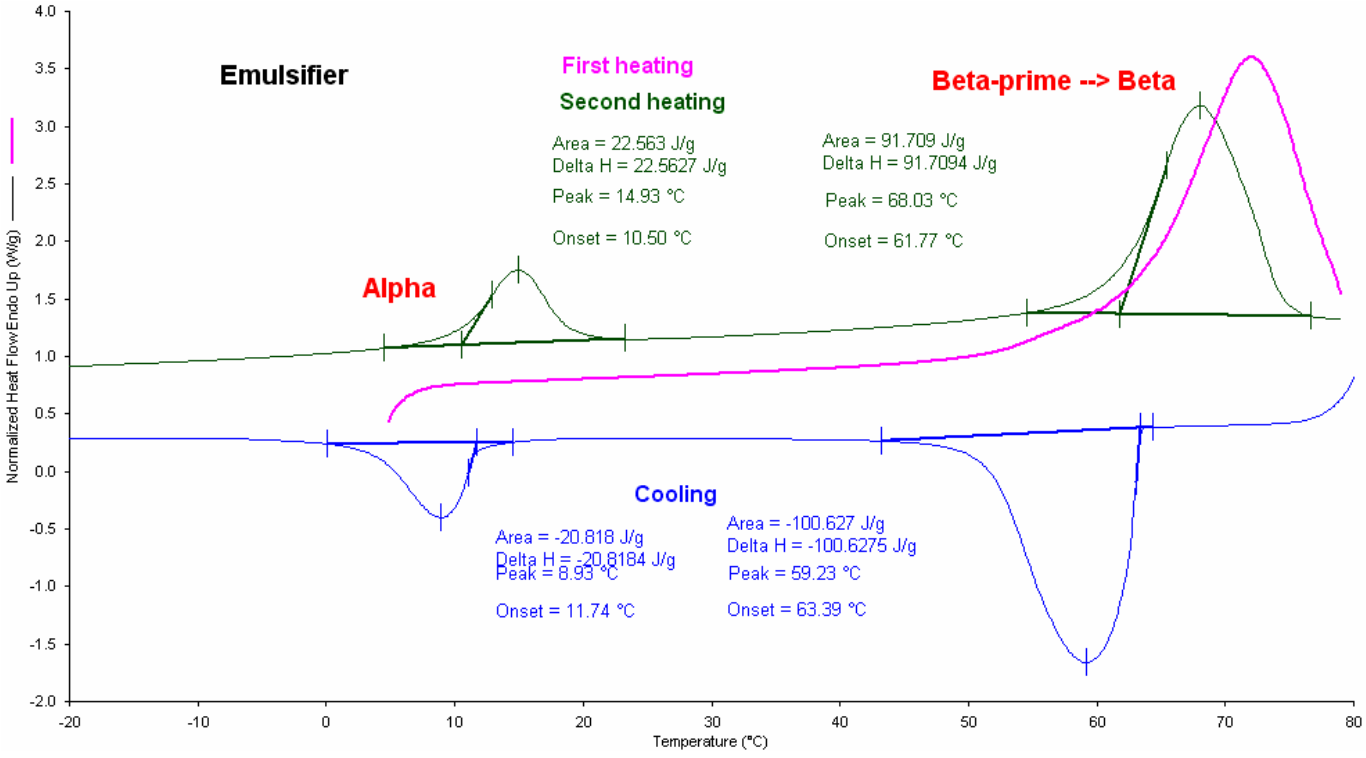

Figure 1. Heat influence on emulsifier.

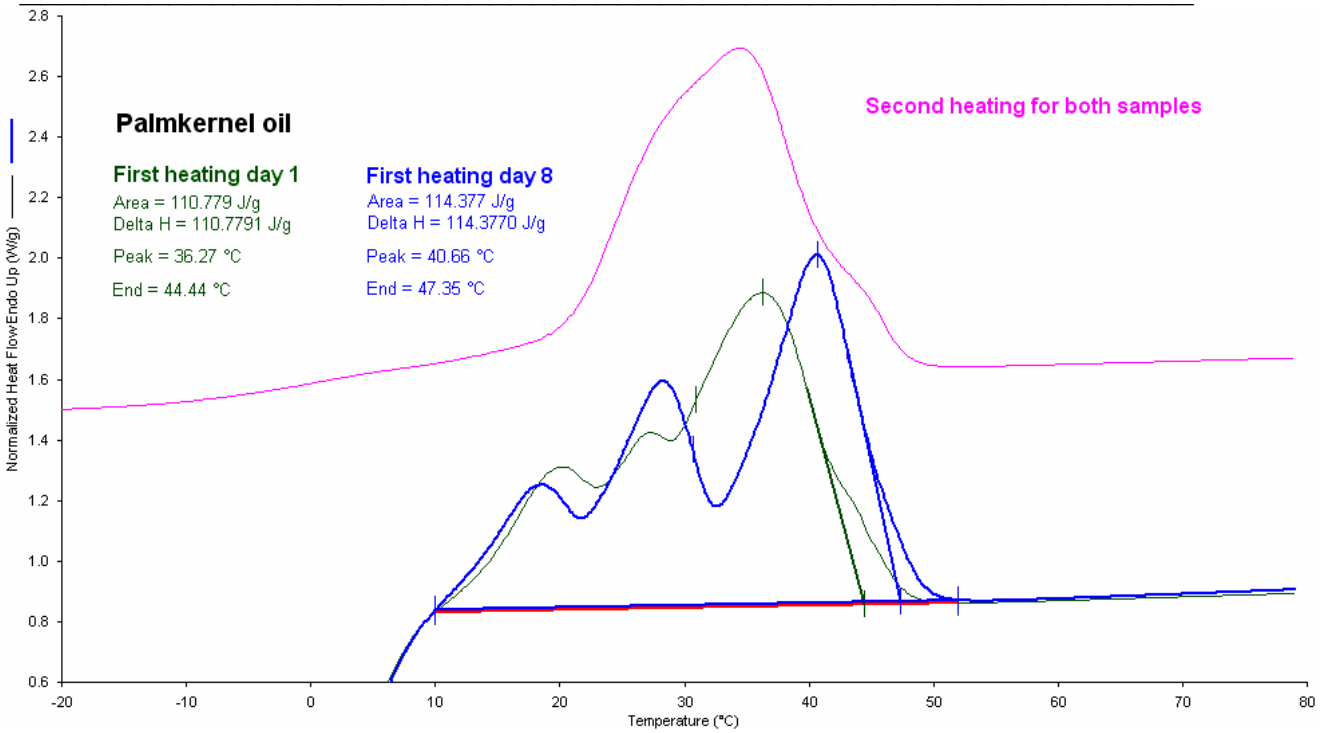

Figure 2. Time influence on palmkernel oil melting behaviour.

DSC is used to study fat phase transitions and melting range. It is one technique to explain the physical and textural properties of fats in bulk and final products. The combination of DSC and XRD is often used to identify the stable β-form, which can result in grainy mouth feel in final products.
DSC is used to compare batches of a product to study the melting behaviour indicating differences in crystallinity of the fat or composition of the end product. Different scanning rates are used to investigate the cooling effect on the crystallisation of a specific fat. The solid fat content (SFC) of a fat system can be determined over a given melting range. The solid fat content values are calculated through the partial areas of DSC heating curves usually between 5-60°C and compared to NMR (Minispec) data [iv, v].
To study the aging of a fat or end product the sample is kept at an isothermal temperature to mimic e.g. refrigerator conditions. Comparing the DSC thermograms of a fresh sample and after a known storage time gives information on phase transitions during these storage conditions.
Other studies [vi] involve tempering to investigate the influence on the final product after temperature abuse or due to transport at ambient. Tempering consisted of warming the systems up to a temperature between 15 and 30 °C and cooling down to 5°C. These results can be correlated with the storage modulus (G').

DSC melting and crystallisation behaviour of different types of oils and fats are studied when replacing them in a product. In a factory and also at lab scale, different ingredients are added at different stages of the production process. Adding an ingredient which is not at the correct temperature can cause encapsulation of other ingredients or may stay present in the product as a particle. The filling temperature of a product is important for example to obtain the desired firmness of a product and to prevent graininess.

An AOCS [vii] method can be carried out for quality control of fats to analyse these raw materials used in food products. This is a “fingerprint” method whereby the

sample is melted, subsequently cooled down with a predefined scanning rate to a low temperature. After crystallisation for a specific time, a heating curve is obtained also with a predefined scanning rate.

DSC of starch samples

Starch [viii, ix], a major structure-forming food hydrocolloid [x], is a polymeric mixture of essentially linear (amylose) and branched (amylopectin) molecules. Small amounts of non-carbohydrate constituents (lipids, phosphorus, and proteins) present in native starch also contribute to its functionality. Starch is used as thickening agent in e.g. dry sauce bases, instant soups, mayonnaise, spreads. Starch pastes can be used as stabilizers for oil emulsions in for instance dressings.

Native starch or modified starch used in these types of food products can show different endothermic peaks in the DSC thermograms respectively, retrogradation (recrystallized amylopectin), gelatinization (50<T<80°C depending on the type of starch), amylose-lipid complex (T>100°C) or recrystallized amylose (T>140°C) can be observed.

Retrogradation is only possible in processed (cooked or modified starch) materials which have been stored at lower temperatures. Retrogradation can expel water from a polymer network also known as syneresis but it can also cause dough to harden.

The hydrogen bond arrangement of amylopectin and amylose makes it difficult for water to penetrate into intact starch granules. When the water is heated the granules swell and gelatinization is observed. DSC measures the temperature at which irreversible changes occur in the granule. This process can also be observed by polarised light microscopy during heating.

The starch powders can be analysed dry to obtain information about the pure sample. Additionally, after adding a known amount of water, information is obtained about the degree of gelatinization. The level of water used is of influence on the gelatinization degree and peak shapes. Starch with low and intermediate water content can show more melting endotherms. The gelatinization information can be used to determine the temperature and time necessary for e.g. rice which is used in instant soups. If the rice has a too high amount of gelatinization left in the product, this will result in hard uncooked rice in the instant soup.

Most starches and rice products contain a lipid (fat) which can form an amylose-lipid complex. This complex can be formed during gelatinization [i]. It is also a thermo reversible complex and should show an exothermic peak on cooling. Sometimes the modification of the amylose with a lipid is performed to control the texture of the final starch.

The composition of plain rice [xi] is starch (76.5%), water (12%), protein (7.5%), fat (1.9%) and minors (2.1%). An example of a native rice (Figure 3) and rice slurry (Figure 4) show the presence of retrogradation and amylose-lipid complex endotherms.

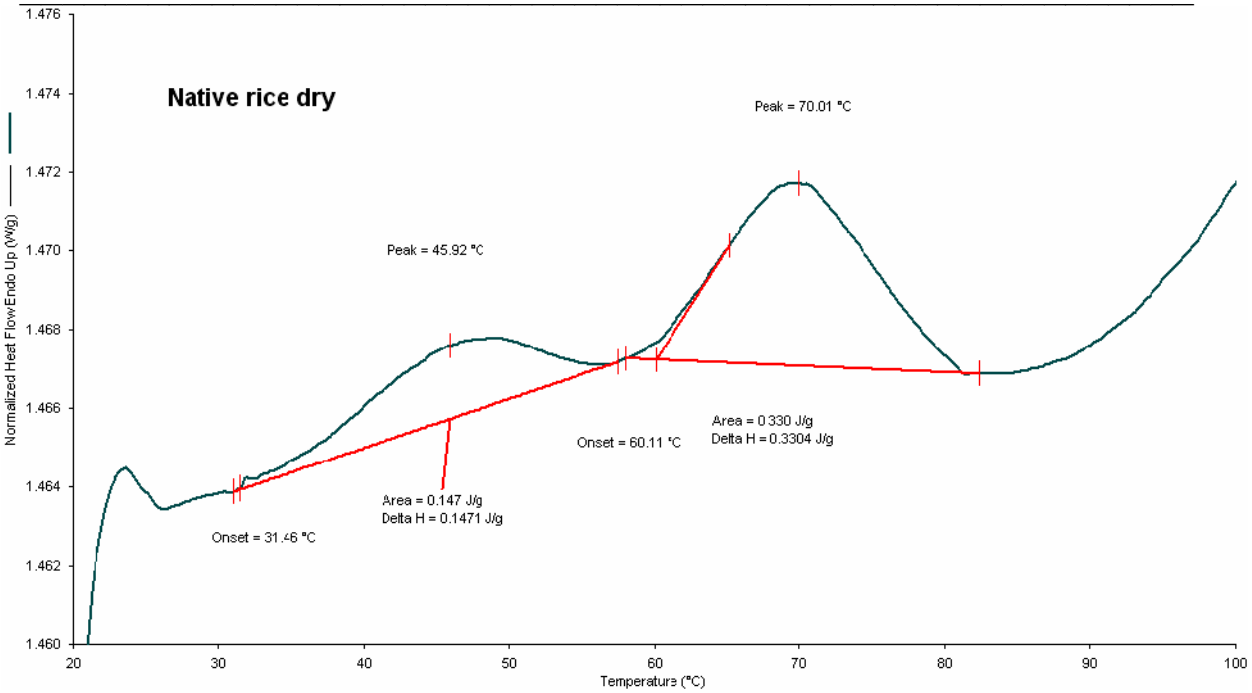

Figure 3. Native rice dry sample showing a retrogradation peak around 45°C and a gelatinization peak around 70°C.

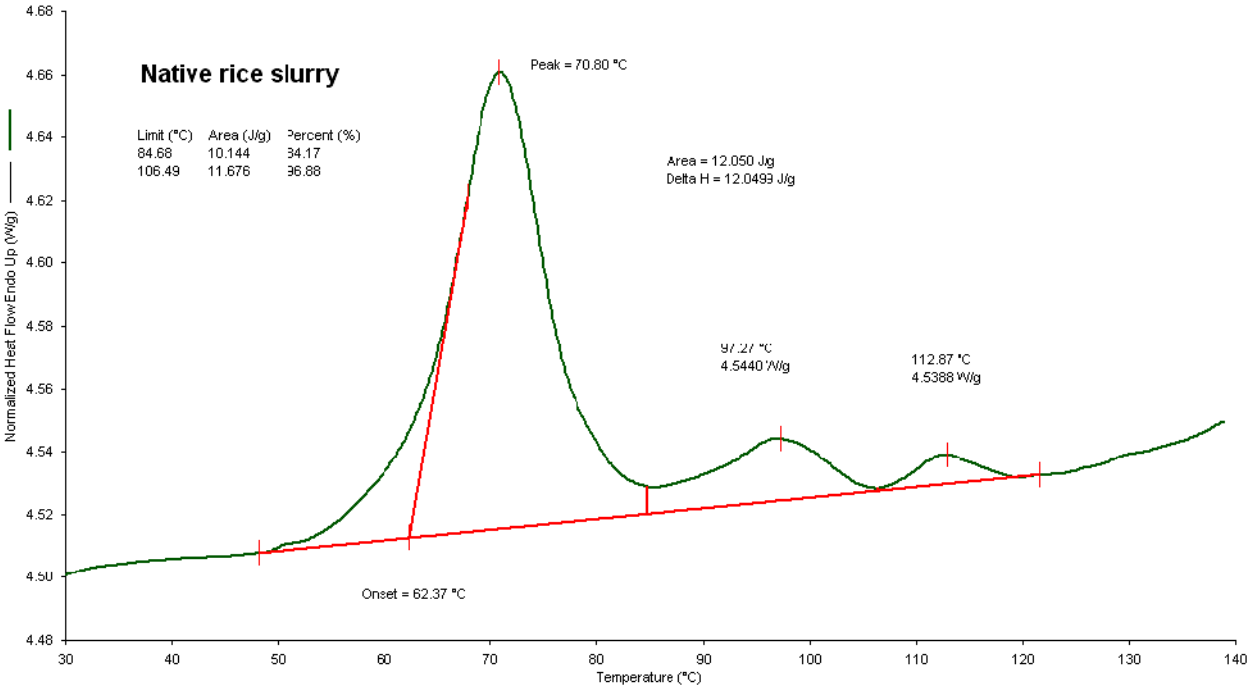

Figure 4. Native rice wet sample showing a gelatinization peak at around 70°C and some amylose-lipid complex at 112°C.

DSC of vegetable powders

Since food products are complex mixtures of several compounds, it is often difficult to determine their glass transition (Tg) temperatures accurately. Understanding the glass transition [xii] phenomenon provides an insight into the causes of the

cohesiveness of many important powders and influencing the wetability or solubility of the powder, which is important for new product development. Food material often contains water which can be present as free or bound water. The free water is related to the wateractivity (Aw). The plasticization effect of water leads to depression of the glass transition temperature causing significant changes in the physicochemical and crystallization properties during storage. Loss of physical stability by the effect of moisture and temperature will reduce flowability and increase caking tendency and, to a smaller extent, affect other physical properties such as colour. A Tg is only observed for amorphous matter. Sugars in a powder can undergo a phase transition from amorphous to crystalline at a given relative humidity during storage and thus have an effect on the glass transition temperature.
DSC is widely used to study glass transition phenomena. The effect of water as a plasticizer on Tg was studied for vegetable powders stored at different Aw values (humidity). At a higher Aw value the samples take up more water. In Figure 5 it is shown that the Tg drops to lower temperatures as the amount of water in the sample increases. The knowledge of Tg in combination with the water activity is important in predicting the physical state of the powder at various conditions, from free flowable to stickiness or phase transitions to crystalline matter.

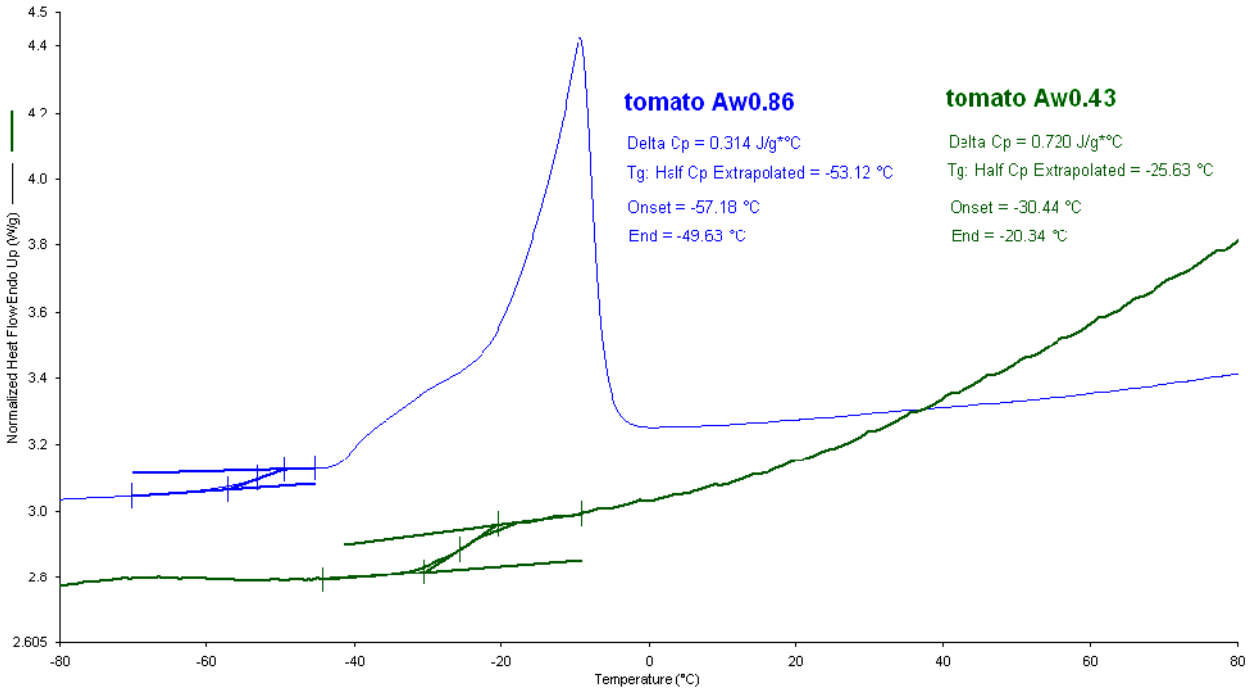

Figure 5. Water influence on Tg of tomato, the Aw 0.86 also shows an endothermic peak which is due to the melting of free water.

Proteins denaturation is also intensively studied by DSC. The influences of pH, salt and polysaccharides were investigated [xiii] for food proteins.

Conclusion

DSC is an essential tool to reveal the underlying phase-compositional principles of food systems. For systems with a clearly established phase-composition-functionality relation, DSC can contribute to the development of novel food products.

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Thermogravimetric Analysis – GC Mass Spectrometry
Application note PerkinElmer

TG-GC/MS Technology –Enabling the Analysis of Complex Matrices in Coffee Beans

Introduction

The combination of a thermogravimetric analyzer (TGA) with a mass spectrometer (MS) to analyze the gases evolved during a TGA analysis is a fairly well-known technique.In cases of complex samples, TG-MS often results in data in which it is nearly impossible to differentiate gases that evolve simultaneously.
Combining TGA with gas chromatography mass spectrometry (GC/MS) allows for a more complete characterization of the material under analysis and precisely determines the products from the TGA.

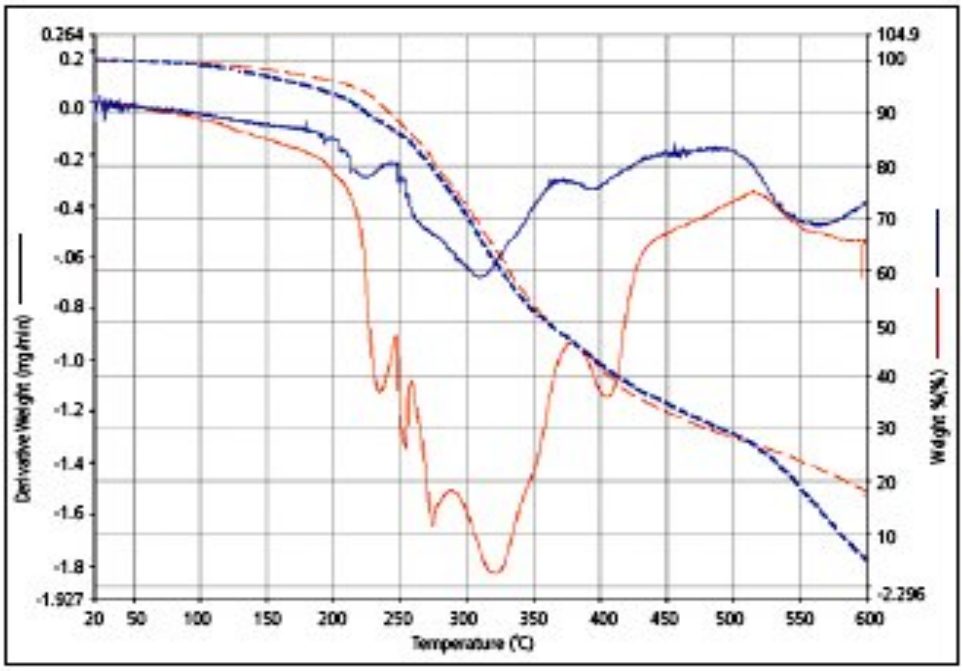
Experimental

This analysis was performed on a PerkinElmer® Pyris™ 1 TGA using alumina pans and the standard furnace. The instrument was calibrated with nickel and iron and all samples were run under helium purge. Heating rates varied from 5 to 40 °C/min, depending on the sample under test. The furnace was burned off between runs in air. Samples were approximately 10-15 mg. Data analysis was performed using Pyris 9.0 Software. During the TG-GC/MS analysis, the PerkinElmer Clarus® 680 C GC/MS was used. A 0.32 mm I.D. deactivated fused-silica transfer line was connected to the GC injector port. The transfer line was heated to 210 °C and connected to the Elite™-1ms capillary GC column. In both cases, data analysis was performed using TurboMass™ GC/MS Software.

Results

In this TG-GC/MS application, coffee beans were analyzed. The TGA resulted in a complex thermogram with many different transitions (Figure 1).

Figure 1. **Resultant thermogram from the analysis of coffee beans. The blue curve is unroasted beans from Africa; the red curve is unroasted beans from Sumatra. The weight loss and the first derivative are shown.**



Complex data was expected as coffee beans are known to contain many different compounds. As a result, it was determined that the evolved gas would likely be too complex for TG-MS, thus TG-GC/MS was determined to be a better approach for this matrix. The goal of the analysis was to search the complex data for two compounds that would be expected in a coffee sample, caffeine (*m/z* 194) and phthalates (*m/z* 149). The caffeine is obviously present in coffee, while the phthalates were a possibility as a result of storage in and contact with plastics.
The resultant GC/MS data is shown in Figure 2 (Page 2), demonstrating a very complex chromatogram. A search for significant peaks resulted in a spectral match

for a phthalate (56 minutes), while a search for *m/z* 194 resulted in a spectral match for caffeine at 60 minutes. As expected, the TGA of coffee beans results in the simultaneous evolution of a large number of gases – TG-GC/MS is able to resolve many of these compounds enabling deeper investigation.

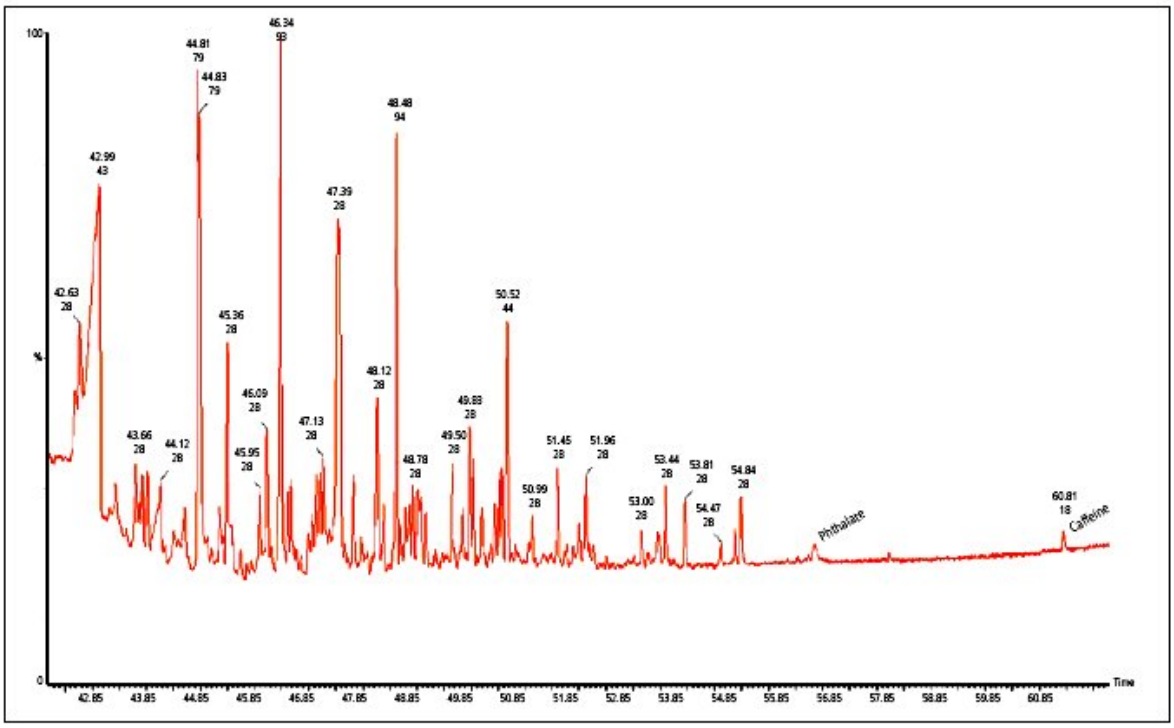


Figure 2. **The GC/MS data resultant from the TGA of African coffee beans.**

Conclusions

TGA analysis allows quantification of the weight loss of a material at specific temperatures. MS increases the power of the technique by providing the ability to identify the species evolved during thermal analysis. TG-GC/MS adds the additional capability of chromatographic separation of co-evolved gases. While not realtime, the improved separation by the GC/MS makes data interpretation easier than TG-MS. This allows the separation of fairly complex mixtures with minimal sample preparation by using the TGA to volatilize components.

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