세부프로그램

FEBRUARY 10

BRIEF ORAL SESSION

10:30 – 12:10

컨벤션 홀

Organizer: 박종호 (한국원자력연구원) / 차상원 (한국외국어대학교)

Chairs: 강덕진 (한국표준과학연구원) / 차상원 (한국외국어대학교)

10:30–10:35 Do-It-Yourself (DIY) Manufacture of a Nano-LC MALDI Spotter Robot using a 3D Printing Technology
이재웅 (서강대학교)

10:35–10:40 Online non-contiguous fractionating and concatenating device coupled to two dimensional reverse phase/reverse phase liquid chromatography system for efficient and comprehensive proteomic analyses
이한겨레 (고려대학교)

10:40–10:45 A metabolomics-driven approach reveals metabolic responses and mechanisms in the rat heart following myocardial infarction
남미소 (한국기초과학지원연구원)

10:45–10:50 Size-dependent analysis of urinary exosomal lipids by flow field-flow fractionation and nanoflow ultrahigh-performance liquid chromatography tandem mass spectrometry (nUPLC-ESI-MS/MS)
양준선 (연세대학교)

10:50–10:55 Label free quantitative proteomics using peptide isotope peak intensities in mass spectrometry
윤기나 (한국기초과학지원연구원)

10:55–11:00 Evaluation of single particle ICP-MS for screening nanoparticles in environmental samples
이상준 (한국표준과학연구원/경희대학교)

11:00–11:05 Comprehensive profiling analysis of 20 urinary neurochemicals using in situ derivatization and liquid chromatography-tandem mass spectrometry
이원웅 (경희대학교)

11:05–11:10 Site-specific characterization of N-glycoproteins in human and mouse plasma samples by LC-MS/MS
이현경 (한국기초과학지원연구원)

11:10–11:15 Korean whole salivary proteome: a preliminary report
조하라 (단국대학교)

11:15–11:20 Comparative study on extraction method of fragrance allergens in water using GC-MS/MS
이인자 (서울물연구원)

11:20–11:25 Simultaneous determination of chlorogenic acid isomers and metabolites in rat plasma using LC-MS/MS
최원구 (가톨릭대학교)

11:25–11:30 UPLC-MS/MS based profiling of eicosanoids in RAW264.7 cells
최유리 (경희대학교)

11:30–11:35 Development of new chemical separation method for uranium age-dating of UO2 materials
최은주 (한국원자력연구원)

11:35–11:40 Steroidal CYP enzyme activities in human amniotic fluid by GC-MS
한소윤 (한국과학기술연구원)

11:40–11:45 Glycomic profiling of serum haptoglobin using nano LC/MS and LC/MS/MS
이성현 ((주)글라이칸)

11:55–11:50 Simultaneous analysis of thiamine and biotin in infant formula by isotope dilution-liquid chromatography mass spectrometry
주자연 (충남대학교)

11:50–11:55 Glycan signatures of human saliva
문한태 (충남대학교 분석과학기술대학원)

11:55–12:00 The effect of Sodium and Potassium ions for sucrose detection by comparing charcoal, DHB and CHCA matrices in MALDI-MS analysis
백지현 (충남대학교)

12:00–12:05 Reactive paper spray ionization mass spectrometry for the analysis of the conjugated ketones
최수빈 (한국외국어대학교)

12:05–12:10 Effect of Ca(II) on the conformation and aggregation process of alpha-synuclein
한종윤 (고려대학교)

Brief Oral Session-1

Do-It-Yourself (DIY) Manufacture of a Nano-LC MALDI Spotter Robot using a 3D Printing Technology

Jae-ung Lee, Han Bin Oh

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The 3D printing technology is growing very rapidly, and is bringing about significant advances in many research areas. On the 3d printing related website, the stories of making 3d printed parts and custom equipment have been posted. In this research, we made a DIY nano-LC MALDI spotter robot using 3D printed custom parts. Using this equipment, nano-LC and MALDI matrix loading can be conveniently coupled online and thus the separated eluents from nano-LC can be loaded automatically onto the MALDI plate. This DIY robot was made of only 3d printed parts and the parts on the online marketplace, so that anyone can make it and carry out maintenance easily and inexpensively. In this DIY robot, the loading speed can be readily controlled using a home-coded software. In addition, a camera is equipped so that the loading process can be monitored.

Brief Oral Session-2

Online non-contiguous fractionating and concatenating device coupled to two dimensional reverse phase/reverse phase liquid chromatography system for efficient and comprehensive proteomic analyses.

Hangyeore Lee, Jeong Eun So and Sang-Won Lee

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In this talk, a novel online two-dimensional reverse-phase/reverse-phase liquid chromatography (2D-RP/RPLC) separation platform, employing a newly developed online non-contiguous fractionationg and concatenating device (NCFC fractionator), will be presented. In bottom-up proteomics analyses of a complex proteome, this system provided significantly improved exploitation of the separation space of the two RPs, considerably increasing the numbers of peptides identified compared to a conventional contiguous 2D-RP/RPLC method. The fully automated online 2D-NCFC-RP/RPLC system bypassed many labor-intensive manual processes (i.e. offline fractionations, manual pooling, clean-up, drying/reconstitution, and autosampler fraction injection) required with the conventional offline 2D-NCFC RP/RPLC method, and thus, it offers minimal sample loss in a context of highly reproducible 2D-RP/RPLC experiments.

Brief Oral Session-3

A metabolomics-driven approach reveals metabolic responses and mechanisms in the rat heart following myocardial infarction

Miso Nam[1,2], Sunhee Jung[1,2], Do Hyun Ryu[2], Geum-Sook Hwang[1,3]

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Myocardial infarction (MI) is caused by myocardial necrosis resulting from prolonged ischemia. However, the biological mechanisms underlying MI remain unclear. We evaluated metabolic and lipidomic changes in rat heart tissue from sham and MI at 1hr, 1day and 10day after coronary ligation, using global profiling based on metabolomics. A time-dependent increase or decrease in polar and lipid metabolite levels was measured. The S-adenosylmethionine (SAM) concentration and the SAM/S-adenosylhomocysteine (SAH) ratio gradually decreased in a time-dependent manner and were significantly downregulated 10 days after MI. Transcriptome analysis revealed that the levels of coenzyme Q (*Coq*)-*3* and *Coq5*, both of which are SAM-dependent methyltransferases, were decreased in the MI groups. These results suggested that dysregulation of SAM may be related to down regulated COQ biosynthetic pathway. In addition, short-chain (C3) and medium-chain (C4-C12) acylcarnitine levels gradually decreased, whereas long-chain acylcarnitine (C14-18) levels increased, owing to a defect in β-oxidation during ischemia. These changes are related to energy-dependent metabolic pathways, and a subsequent decrease in adenosine triphosphate concentration was observed. The comprehensive integration of various omics data provides a novel means of understanding the underlying pathophysiological mechanisms of MI.

Brief Oral Session-4

Size-dependent analysis of urinary exosomal lipids by flow field-flow fractionation and nanoflow ultrahigh-performance liquid chromatography tandem mass spectrometry (nUPLC-ESI-MS/MS)

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Exosomes are small membrane vesicles (diameter of 20 to 100 nm) that are secreted by various kinds of cells. Exosomes contain biological molecules such as mRNA, proteins, and lipids that are originated from cells and they transport these molecules between cells. The cell-to-cell communication process, which is related to the immune system, affects transition of pathogens or growth of tumor cells and recent studies on exosomes have been focused on understanding its role and discovering biomarkers of diseases.

Exosomes are found in various kinds of body fluids, such as blood or urine, and urinary exosomes are usually originated from prostate or kidney cells. Closely related to prostate cancer (PCa), the size of PCa derived urinary exosomes is reported to be different from that of normal ones.

Flow field-flow fractionation (FlFFF) is an elution based analytical technique that separates sample components according to their sizes. In this study, urinary exosomes of controls and PCa patients were first retrieved by using ultracentrifugation and asymmetrical FlFFF (AF4) was adopted to sort out urinary exosomes according to their sizes. Exosomes in different sizes were collected and lipids within them were analyzed to discover any possible biomarker candidates. The overall lipid amounts were increased in PCa patient exosomes and lipids from small exosomes showed more changes than larger exosomes.

Brief Oral Session-5

Label free quantitative proteomics using peptide isotope peak intensities in mass spectrometry

Ki Na Yun[1,2], Gun Wook Park[1], Ju Yeon Lee[1], Eun Sun Ji[1], Mee-Jung Han[3], Han Bin Oh[2], Jong Shin Yoo[1], Jin Young Kim[1]

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[2]Department of Chemistry, Sogang University, Seoul, Korea

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We have developed an automated label-free protein quantification method that utilizes the combined intensity of top three isotope peaks at three highest MS spectral point. It was named three isotopes quantification (TIQ) that allows for a comparative protein analysis in a computational manner. The efficiency of TIQ was demonstrated by a benchmark dataset with two proteomes at known ratios. We accurately detected the mixing ratio over the entire protein expression range, with greater precision for abundant proteins. The performance of TIQ was also compared to that of SWATH-MS in terms of the number of quantified peptides and proteins and the specificity to detect differentially abundant proteins, where SWATH-MS is another approach for label free protein quantification utilizing the MS/MS intensity. There are a few advantages to TIQ. First, because it requires no peak area generation from the extracted ion chromatogram (XIC), it allows high-speed quantitation. Second, it is effective to remove signal interference from co-eluted ions with similar m/z values by evaluating the isotope pattern. And third, considering top three isotope peaks provides more sensitive results with better S/N ratios.

Brief Oral Session-6

Evaluation of Single Particle ICP-MS for Screening Nanoparticles in Environmental Samples

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Increased use of engineered nanoparticles (NPs) in various fields of industry and consumer products has imposed potential risks to the environment and human health. Therefore, it is important to characterize NPs from the manufacturing to the final disposal in the environment for better understanding of the life-cycle of NPs and its impact. Recently, single particle (SP) ICP-MS has been attracted a lot of attentions to characterize the NPs, since it can simultaneously provide the information on elemental composition, particle size, and particle number concentration of a nanoparticle. It also allows detection of small numbers of NPs in a sample which is quite suitable for detection of low-abundant NPs in environmental samples. In a favorable condition, dissolved ion signals are distinguishable from NPs signals and provide additional information on dissolve ions. SP ICP-MS can be developed as a fast screening method for NPs in a real-world sample due to its decent analytical characteristics. For this purpose, we carried out preliminary investigation focused on technical limitations of SP ICP-MS. Relatively well-characterized Au and Ag NPs were used as the test samples. Element-dependent detection limits for NPs size, the influence of blank signal drift of easily dissoluble NPs, and separation of NPs pulses from electronic noises were investigated.

Brief Oral Session-7

Comprehensive profiling analysis of 20 urinary neurochemicals using *in situ* derivatization and liquid chromatography-tandem mass spectrometry

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Dopamine, serotonin, GABA and their metabolites play a key role in multiple regulatory systems and the change of their physiological levels are closely associated with neurological disorders. Thus the development of a reliable analytical method of neurochemicals in biological fluids is important to discover potential biomarkers for the diagnosis, treatment and prognosis of neuronal disease. However, the analysis of neurochemicals in biological sample was challenging, because of highly different polarities between basic precursor and acidic metabolites, their low physiological amounts and high matrix interferences in biological samples. In this study, we developed a liquid chromatography-tandem mass spectrometry (LC-MS/MS) combined with Fischer esterification for comprehensive profiling of 20 neurochemicals in urine. *In situ* Fischer esterification could greatly improve the peak separation capacity and MS detection in a single run LC-ESI-MS/MS-positive ion mode due to reducing distinct physicochemical properties. After esterification, desalting process could significantly reduce the ion suppression of some analytes in MS detection. Esterified acidic neurochemicals were well retained on reversed-phase C18 column and separated with other basic neurochemicals within 6 min. Also, esterification analytes produced specific fragment ions to provide high sensitivity and selectivity in MRM mode. Established method was validated in terms of linearity, precision, accuracy, recovery, and matrix effect. Human urine samples collected from patients with Parkinson's disease and controls (patients; 21, controls; 10) were successfully analyzed to explore important biomarkers caused in metabolic disorder. In conclusion, this method may be helpful for comprehensive studying of neuropathological mechanism and discovering biomarkers for neurological disease.

Brief Oral Session-8

Site-specific characterization of N-glycoproteins in human and mouse plasma samples by LC-MS/MS

Hyun Kyoung Lee[1,2], Ju Yeon Lee[1], Gun Wook Park[1,2], Jin Young Kim[1] and Jong Shin Yoo[1,2]

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Mouse has been used as an animal model for scientific research owing to its physiological similarity to human. However, their N-glycosylation of protein showed many differences between mouse and human. Usually N-glycosylation is directly involved in biological process and plays crucial role in human diseases due to their unusual biological sensitivity. Therefore, the specific characterization of N-glycosylation in model mouse is necessary in order to investigate progression of disease.

This study provided a method to characterize the site-specific N-glycosylation of human and mouse plasma. We compared site-specific N-glycosylation in human and mouse plasma samples using LC-MS/MS with GPA (GlycoProteome Analyzer) system[1]. As reported previously, we confirmed that the sialic acid of N-glycopeptides was almost entirely Neu5Gc in mouse plasma, while in human plasma was Neu5Ac. Especially, a unique trisialylated biantennary N-glycopeptide (peptide_$Hex_2HexNAc_2NeuGc_3$+$Man_3GlcNAc_2$) was specifically identified from several glycoproteins in mouse plasma. The trisialylated biantennary glycoform was recently reported in mouse serum, although it could not determine the binding position of the third Neu5Gc. We first report that it is directly linked to GlcNAc with evidence of specific oxonium ions and glycopeptide fragment ions in MS/MS spectra. This clearly proves that the new structure of trisialylated biantennary N-glycopeptide found only in mouse plasma.

Reference

1. Gun Wook Park and Jin Young Kim et al., *Scientific Reports*, 6:21175 (2016)

Brief Oral Session-9

Korean whole salivary proteome: a preliminary report

Ha Ra Cho, Han Sol Kim, Yong Seok Choi*

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Saliva is considered as a good biological fluid for the purpose of monitoring biomarkers due to its suitable characteristics as a biological sample, for example, the non-invasive nature during its sampling and the easiness of collecting the relatively large volume of a sample. However, while proteomic studies on various types of saliva have been carried out in the United States and Europe over a decade, any proteomic research on saliva was never tried in Korea, yet. Thus, as the first step of Korean salivary proteomics, we are conducting a study to construct the first Korean reference salivary proteome, and its preliminary report is presented here. From the proteomic analyses of whole saliva (WS) samples from healthy Korean volunteers, many proteins in Korean WS have been being identified. While gene ontology distributions of Korean WS proteome are similar with those previous reported from other countries, a large portion of proteins in Korean WS is found to be unique by the comparisons with salivary proteome databases. Thus, the distinctiveness of Korean salivary proteome is strongly expected and the results from this on-going study could be widely used as the basement of future researches on the discovery/application of disease biomarkers from Korean WS.

Brief Oral Session-10

Comparative study on extraction method of fragrance allergens in water using GC-MS/MS

IN JA LEE*, Haksun Kwon, Chi-hwa An, Jae-Chan Ahn, Bogsoon Kim

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Products containing 26 of these compounds, which are fragrance allergens likely to cause contact allergies, are required under domestic cosmetic law to be labeled when their concentrations exceed 0.01% for rinse-off products (e.g. cleansers, shampoos), and 0.001% for leave-on products (e.g. lotions, deodorants) beginning in 2008. Fragrance allergens are continuously introduced into the environment via urban waste water effluents because they are important components of products used in daily life such as soaps, shampoos and lotions, so it is needed to develop the analysis to investigate those fragrance allergens.

Methods based on solid phase micro extraction(SPME) and liquid-liquid extraction(LLE) followed by GC-MS/MS have been studied for the analysis of 24 fragrance allergens excepting for 2 natural materials in water. Extraction conditions such as the kind of fiber, extraction temperature, type of solvent, amounts of sodium chloride were optimized using a multivariate approach.

In the case of using SPME, 15 of the 24 fragrance allergens were analyzed, and the correlation coefficient (r^2) of the calibration curve for quantification showed linearity of 0.9969 or more, and the method detection limits (MDL) and the limits of quantification (LOQ were 0.078 ~ 0.582 ug/L and 0.261 ~ 1.940 ug/L, respectively.

In the case of using LLE, 24 fragrance allergens were analyzed, and the correlation coefficient (r^2) of the calibration curve for quantification showed linearity of 0.9957 or more, MDL and LOQ were 0.020 ~ 0.138 ug/L and 0.065 ~ 0.440 ug/L, respectively.

It was concluded that the LLE pre-treatment method with low detection limit and more simultaneous analysis items was more effective to analyze fragrance allergens in water.

Brief Oral Session-11

Simultaneous determination of chlorogenic acid isomers and metabolites in rat plasma using LC-MS/MS

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A selective, sensitive and reliable liquid chromatography-tandem mass spectrometry method for the simultaneous determination of chlorogenic acid, neochlorogenic acid, cryptochlorogenic acid, caffeic acid, caffeic acid 3-O-glucuronide, caffeic acid 4-O-glucuronide, and ferulic acid in rat plasma was developed. After liquid-liquid extraction with ethyl acetate as sample preparation, seven analytes were seperated on Halo C18 column with gradient elution of 0.1% formic acid in water and methanol. The analytes were quantified by an electrospray ionization tandem mass spectrometry in the selected reaction monitoring mode. The standard curves were linear over the concentration range of 0.5-200 ng/mL for chlorogenic acid and neochlorogenic acid, 2.5-1000 ng/mL for cryptochlorogenic acid, caffeic acid, caffeic acid 3-O-glucuronide, and caffeic acid 4-O-glucuronide, and 12.5-5000 ng/mL for ferulic acid, respectively. The intra- and inter-day coefficient variations and relative errors were 4.1 to 18.1% and -8.8 to 16.0% at LLOQ and were 2.0 to 12.5% and -10.0 to 10.4% at three QC concentrations. This method was successfully applied to the pharmacokinetic study of chlorogenic acid, cryptochlorogenic acid, neochlorogenic acid, caffeic acid, caffeic acid 3-O-glucuronide, caffeic acid 4-O-glucuronide, and ferulic acid after an oral administration of the extract of *stauntonia hexaphylla* leaf at a dose of 100 mg/kg in male Sprague-Dawley rats.

Brief Oral Session-12

UPLC-MS/MS Based Profiling of Eicosanoids in RAW264.7 Cells

Yu-Ri Choi[1], Jae Won Lee[1], Hyuck Jun Mok[1], Seung Cheol Park[1], Hyung Don Kim[2], Kwang Pyo Kim[1*]

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Although the pro-inflammatory and anti-inflammatory effects of various eicosanoids have been widely studied, changes in the levels of various eicosanoids during inflammation have not yet comprehensively studied. Thus, we designed two experiments in order to measure the levels of eicosanoids. We assessed the effect of lipopolysaccharide (LPS) treatment on the levels of eicosanoids in macrophage cells, and treated with LPS and 20(S)-ginsenoside-Rg3 (Rg3) for 12h, 24h. UPLC-MS/MS-based lipidomics analysis was used to profile various eicosanoids from macrophage cells treated with LPS and Rg3. The profiling data were statistically analyzed by principal component analysis, hierarchical clustering analysis, analysis of variance, and volcano plot. We have found that thirty-nine eicosanoids were upregulated, seven were down-regulated by LPS treatment in a concentration-dependent manner, and eighteen eicosanoids were recovered by Rg3 treatment.

Brief Oral Session-13

Development of new chemical separation method for uranium age-dating of UO_2 materials

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[2]*Radiochemistry & Nuclear Nonproliferation, University of Science & Technology, Korea*

Age-determination of uranium samples is an important technique for nuclear forensics by analyzing a daughter-mother radionuclide pair such as $^{230}Th/^{234}U$, $^{231}Pa/^{235}U$, $^{232}Th/^{236}U$. $^{230}Th/^{234}U$ is one of the most commonly used isotope pair due to relatively rapid ingrowth of ^{230}Th in comparison with others and availability of high precision. For accurate and precise determination of $^{230}Th/^{234}U$ ratio, Th and U must be purified by removing interfering species from uranium samples prior to analysis as much as possible. Additionally, ^{232}Th impurities during chemical procedures should be minimized and well evaluated because standard ^{232}Th is used as a spike for isotope dilution technique.

In this study, we have developed new chemical separation method using UTEVA resin and optimized separation conditions. This new chemical separation method is expected to be more versatile than previous method using TEVA resin or ion exchange chromatograpy because it is possible to evaluate Pu age by analyzing $^{241}Am/^{241}Pu$ as well as $^{230}Th/^{234}U$ at the same time. For testing this method, we prepared simulated uranium samples. Elution curve and recovery yield were obtained from newly developed separation schemes. The optimal volumes of Th eluent (5 M HCl) was 6 mL and the recovery yield was 99.5 %. In addition we also verified this method with UO_2 reference materials and isotopic ratio measurements of $^{230}Th/^{234}U$ were performed using MC-ICP-MS equipped with desolvation system (Aridus-Ⅱ).

Brief Oral Session-14

Steroidal CYP enzyme activities in human amniotic fluid by GC-MS

Soyun Han[1,2], Ju-Yeon Moon[3], Jae-Hong Kim[2], Man Ho Choi[1]

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[2]*College of Life Sciences and Biotechnology, Korea University*
[3]*Department of Pharmacy, The Catholic University of Korea*

Although the potential risk factors of preeclampsia are associated with placental oxidative stress and altered steroid metabolism, its pathogenesis has not fully been identified. To investigate whether human cytochrome P450 (CYP) enzymes are responsible to oxidative metabolism of endogenous steroids, gas chromatography–mass spectrometry in the selected-ion monitoring (GC–SIM/MS)-based steroid profiling was, firstly, developed for simultaneous quantification of CYP-mediated regioselective hydroxysteroids and their substrates, including 15 androgens, 7 estrogens, 4 progestins, 6 corticoids, and 8 sterols, with Oasis HLB™ solid-phase extraction. This CYP-mediated steroid signatures allows simultaneous assessment of CYP1A, CYP1B, CYP2C, CYP3A, CYP11B, CYP17A, CYP19A, and CYP21A. Then, the devised assay was applied to amniotic fluids obtained from patients with preeclampsia and normotensive controls. Due to its compositional changes of amniotic fluids along with gestational age according to the process of the fetal development, the assessment of steroidal CYP enzyme activities in amniotic fluids could serve as a useful tool for assessing the diagnostic biomarkers.

Brief Oral Session-15

Glycomic profiling of serum haptoglobin using nano LC/MS and LC/MS/MS

Sung Hyeon Lee

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Glycosylation changes have been reported in a wide variety of human diseases, including immune disorders and cancers, and even is associated with malignant transformation. Recently, a targeted glycoproteomic approach has gained considerable attention as a novel method for biomarker discovery to improve the specificity and sensitivity for clinical use. Here, we comprehensively investigated the indirect and direct glycomic profile of a target glycoprotein, serum haptoglobin (Hp) by chip-based nano LC-QTOF MS and MS/MS analysis following antibody-assisted purification. From the results of significant N-glycan variations between GC patients and healthy controls, we conclusively suggest that aberrant glycans of serum Hp are associated with patients with gastric cancer and might be a promising marker for GC screening/monitoring.

Brief Oral Session-16

Simultaneous analysis of thiamine and biotin in infant formula by isotope dilution-liquid chromatography mass spectrometry

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Thiamine and biotin are part of vitamin B complex and play a key role as a coenzyme in biochemical reaction in human body. A definite method for the analysis of water-soluble vitamins is necessary to produce reliable and SI traceable measurement data.

The aim of this study is to simultaneously determine thiamine and biotin in infant formula using isotope dilution-liquid chromatography mass spectrometry. Acid hydrolysis at room temperature was performed to extract thiamine and biotin in infant formula. Thiamine-[$^{13}C_3$] and biotin-[$^{2}H_2$] standard materials were spiked as internal standard. Waters X-bridge C18 column (4.6 x 150 mm, 3.5 μm) was selected for proper separation of thiamine and biotin, and 10 mmol/L ammonium formate in H_2O, pH 3.8 and methanol were decided as mobile phases. The post-column infusion method was used to study matrix effects originating from sample matrix in electrospray ionization mode.

For the quantification, selected reaction monitoring mode is applied to monitor the collisionally induced dissociation channels of m/z 265.1→122.0 and 245.1→227.1 for thiamine and biotin, respectively, and m/z 268.1→122.0 and 247.1→229.1 for corresponding isotope compounds. The repeatability and reproducibility test in infant formula showed less than 2 % of relative standard deviation.

An LC/MS/MS-based isotope dilution mass spectrometric method has been evaluated as a candidate reference method for the simultaneous determination of thiamine and biotin in infant formula.

Brief Oral Session-17

Glycan signatures of human saliva

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[2]*Asia-Pacific Glycomics Reference Site, Chungnam National University, Daejeon*

In recent years, saliva has received particular attention among researchers especially in the field of forensic sciences. Saliva encountered at crime scene is one of the most significant evidence for crime investigation and thus, to identify saliva from other human fluids and non-human fluids is very important. Conventional methods including enzymatic amylase and starch-iodine test to determine saliva have low sensitivity in trace samples and lack of specificity due to cross-reaction with other fluids. In order to overcome weakness in saliva identification, various studies have been attempted based on biochemical components. Glycoproteins which are highly sensitive to the biochemical environment are a major constituent in saliva and play an important and vital role in maintenance of oral health. Here, we have explored the possibility if glycan can be used as a bio-signature to identify and differentiate human saliva compared with other fluids. Briefly, N-glycans in human saliva (male: 7 and female: 11, age: on average 27) were enzymatically released and were enriched by PGC-SPE. The global characterizations of human saliva N-glycans were carried out by nano LC-PGC chip/Q-TOF MS. We could determine highly fucosylated N-glycans are saliva-specific molecule. Sensitivity was evaluated by comparisons of glycan profiles of 2.5 to 100 μL of saliva. In future work, we will expand this approach to find glycan signatures for differentiating the human blood and semen.

(1,480 / 1,500)

Brief Oral Session-18

The effect of Sodium and Potassium ions for sucrose detection by comparing charcoal, DHB and CHCA matrices in MALDI-MS analysis

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Matrix-assisted laser desorption/ionization (MALDI) is one of the most commonly used soft ionization method for the determination of large molecules such as proteins or peptides. MALDI conventionally uses organic matrices such as 2,5-dihydroxybenzonic acid (2,5-DHB) and α-cyano-4-hydroxycinnamic acid (α-CHCA). However, organic matrices usually break up under laser irradiation. Moreover, the product of the matrices have signal interferences with high intensity in the low molecular weight ranges (m/z<500). Many alternative matrices such as activated charcoal, carbon nanotubes, and porous silicon surface have been used to overcome the interferences of matrix-related ions. In this investigation, sucrose which has molar mass of 342.29, was analyzed using 2.5-DHB, CHCA, and charcoal. Among the three matrices, charcoal was found to be best since it provides the highest sucrose peak intensity and the lowest interferences. However, when using charcoal matrix and sodium ion addition, it was observed that sucrose was cleaved into glucose generating [glucose + Na]$^+$ peak. Therefore, it was necessary to explore new method for the detection of only intrinsic sucrose by MALDI. Lowering the laser intensity decreases the glucose peak intensity to only a certain extent and changing the additive cation from Na^+ to K^+ successfully removed the glucose peak. The addition of K^+ cation was found to be an efficient way for the determination of sucrose.

Brief Oral Session-19

Reactive paper spray ionization mass spectrometry for the analysis of the conjugated ketones

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Paper spray ionization (PSI) is an ambient ionization method which utilizes a triangular paper tip as a sampling base as well as an electrospray tip. In PSI, sample solution is usually deposited onto a paper tip and dried. Analytes in a sample spot are then extracted, transported to the end of the paper tip, and finally ionized by applying an electrospray solution and high voltage on a paper tip. In case an electrospray solution contains a reactant which can readily react with target analytes, *in situ* derivatization of target analytes can occur during PSI processes and this method is referred to as reactive PSI. In this presentation, we demonstrated reactive PSI mass spectrometric analysis of conjugated ketones including quinones and isothiazolones. The reactant for this application was cysteamine which readily reacts with a conjugated ketone *via* Michael addition reaction. Since the reaction product has an amine group which can be easily protonated, sensitivity was greatly enhanced by this approach. In addition, conjugated ketones could be selectively detected by monitoring the specific fragment ions of the reaction products.

Brief Oral Session-20

Effect of Ca(II) on the conformation and aggregation process of alpha-synuclein.

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Parkinsons's disease (PD) is a neurodegenerative disease, characterized by aggregation of alpha-synuclein (αSyn). To understand factors affecting αSyn to form abnormal aggregates, chemical compounds and metal ions have been investigated *in vitro*. Among them, Ca(II), one of the most crucial metal ions in life, was shown to promote αSyn aggregation and it has been considered to have a relationship with PD. Ca(II) was observed to interact with C-terminal domain of αSyn and their binding affinity was measured (K_d ~ 1 mM). However, how the interaction affects the aggregation process of αSyn is not clearly understood. In this study, we investigated the effect of Ca(II) on the conformation and aggregation process of αSyn using mass spectrometry (MS), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). Our MS and SAXS results showed that interaction between Ca(II) and C-terminal of αSyn promotes conformational change of αSyn into extended structure. The conformation change is considered as a cause of increased rates of αSyn aggregation. Furthermore, we observed that Ca(II) can affect the aggregation process during nucleation and elongation steps, and even mature fibril. Our study will provide physicochemical understanding of interaction between αSyn and Ca(II) and the aggregation process of αSyn.