2011 Annual Meeting Abstacts

Analytical

MONDAY

MORNING

ANA 1 / BIO 1: Lipidomics and Metabolic Analysis

Chair(s): W.C. Byrdwell, USDA, ARS, USA; and R. Weselake, University of Alberta, Canada

Plant Lipidomics to Identify the Roles of Lipids in Plant Stress Responses. R. Welti[1], H.S. Vu[1], M. Roth[1], P. Tamura[1], S. Shiva[1], S. Sarowar[2], V. Nalam[2], G. Klossner[2], K. Lorenc Kukula[2], M. Li[3,4], G. Gadbury[1], J. Shah[2], X. Wang[3,4], [1]Kansas State University, Manhattan, KS, USA, [2]University of North Texas, Denton, TX, USA, [3]University of Missouri at St. Louis, St. Louis, MO, USA, [4]Danforth Plant Science Center, St. Louis, MO, USA

Our group is investigating how membrane lipids change when plants are exposed to environmental stresses. Direct infusion electrospray ionization triple quadrupole mass spectrometry, quadrupole time-of-flight, collision induced dissociation time-of-flight, and Fourier transform ion cyclotron resonance mass spectrometry are being employed to profile lipids as a function of plant genotype and treatment. Currently we are analyzing a large-scale experiment examining the role of oxidized lipids in plant response to biotic and abiotic stresses, including freezing, salinity, bacterial infection, and fungal infection.

Acylated Monogalactosyldiacylglycerols: Their Detection and Possible Biological Roles in Plant Stress Responses. H.S. Vu[1], R. Welti[1], M. Roth[1], P. Tamura[1], S. Shiva[1], S. Sarowar[2], V. Nalam[2], M. Li[3,4], G. Gadbury[1], J. Shah[2], X. Wang[3,4], [1]Kansas State University, Manhattan, KS, USA, [2]University of North Texas, Denton, TX, USA, [3]University of Missouri at St. Louis, St. Louis, MO, USA, [4]Danforth Plant Science Center, St. Louis, MO, USA

Although acylated monogalactosyldiacylglycerols were first discovered almost four decades ago, they have been ignored due to the lack of evidence to support their biological roles. We have developed various mass-spectrometry-based methods to profile monogalactosyldiacylglycerols acylated with both oxidized and non-oxidized fatty acids. Many acylated monogalactosyldiacylglycerols significantly increase in Arabidopsis leaves challenged by different stresses. In responses to biotic stresses, oxidized acylated monogalactosyldiacylglycerols are induced to a much greater extent by avirulent bacterial interactions than by virulent interactions. When challenged by abiotic stresses such as mechanical wounding, freezing or salinity, unique patterns of induction are also observed.

Carbon Flux Analysis in Oil Crops. I.A. Guschina[1], M. Tang[1], U.S. Ramli[2], J.J. Salas[3], P.A. Quant[4], R.J. Weselake[5], J.L. Harwood[1], [1]Cardiff University, Cardiff, Wales, UK, [2]Malaysian Palm Oil Board, Kuala Lumpur, Malaysia, [3]CSIC, Seville, Spain, [4]Oxford University, Oxford, UK, [5]University of Alberta, Edmonton, Canada

Oil-producing plants represent an extremely important group of agricultural crops. The demand for their products has been increased recently by their use (and potential use) for chemical feedstocks, speciality nutraceuticals and, possibly, for biofuels. This is in addition to providing basic edible oils. In order to optimise oil production by crops we need to know how it is regulated both qualitatively and quantitatively. For the latter, flux analysis provides much useful information. We have applied one particular method (top-down flux control analysis) to a variety of important oil crops. Our data show that different crops show distinct properties, making wide generalisations difficult. However, it is possible to use the information from flux control analyses to inform genetic manipulations. This emphasises the importance, as well as the utility, of defining the details of carbon flux to plant storage oils.

Core Aldehydes of PtdCho as Possible Activators of Hydrolysis of Plasma Lipoproteins by Group IIA sPLA2. A. Kuksis, A. Ravandi, W. Pruzanski, University of Toronto, Toronto, ON, Canada

Recent studies have demonstrated that bee venom PLA2 (group III PLA2), which possesses structural similarity to group IIA sPLA2, is activated in liposomes by 1-palmitoyl-2-(9?-oxo-nonanoyl) GroPCho (a core aldehyde) and has suggested that other lipid oxidation products might produce similar effects. Other work had shown that group IIA sPLA2 preferentially attacked the hydroxyl and hydroperoxy linoleates and other oxygenated fatty acids, which were released from PtdCho of plasma lipoproteins at early times of incubation. Later oxygenated arachidonates (isoprostanes) were also identified among the products of plasma lipoprotein hydrolysis by group IIA sPLA2. In the present work we have identified both 1-palmitoyl(stearoyl)-2-[(5-oxo- valeroyl(9-oxo-nonanoyl)] GroPCho among the products of group IIA sPLA2 incubation of HDL and LDL of normal and acute phase plasma. The aldehydes were identified by LC/ESI-MS with reference to synthetic core aldehyde standards. The above liposomal studies and the present demonstration of formation of core aldehydes during a prolonged enzyme digestion provides a plausible explanation for the increased activity of group IIA sPLA2 observed occasionally with PtdCho, but which until now had remained unaccounted for.

Rapid Characterization of Lipids by MALDI MS. J.O. Lay, Jr., J. Gidden, R Liyanage, University of Arkansas, Fayetteville, AK, USA

Lipids can be analyzed after minimal processing in crude extracts without resort to hydrolysis and esterification. For glycerol lipids direct MALDI results in detection of sodium adduct ions of intact triacylglycerols (TAGs) and abundant diacylglycerol (DAG) like fragments. Unless protonated molecule formation is suppressed these fragments are abundant and preclude detection of DAGs in mixtures. DAGs like fragments can be eliminated by addition of base to preclude formation of unstable precursor protonated molecules during ion formation. With phospholipids the loss of the head group can be competitive with fatty acid loss. This can be useful for elucidation of phospholipids class. Indeed direct MS/MS of phospholipids in crude mixtures is very useful for the confirmation of the lipid class when obtaining phospholipids profiles because of the ability to establish parent-ion and product-ion relationships directly from mixtures. Lipid mixtures containing both glycerol- and phospho-lipids show only the

phospholipids by direct MALDI because of suppression of the TAGs by the more polar phospholipids. We have developed rapid SPE separation approaches to produce separate TAGs and phospholipids fractions. We have applied these techniques to the analysis of lipids, lipids-decomposition, olive oil adulteration, microbial taxonomy, lipid metabolism/biochemistry, and lipid oxidation.

Triple Parallel Mass Spectrometry (LC1/MS3) Method for Lipidomic Analysis of Vitamin D and Plant Triacylglycerols in Dietary Supplement Capsules. W.C. Byrdwell, USDA, ARS, BHNRC, FCMDL, Beltsville, MD, USA

Three methods are demonstrated for a complete analysis of vitamin D and triacylglycerols (TAGs) in fortified dietary supplements that virtually eliminates all chemical pretreatment prior to analysis. Three mass spectrometers, in parallel, plus a UV detector, an evaporative light scattering detector (ELSD), and a corona charged aerosol detector (CAD) were used simultaneously. The contents of gelcaps that contained 1000 IU (25 mcg) vitamin D3 in safflower oil and 2000 IU (50 mcg) vitamin D3 in rice bran oil were analyzed without the need for lengthy saponification and extraction. Three to five gelcaps were analyzed, each in triplicate or quintuplicate, using vitamin D2 as an internal standard. Vitamin D3 was analyzed using UV detection, selected ion monitoring (SIM) atmospheric pressure chemical ionization mass spectrometry (APCI-MS), and two transitions of multiple reaction monitoring (MRM) APCI-MS. The triacylglycerols in the oils were analyzed using full-scan APCI-MS, electrospray ionization (ESI) MS, up to MS4, the ELSD and the CAD. Triacylglycerols (TAG) containing fatty acids up to 28 carbons in length were identified. The gelcaps contained more than the label amount of vitamin D3 and differences were seen between synthetic vitamin D and that from fish oil.

LC-MS/MS as a Tool for Probing Industrial Oil Biosynthesis in Seeds. J.M. Dyer[1], T.R. Larson[2], L. Whitehead[2], A. Gilday[2], C.R. Dietrich[3], P. Yang[3], J.M. Shockey[4], C. Lu[5], E.B. Cahoon[6], I.A. Graham[2], [1]USDA-ARS, US Arid-Land Agricultural Research Center, Maricopa, AZ, USA, [2]Center for Novel Agricultural Products, University of York, York, UK , [3]Donald Danforth Plant Science Center, Saint Louis, MO, USA, [4]USDA, ARS, Southern Regional Research Center, New Orleans, LA, USA, [5]Department of Plant Sciences and Plant Pathology, Montana State University, Bozeman, MT, USA, [6]Center for Plant Science Innovation, University of Nebraska-Lincoln, Lincoln, NE, USA

The seed oils of crop plants, composed primarily of triacylglycerols (TAGs), represent a major source of calories for human and animal nutrition and an excellent feedstock for the production of biofuels. In recent years, there has been increasing interest in engineering plants to accumulate high amounts of industrially important fatty acids in the oil, which can substitute for similar types of oleochemicals that are typically derived from non-renewable petroleum. The genes and enzymes required for producing high amounts of industrial oils in plants, however, are not fully understood, and host plants often respond in unexpected ways that limit the production of desired fatty acids. As such, sophisticated analytical techniques are needed to help identify the enzymes and metabolic processes that influence the production of industrial fatty acids in seeds. We have recently developed LC-MS/MS procedures for identifying and quantifying individual TAG molecular species. Application of these techniques to the study of plants producing either

hydroxylated or conjugated fatty acids has shed light on both the mechanisms of fatty acid "channeling" into TAG, as well as several bottlenecks that limit the production of industrial fatty acids in developing seeds. Implications for producing industrial oils in transgenic plants will be discussed.

Applying Genomics and Biotechnology to Design Soybeans for 21st Century Markets. Richard F. Wilson, United Soybean Board, Raleigh, NC, USA

Future gains in U.S. soybean productivity will be a function of superior technology. Advances in soybean genetics and biotechnology will: 1) help ensure an adequate supply, 2) provide cost-effective ways to adapt to government regulations, 3) help sustain domestic livestock markets, and 4) provide health conscience consumers with high quality foods. The United Soybean Board has enabled genetic modifications of soybean composition and yield enhancement that are now filling seed-industry pipelines with a series of elite soybean cultivars distinguished by specific quality traits. For example, soybeans that produce high-oleic oils under private labels are now becoming commercially available. Looking forward, knowledge gained from the sequence of the soybean genome will accelerate the development and deployment of additional traits that will continue to reset the ingredient paradigm for food and feed products. Soybeans with high levels of omega-3 fatty acids, and soybean meal with greater amounts of digestible phosphorus are among the soybean quality trait innovations. This review envisions how these next generation technologies will influence soybean consumption and trade in oilseed markets that are increasingly driven by customer demand for quality, nutrition and value.

Sterol Glycosides in Various Plant Materials Reflect Unique Sterol Patterns. L. Nyström[1], A. Schär[1], A.-M. Lampi[2], [1]ETH Zurich, Zurich, Switzerland, [2]University of Helsinki, Helsinki, Finland

Plant sterols from various plant materials have gained significant scientific interest in the past decades due to their use in functional foods. Recent studies have shown that also glycosylated sterols and natural intake levels of plant sterols can inhibit the cholesterol absorption in the gut. Very little information is available of the occurrence of these polar sterol conjugates in food materials, and even less information is available on the sterol composition found as sterol glycosides. We have demonstrated that the sterol composition as sterol glycosides (SG) and acylated sterol glycosides (ASG) can be significantly different from the total sterol composition found in various edible plant materials (e.g. beans, seeds, fruits, vegetables), and that there are unique patterns of sterol composition in SG from various plant families. Unlike commonly stated in the literature, sitosterol may not always be the most abundant sterol in the glycosylated sterols. Due to their more polar nature, incorporation of glycosylated sterols provides new dimensions to formulation of plant sterols in functional foods. Further, the sterol composition of SG mixtures may be modified by selection of SG source.

Biotechnological Approaches to Remove Chlorophyll Components in Plant Oils. Rene Mikkelsen[1], Janne Brunstedt[1], Birgitte Wittschieben[1], Heidi Pedersen[1], Lis Byrsting Møller[1], Charlotte Poulsen[1], Masoud Zargahi[1], Susan Madrid[2], Ken Carlson[3], [1]Danisco, Brabrand, Denmark, [2]Danisco USA, Palo Alto, CA, USA, [3]Danisco USA, New Century, KS, USA

Plant oils contain a vast number of compounds which potentially interfere with processing, stability, organoleptic properties, health effects etc of the final oil. For example, vegetable oils derived from oilseeds such as soybean and rape seed (canola) typically contain some chlorophyll which has to be removed in the final oil. Modern biotechnology provides a new powerful toolbox to modulate and control the properties of various components found in plant oils. Part of this toolbox is recombinant DNA and protein engineering technologies that make it is possible to create new enzymes targeted specifically towards selected compounds found in plant oils. This combined with modern and improved enzyme production capabilities have made it possible to generate new enzyme solutions for the fats and oil industry. We have isolated enzyme candidates from the chlorophyllase family of enzymes and tested the ability to degrade different chlorophyll components in an oil matrix.

ANA 1.1 / S&D 1.2: Advances in Analytical Methods for Surfactants and Detergents

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Chair(s): D. Scheuing, The Clorox Company, USA; and K. Ma, Cognis Corp., USA

Quantifying Adsorption of Surfactants and Polyelectrolyte Complexes at the Solid-Liquid Interface by Quartz Crystal Microgravimetry with Dissipation. Mona Marie Knock, David R. Scheuing, Michael I. Kinsinger, Clorox Technical Center, Pleasanton, CA, USA

The suitability of quartz crystal microgravimetry with dissipation (QCM-D) for measuring the adsorption of surfactants and polyelectrolyte complexes at the solid-liquid interface is examined. The effect of sensor hydrophobicity on surfactant adsorption is investigated for sodium dodecyl sulfate (SDS), ′dioctyl′ sulfosuccinate sodium salt (AOT), hexadecyltrimethylammonium bromide (CTAB), and dihexadecyldimethylammonium bromide (DHDAB). Surfactant solutions were studied above their respective critical micelle concentration (CMC) and Krafft point in the absence of added electrolyte. Surfactant adsorption at the hydrophobic octadecanethiolate sensor surface was compared with adsorption on hydrophilic gold and silicon dioxide sensor surfaces. The adsorption behavior of net anionic and cationic polyelectrolyte complexes on silicon dioxide was also characterized.

Consumer-preferred Rheology of Surfactant-thickened Cleaning Products. D. Fritter, The Clorox Company, Pleasanton, CA, USA

Surfactants are commonly used to thicken oxidant-containing cleaners through the formation of a viscoelastic network of cylindrical micelles. These systems can exhibit a range of flow properties that influence ease of use and consumer perception of the product. Relevant measures go beyond the traditional thin-to-thick scale of viscosity and include ease of dispensing, elasticity, and cling to vertical surfaces. Rheological characterization provides a way to quantitate flow behavior that allows definition of the consumer-preferred space for a particular application.Viscoelastic materials can be characterized by the zero-shear viscosity, relaxation time, and static shear modulus, as obtained from a Frequency Sweep. For surfactant-thickened formulations, the consumer-preferred rheology for a product that is squirted or sprayed onto a vertical surface is a relaxation time less than about 0.01 s and a zero-shear viscosity greater than about 100 cP. The low relaxation time ensures a smooth and fluid appearance as the product hits and covers the surface, while the zero-shear viscosity requirement ensures that the coating doesn't drain too

quickly. This combination of parameters leads to a product with consumer-preferred cling to vertical surfaces.

Applications of Fourier Transform Infrared Spectroscopy to Studies of Surfactant Behavior. David R. Scheuing, Clorox Services Company, Pleasanton, CA, USA

Liquid water is an intense absorber of infrared light and is thus commonly considered to interfere significantly in the analysis of aqueous systems via FT-IR. However, when the pathlength through the sample is restricted to below about 20 micrometers, a variety of analyses of surfactants in aqueous systems can be readily accomplished with FT-IR. Modern spectrometers, coupled with newer designs of optical accessories, can be used routinely and efficiently to characterize the behavior of surfactants or formulations on clean surfaces or on controlled dirty surfaces through the use of internal reflection (attenuated total reflectance or ATR) techniques. Due to the short effective pathlengths achieved with ATR and the excellent reproducibility of signals in the frequency domain with modern instruments, the elimination of the normally intense absorption due to water can be readily achieved via spectral subtraction or ratio techniques. Spectra of a variety of water-solid interfaces can be obtained, and hence the chemical analysis of these interfaces, including time-resolved changes is possible. The combination of FT-IR data with results from other surface analytical techniques can be used to probe formulation performance or more fundamental properties of phase separation of aqueous systems of practical interest.

Application of LC-MS to Surfactant Analysis. David Dabney, Stepan Company, Northfield, IL, USA

Mass spectrometry has taken an increasing role in all segments of analytical analysis over the last 20 years. From quantitative analysis related to biologics to structural elucidation of novel compounds, mass spectrometry continues to improve our understanding of the materials we use everyday. The application of mass spectrometry to the study of surfactants while not new has generally been limited to the identification of surfactants related to biologic matrices. Here we apply mass spectrometry to the analysis of surfactants for the purpose of understanding the composition and properties of the surfactant as a stand alone entity. By understanding the total composition of our materials we provide for the information necessary for regulatory, manufacturing, performance and quality of the surfactants. Mass spectrometry is well suited for this endeavor due to its dynamic range, ability to be coupled to various separation techniques and array of ionization and mass selection configurations as well as rapidly improving data evaluation techniques. In this talk, the basic principles of mass spectrometry will be reviewed along with examples of mass spectrometry being applied to the evaluation of various surfactant chemistries.

Emerging Ambient Ionization Methods and Their Use to Characterize Substrate Modifications. Ismael Cotte-Rodriguez , The Procter & Gamble Co., Global Analytical, Cincinnati, OH 45252, USA

Tools that allow rapid in-situ analysis of ambient surfaces with minimal or no sample preparation are ideal to monitor substrate modifications. This presentation focuses on the use of desorption

electrospray ionization (DESI) as an imaging tool to understand substrate modification. DESI is a powerful ambient ionization method that combines features of desorption ionization with those of spray ionization. DESI allows mass spectrometry to be performed on samples that are in ambient environments. The method is based on directing a pneumatically-assisted electrospray onto a given surface, from which small organics and large biomolecules are picked up, ionized and delivered as desolvated ions into the mass spectrometer. Increased selectivity is achieved both by MS/MS and by including additives in the spray solvent (Reactive-DESI). DESI has high sensitivity, is suitable for characterization of both large and small molecules, and allows the direct analysis of pure compounds and formulated mixtures deposited on surfaces or in tissue without sample preparation. Examples of applications in consumer product development will be covered including analyte-substrate interactions and quantitation approaches for selected analytes.

Analytical Toolbox to Unveil Complex Mixtures of Surfactant-Based Systems. Michele Mangels[1], José Andrés Rojo[1], Bob Strife[2], Kevin Garber[2], [1]The Procter & Gamble Co., Miami Valley Innovation Center, Cincinnati, Ohio, USA, [2]Mason Business Center - Analytical GCO, Cincinnati, Ohio, USA

The characterization of the complex mixtures found in many surfactant-based systems and detergent products poses unique analytical challenges. The surfactant raw materials themselves are often intricate mixtures of active molecules that generally need to be formulated into blends with other raw materials involving co-surfactants, functional polymers and many other organic and inorganic chemicals and solvents. A variety of analytical approaches are available for the characterization of these mixtures. Presented are a broad suite of analytical techniques currently in use for understanding various polar and non-polar surfactants with nonionic, cationic, or anionic functionalities. Chromatographic approaches discussed range from the use of gas and high pressure liquid chromatography, including the use of supercritical fluids and the so-called aqueous normal phase separation mode. Detection techniques discussed which prove useful in the characterization of these complex systems include flame ionization, evaporative light scattering, and both low and ultra-high resolution mass spectrometry with various types of ionization sources. Also discussed are some approaches used to help visualize the complex data sets generated by these techniques.

AFTERNOON

ANA 2: Advances in Spectroscopic Techniques

Chair(s): T. Mason-West, Bunge, USA; and TBD

E-Nose and TD GCMS on Oxidized Canola Oils. M.D. Evenson, J.A . Flook, T.G. Patterson, A. Syed, C.J . Kahl, D.H. Meyer, Dow AgroSciences, Indianapolis, IN, USA

Oxidative stability is a key factor in the selection of oils for food applications. Volatile compounds generated during the oxidation of oil will impact both the flavor and aroma characteristics of cooked food products. A comparative study was conducted to evaluate the

composition and sensory attributes of volatiles emitted from two different cooking oils using Thermal Desorption Gas Chromatography Mass Spectroscopy (TD/GCMS) and Electronic Nose (E-Nose) technologies. Over one hundred volatile compounds were identified by TD/GCMS from used oils. Many were common to both oils and show a linear relationship to the accelerated aging, several had a plateau at a specific time point and others were specific to the individual oils. The same sample set was also evaluated on the E-Nose and aroma maps were generated. Aroma sensing by E-Nose offers a powerful new technology for determining oil quality and characteristics on the basis of an aroma profile from a complex mixture of volatile compounds. As detailed information is generated on the aged oils, specific compounds that produce undesired or desired aromas or flavors could be determined, altered or masked in the oil to improve the stability or sensory profiles.

Analysis of Color Bodies in Vegetable Oil. J.B. Soe, R. Mikkelsen, L. Lauridsen, T. Jorgensen, Danisco A/S, Brabrand, Denmark

Vegetable oils like soya oil and rapeseed oil produced form extraction of beans or seeds contain a number of oil soluble minor components including carotene, tocopherols, chlorophylls or degradation products of chlorophylls like pheophytins and pyropheophytins. Some of these components are crucial for the quality of oil.Over the years a number of analytical methods have been developed to analyse these minor components and methods can among others be found as AOCS standard methods.Many of these methods rely on photometric measurements, which can be used in the quality control during refining of vegetable oils.Analysis of chlorophyll, pheophytin and pyropheophytin is however a challenging task,at least in refined oil where these components are found in low ppb level.In order to understand the effect of enzymatic degradation of green color bodies it is crucial to be able to analyse these components.Development of a analytical method based on advanced HPLC/MS equipment, is shown to give the possibility for detection of chlorophyll, pheophytin and pyropheophytin components individually as well as their degradation products in the low ppb range.In the presentation examples of analysing these colour components in oil samples from crude to refined oil will be shown.

Updating a Synchronous Fluorescence Spectroscopic Virgin Olive Oil Adulteration Calibration to a New Geographical Region. J.H. Kalivas[1], M.R. Kunz[1], J. Ottaway[1], C.A. Georgiou[2], G.A. Mousdis[3], [1]Idaho State University, Pocatello, ID, USA, [2]Agricultural University of Athens, Athens, Greece, [3]National Hellenic Research Foundation, Athens, Greece

Detecting and quantifying extra virgin olive adulteration is of great importance to the olive oil industry. Many spectroscopic methods in conjunction with multivariate analysis have been used to solve these issues. Successes to date are limited as analyses are specific to included geographical regions, growing seasons, cultivars, etc. (the composite primary condition). Samples from new geographical regions, growing seasons, etc. (secondary conditions) are not always correctly predicted by the primary data due to the secondary conditions not matching the primary conditions. Three Tikhonov regularization (TR) variants are used in this presentation to allow adulterant (sunflower oil) concentration predictions in samples from geographical regions not part of the original primary domain. Of the three TR variants, ridge regression with an additional 2-norm penalty provides the smallest validation sample prediction errors. While the

presentation reports on using TR for model updating to predict adulterant oil concentration, the methods are applicable to updating multivariate analyses distinguishing adulterated samples from pure extra virgin olive oil. Additionally, the approaches are general and can be used with other spectroscopic methods and adulterants as well.

On-line Monitoring of the Transesterification Reaction Between Triglycerides and Ethanol Using Near Infrared (NIR) Spectroscopy. R. Richard[1,2], B. Dubreuil[1,2], S. Thiebaud-Roux[1,2], L. Prat[3], [1]Université de Toulouse; INPT; LCA (Laboratoire de Chimie Agro-Industrielle); ENSIACET, F-31030 Toulouse, France, [2]INRA; LCA (Laboratoire de Chimie Agro-Industrielle), F-31030 Toulouse, France, [3]Université de Toulouse; INPT; CNRS; Laboratoire de Génie Chimique; UMR 5503, F-31030 Toulouse, France

To substitute fossil fuels, biodiesel can be produced from vegetable oils, animal fats, and waste cooking oils by transesterification with ethanol. Various factors such as free fatty acid content, water content, type/amount of catalyst, vegetable oil to alcohol molar ratio, or temperature can affect this process. Many analytical procedures using gas chromatography and high performance liquid chromatography have been developed to determine the composition of crude transesterification products but these techniques are long to handle, unreliable and expensive methods of on-line monitoring. In this work, an innovative method using NIR spectroscopy to on-line monitor the transesterification reaction of high oleic sunflower oil with ethanol in a one-liter-batch reactor was developed. Partial least squares regression was used to develop calibration models between NIR spectral data and analytical data obtained by a reference method: gas chromatography with flame ionization detection (GC-FID). The results indicated that the use of NIR spectroscopy is an appropriate technique to research optimal reaction parameters and obtain kinetic data for a range of temperature from 30°C to 80°C. It was also shown that the water content in ethanol or oil has a negative influence on ethyl ester production.

Using Fourier Transform Near Infrared (FTNIR) in Evaluation of Monoacylglycerides and Propyleneglycolmonoester in Edible Fats and Oils. Gabriela Sekosan, Tiffanie West, Bunge North America, Bradley, IL, USA

A rapid and new method for the quantitation of the amount of monoacylglycerides, α-monoacylglycerides and propyleneglycolmonoester in both emulsifier and oils and fats containing emulsifiers, was developed using NIR. For the calibration of the instrument more than 100 samples with ranges of 0-75% were used. The new method reduces the preparation and analysis time from 3 hours to less than 10 minutes and is eliminating the solvent use.

Analysis of Epoxidized Soybean Oil using Fourier Transform Near Infrared Spectroscopy (FT-NIR). H. Li[1], M. Ochs[2], M. Gulden[2], [1]Bruker Optics, Inc., USA, [2]CHS, Inc., USA

Epoxidized soybean oil (ESBO) is widely used as a plasticizer and heat stabilizer for polyvinyl chloride (PVC) plastics. There are several parameters used to control the epoxidiation process and the quality of the finish product. Iodine value (IV) is used to help determine when all the carbon-to-carbon double bonds have been opened and when to stop the reaction. Moisture content is used to determine the moisture residule in finish product from the washing procedure, of which the value should be very low since water can cause degradation of epoxide group. The

oxirane value (OV) is another measurement to determine if the epixidation reaction was completed during the reaction. While acid value (AV) needs to be checked to determine if any residual acid that is used in the reaction remains in the ESBO product.Fourier transform near infrared (FT-NIR) spectroscopy was used to in this study to analyze multiple measurement parameters in washed ESBO during process and finish ESBO production samples. For washed ESBO, partial least squares (PLS) calibration model was developed for IV and an independent test set validation of the calibration model yielded root mean square error of prediction (RMSEP) value of 0.79 (mg I_2/g). A set of finish ESBO samples were used for developing PLS calibration models for measuring acid value, iodine value, moisture and oxirane value, and leave-one-out cross validations for each model gave values for RMSECV of 0.38 (mg KOH/g), 0.88 (mg I_2/g), 0.05% and 0.14% respectively. Overall, the results of this study demonstrate the feasibility of FT-NIR spectroscopy for the routine analysis of ESBO finish product and process control of epoxidization of soybean oil.

TUESDAY

AFTERNOON

ANA 3.1 / LOQ 3: Antioxidants and Oxidation Control: Analytical Methodologies and Efficacies

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Chair(s): D. Luthria, USDA, ARS, USA; and F. Shahidi, Memorial University of Newfoundland, Canada

Efficacy and Measurement of Antioxidants. F. Shahidi, Department of Biochemistry, Memorial University of Newfoundland, St. John's, NL, Canada

Antioxidants in food and biological systems have received increasing attention in recent years due to better appreciation of their role in food preservation as well as in health promotion and disease risk reduction. The efficacy of antioxidants from natural origin in foods depends on the source material, activity of the relevant phytochemicals related to their structural characteristics and lipophilicity/hydrophilicity. In addition, concentration of antioxidants, presence of other food constituents and storage conditions, among others, are important factors affecting antioxidant activity. The mechanism of action of antioxidants may be quite varied and testing of their efficacy should include several assays that are complementary to one another. In addition, sampling techniques as well as release of bound antioxidants from food matrix is essential when correlating in-vitro data with in-vivo results.

Comparison of Extraction Solvents on Assay of Phenolics Form Foods. Devanand Luthria, USDA, ARS, ERRC, USA

Increased interest in bioactive food components and phytochemicals has arisen from numerous epidemiological studies that suggest that certain phytochemicals can reduce risk of chronic diseases. This presentation will illustrates with examples the significance of optimization of extraction procedures in developing analytical methodologies for accurate estimation of bioactive compounds present in foods and dietary supplements. It will discuss the importance of

different sample preparation parameters such as extraction solvent composition, solid-to-solvent ratio, temperature, and particle size for the accurate assay of phenolic compounds in different food matrices. Furthermore, effect of drying and grinding procedures on the assay of phenolic compounds from plant and food samples will also be presented. A comparison of current (pressurized-liquid, ultrasonic irradiation, and microwave-assisted) and classical (stirring, Soxhlet, shaker, vortex) extraction procedures on the assay of phenolic phytochemicals will also be discussed. A systematic protocol for optimizing sample preparation procedure for extraction and assay of phytochemicals from different plant matrices will also be presented. Accurate analysis of bioactive compounds is critical for their precise and reproducible quantification in different foods, establishing appropriate dietary intake and safety guidelines, and understanding their role in human health and nutrition.

Extraction and Analysis of Soluble and Bound Fruit Polyphenols. L. Howard, B. White, University of Arkansas, Dept. Food Science, Fayetteville, AR, USA

Polyphenols in fruits and their co-products are typically extracted with aqueous-organic solvent mixtures prior to HPLC analysis or determination of antioxidant capacity. Evidence is increasing that significant quantities of polyphenols in fruits, especially hydrolysable and condensed tannins are entrapped or bound to cell wall polysaccharides and resist extraction using conventional extraction techniques, suggesting levels of fruit polyphenols reported in the literature have been vastly underestimated. The release of bound polyphenols from fruits following conventional extraction can be performed using acid or alkaline hydrolysis methods, but both methods have limitations due to the lability of polyphenols and formation of side products under harsh chemical conditions, and lack of authentic standards for quantification. These methods along with their advantages and disadvantages will be discussed as well as the potential implication of bound polyphenols on gastrointestinal health.

Challenges with Antioxidant Analysis: Strengths and Weaknesses. W. Ellefson, D. Sullivan, Covance Laboratories, Madison, WI, USA

Today?s marketplace reflects consumers demand for healthy products. Products that are high in antioxidant content are one area of major interest. There are a variety of general methods (ORAC, DPPH, Folin-C, FRAP, etc.) to measure antioxidant potential. In addition there are many methods that assess the level of individual categories (e.g., catechins, isoflavones, etc.) or individual compounds. All methods have strengths and weaknesses. This presentation will focus primarily on these strengths and weaknesses. An overview of the application of a selected number of these methods will be presented along with estimates of what compounds each test is capable of measuring. Specific examples will be highlighted, including the stability indicating nature of some of these test methods. This discussion will provide an overview of many of the analytical techniques and highlight the need for harmonized methods of analysis. Some of these methods have more specific applications with selected matrices, while others have a broader application. When there are numerous methods for the same analyte there is significant room for disagreement. We will highlight a process to come together, discuss common methods, agree on an approach, and complete a study to develop