

**2011 China-Japan-Korea Symposium
On Analytical Chemistry**

Program and Abstracts

October 31 to November 2, 2011
Jeju, Korea

2011 China-Japan-Korea Symposium on Analytical Chemistry

<http://cjk2011.weebly.com/>

October 31 – November 2, 2011

Grand Hotel, Jeju, Korea

Organized by

*The Korean Analytical Science Research Group
China-Japan-Korea Analytical Science Discussion Group
Korea Food Research Institute*

Supported by

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Message from Chairman

Welcome to CJK Symposium 2011, the China-Japan-Korea Symposium on Analytical Chemistry on Food, Environment and Nano-technology, which is held from Oct. 31 to Nov. 2, 2011 at Jeju Grand Hotel, Korea. We have chosen a beautiful Jeju island with wonders of nature and friendly people. This CJK Symposium can be traced to the China-Japan Symposium held in 2002 in Beijing. And, in 2003, Korea-Japan Symposium on Gas Chromatography was held in Seoul, Korea. The first CJK Symposium on Environmental Analytical Chemistry was held in Beijing, in 2004. Since 2004, former CJK Symposiums were in Chiba (2005), Chongqing (2006), Jeju (2007) jointly with ASIANALYSIS, Xiamen (2008), Chiba (2009) and Wuhan (2010). From 2009, the name of symposium was changed into “China-Japan-Korea Symposium on Analytical Chemistry”. Now we organized 8th CJK Symposium in Jeju again.

As you already have noted in preliminary announcement, the organizing committee has put together superb plenary lectures, key-note lectures, oral and poster presentations that should have something of interest for all attendants. You will experience rapid changes in the world of analytical science as you look the lectures, key-note or oral presentations and poster sessions. The Abstract book will be helpful to attendants who want to know more about presentations being given in the scientific program.

In this opportunity the organizing committee appreciates to Dr. Suk-Hoo Yoon, the President of Korea Food Research Institute, and several sponsors, Prof. Jin-Ming Lin and Dr. Haifang Li of China delegate, Prof. Hiroshi Nakamura and Dr. Tsuneaki Maeda of Japan delegate, Dr. Jaeho Ha of Korea delegate for their all consideration for this symposium. We are pleased to have you join us to share your very recent research ideas and activities, and to extend our friendship. I wish that you will be both a professionally rewarding and most enjoyable experience.

Dong –Sun Lee, Prof. Ph.D.

Chair of the Organizing Committee of CJK Symposium 2011.

ORGANIZING COMMITTEE

Chairperson : Prof. Dong-Sun Lee

Dept. of Chemistry, Seoul Women's University, Seoul 139-774, Korea
dslee@swu.ac.kr Tel:+82-2-970-5654, Fax: +82-2-970-5972

Organizer : Dr. Jaeho Ha

Food Analysis Center

Korea Food Research Institute

516 Baekhyun, Bundang, Songnam, Gyeonggi 463-746, Korea
jhfri@kfri.re.kr, Tel: +82-31-780-9127, Fax: +82-31-780-9280

COMMITTEE MEMBERS

KOREA

Prof. Dong-Sun Lee

Seoul Women's University

Prof. Myeong-Hee Moon

Yonsei University

Dr. Jaeho Ha

Korea Food Research Institute

Dr. Dongbin Shin

Korea Food Research Institute

Dr. Homoon Seog

Korea Food Research Institute

Prof. Sun-Young Bae

Seoul Women's University

Prof. Man-Goo Kim

Kangwon National University

Dr. Man-Ho Choi

KIST

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Prof. Jin-Ming Lin
Tsinghua University

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Southwest University

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Northeast University

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Institute of Chemistry, CAS

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Huazhong University

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Hunan University

Prof. Zilin Chen
Wuhan University

Dr. Yuki Hashi
Shimadzu(Shanghai) Company

Prof. Gongke Li
Sun Yat-sen University

Prof. Lehui Lu
Changchun Institute of Applied Chemistry, CAS

Prof. Chengxiao Zhang
Shanxi Normal University

JAPAN

Prof. Hiroshi Nakamura
Chair of the Japan Society for Analytical Chemistry

Emeritus Prof. Toshiyuki Hobo
Tokyo Metropolitan University

Dr. Osamu Niwa
AIST

Prof. Hideaki Hisamoto
Osaka Prefecture University

Prof. Kinichi Tsunoda
Gunma University

Prof. Masami Shibukawa
Saitama University

Prof. Katsumi Uchiyama
Tokyo Metropolitan University

Prof. Koichi Oguma
Chiba University

Dr. Tsuneaki Maeda
AIST

Dr. Takumi Takasuga
Shimadzu Techno-Research Inc.

Prof. Toyohide Takeuchi
Gifu University

Prof. Tadao Sakai
Aichi Institute of Technology

Prof. Kazuhiko Tanaka
Hiroshima University

Prof. Shoji Motomizu
Okayama University

Dr. Akemi Yasui
National Food Research Institute

SCIENTIFIC PROGRAMME

MONDAY, OCTOBER 31th

Afternoon

13:00 - 18:00 Registration

TUESDAY, NOVEMBER 1st

(Room Jade)

Morning

08:00 - 08:40 Opening Ceremony

PLENARY LECTURES

(Room Jade)

Chairpersons : Prof. Man-Goo Kim and Prof. Chengzhi Huang

08:40 - 09:05 - Prof. Hanfa Zou, China

The application of monolithic and mesoporous materials in analysis of biological samples

09:05 - 09:30 - Prof. Katsumi Uchiyama, Japan

Development of micro-gas chromatography system for on-site measurement

09:30 - 09:55 - Prof. Myeong-Hee Moon, Korea

Flow field-flow fractionation: A new pipeline to proteomics

09:55 - 10:20 - Prof. Yi Chen, China

SPME and GC-MS of polycyclic aromatic hydrocarbons from different sources

10:20 - 10:35 - Coffee Break

10:35 - 11:00 - Dr. Osamu Niwa, Japan

Nano-structured carbon film for direct electron transfer with biomolecules

11:00 - 11:25 - Dr. Jaeho Ha, Korea

Determination of E,E-farnesol in Makgeolli using stir bar sorptive extraction coupled with gas chromatography – mass spectrometry

11:25 - 11:50 - Prof. Mengsu(Michael) Yang, China

High-throughput and real-time analysis of cell communication by integrated microfluidics

11:50 - 13:00 Lunch/Poster Presentations

Poster should be put up 11:30 to 15:00

Afternoon

13:00 - 15:00 Poster Presentations & Exhibition

KEYNOTE LECTURES

(Room Jade)

Chairpersons : Prof. Katsumi Uchiyama and Prof. Zilin Chen

13:00 - 13:20 - Prof. Hideaki Hisamoto, Japan

Combinable PDMS capillary (CPC) sensor array towards the development of single step and multiple biosensing microdevices

13:20 - 13:40 - Prof. Xinghua Xia, China

Interfacial behavior of biomolecules and bioelectrochemical analysis

13:40 - 14:00 - Prof. Man-Goo Kim, Korea

A novel investigation method of VOC emission from car interior components by μ -chamber

14:00 - 14:20 - Prof. Jianhua Wang, China

Biomass/cell manipulation for arsenic analysis and removal from water samples

14:20 - 14:40 - Prof. Kei Toda, Japan

Atmospheric isoprene and formaldehyde analyzers utilizing chemiluminescence detection and microchannel scrubber

14:40 - 14:50 Coffee Break

ORAL PRESENTATIONS

(Room Jade)

Chairpersons : Prof. Mengsu(Michael) Yang and Prof. Hiroshi Nakamura

14:50 - 15:05 - Prof. Jin-Ming Lin, China

Preparation of hydrogel microarrays in microchannels and its application for cell research

15:05 - 15:20 - Prof. Kinichi Tsunoda, Japan

Application of electrospary ionization mass spectrometry to the determination of inorganic ions in environmental samples

15:20 - 15:35 - Prof. Xi Chen, China

Electrochemically enhanced solid-phase microextraction

15:35 - 15:50 - Dr. Cheong-Tae Kim, Korea

Determination of melamine and its analogues in various processed foods by using tandem mass spectrometry

15:50 - 16:05 - Prof. Cheng Zhi Huang, China

On the analytical chemistry of phosphate-containing anions

16:05 - 16:15 Coffee Break

Chairpersons : Prof. Xi Chen and Dr. Cheong-Tae Kim

16:15 - 16:30 - Prof. Lehui Lu, China

Bi₂S₃ nanodots as a contrast agent for *in vivo* x-ray computed tomography imaging

16:30 - 16:45 - Prof. Koichi Oguma, Japan

Speciation of vanadium using difference in rate of complex formation with xylenol orange

16:45 - 17:00 - Prof. Yang Tian, China

A ratiometric fluorescent sensor for intracellular metal ions based on inorganic-organic nanocomposites

17:00 - 17:15 - Prof. Xiangying Sun, China

Synthesis of dual-fluorescence nanocomposites and ratiometric fluorescence sensing for Hg²⁺

17:15 - 17:30 - Prof. Zilin Chen, China

Analysis of active components in Chinese herbs by LC/CE with MS and electrochemical detections

TUESDAY, NOVEMBER 1st

(Room Armethyst)

KEYNOTE LECTURES

Chairpersons : Prof. Jin-Ming Lin and Dr. Kangbong Lee

13:00 - 13:20 - Dr. Man Ho Choi, Korea

Mass spectrometry-based hair metabolomics in biomarker discovery of hormonal-dependent diseases

13:20 - 13:40 - Dr. Takumi Takasuga, Japan
Application of GC-HRTOFMS for environmental analysis: A comprehensive screening and identification techniques for trace organohalogen Compounds in environmental matrices

13:40 - 14:00 – Dr. Yuki Hashi, China
Determination of carbamate pesticides in vegetables and fruits by on-line GPC-LCMS system

14:00 - 14:20 - Prof. Masami Shibukawa, Japan
Liquid chromatography with a gas-liquid hybrid stationary phase

14:20 - 14:40 - Prof. Sunyoung Bae, Korea
Hydrochar of cabbage by hydrothermal carbonization Reaction and its sorption capacity

14:40 - 14:50 Coffee Break

ORAL PRESENTATIONS

(Room Armethyst)

Chairpersons : Prof. Myeong Hee Moon and Prof. Koichi Oguma

14:50 - 15:05 - Dr. Kangbong Lee, Korea
Monitoring of corticosteroids in cosmetic products manufactured in Korea

15:05 - 15:20 - Prof. Bi-feng Liu, China
Neuronal analysis in vivo with microfluidic chip

15:20 - 15:35 - Dr. Shinya Tahara, Japan
Current eating habit of Japanese and their effect on fecal odor

15:35 - 15:50 - Prof. Cheng-Xiao Zhang, China
Electrogenerated chemiluminescence biosensor for protein and bacteris

15:50 - 16:05 - Mr. Daisuke Kozaki, Japan
Preliminary study on ion-exclusion/cation-exchange chromatography for determining simultaneously radioactive anions and cations released from nuclear power plant

16:05 - 16:15 Coffee Break

Chairpersons : Prof. Hideaki Hisamoto and Prof. Jianghua Wang

16:15 - 16:30 - Prof. Gongke Li, China

Hybrid field-assisted solid-liquid-solid dispersive extraction for the determination of organochlorine pesticides in tobacco by gas chromatography

16:30 - 16:45 – Dr. Jang-Hyuk Ahn, Korea

A novel sample preparation method by rapid and simple no-heating saponification for the determination of cholesterol in infant formula

16:45 - 17:00 - Prof. Bin Liu, China

Urea electrochemical sensor based on molecularly imprinted chitosan film doped with CdS QDs

17:00 - 17:15 - Prof. Dong-Sun Lee, Korea

A new needle packed with poly(dimethylsiloxane) having a micro-bore tunnel as alternative solid phase microextraction

17:15 - 17:30 - Prof. Hai-Long Wu, China

Aspects of recent developments of chemical multiway calibration methodologies

List of Participants from Korea

| Name | Organization | E-mail |
|------------------------|--|----------------------|
| Dong-Sun Lee, Prof. | Department of Chemistry, Seoul Womens University | dslee@mail.swu.ac.kr |
| Man-Goo Kim, Prof. | Department of Environmental Science, Kangwon National University | mgkim@kangwon.ac.kr |
| Myeong-Hee Moon, Prof. | Department of Chemistry, Yonsei University | mhmoon@yonsei.ac.kr |
| Jaeho Ha, Dr. | Korea Food Research Institute | jhkfri@kfri.re.kr |
| Dongbin Shin, Dr. | Korea Food Research Institute | dbshin@kfri.re.kr |
| Homoon Seog, Dr. | Korea Food Research Institute | hmoon@kfri.re.kr |
| Sanghee Lee, Dr. | Korea Food Research Institute | shlee@kfri.re.kr |
| Miyoung Yoo, Dr. | Korea Food Research Institute | myyoo@kfri.re.kr |
| Yooshin Shim, Mr. | Korea Food Research Institute | ysshim@kfri.re.kr |
| Dongwon Seo, Mr. | Korea Food Research Institute | dwseo@kfri.re.kr |
| Eunhwa Kang, Ms. | Korea Food Research Institute | ehkang@kfri.re.kr |
| Yongsun Cho, Ms. | Korea Food Research Institute | yscho@kfri.re.kr |
| Jinbong Hwang, Dr. | Korea Food Research Institute | hwangjb@kfri.re.kr |
| Nahmgung Bae, Dr. | Korea Food Research Institute | baeng@kfri.re.kr |
| Sun-Young Bae, Prof. | Department of Chemistry, Seoul Womens University | sbae@swu.ac.kr |
| Kangbong Lee, Dr. | Korea Institute of Science and technology | leekb@kist.re.kr |
| Seongweon Jeong, Dr. | Korea Food Research Institute | donow@kfri.re.kr |
| Man-Ho Choi, Dr. | Korea Institute of Science and Technology | mh_choi@kist.re.kr |
| Cheong-Tae Kim, Dr. | Nong Shim Co., Ltd. | kctmass@hanmail.net |
| Jang-Hyuk Ahn, Dr. | Namyang Dairy Co., Ltd. | ahn5470@daum.net |
| Hye-Young Seo, Dr. | World Institute of Kimchi | hyseo@kfri.re.kr |
| Sung-Hee Park, Dr. | World Institute of Kimchi | |
| Ji-Hee Yang, Ms. | World Institute of Kimchi | |
| Se Mi Kang, Ms. | Korea Institute of Science and Technology | |
| Su Hyeon Lee, Ms. | Korea Institute of Science and Technology | |
| Joongmok Jung, Mr. | Young In Scientific Co., Ltd. | |
| Haejin Wang, Ms. | Korea Food Research Institute | |
| Hyejin Jang, Ms. | Korea Food Research Institute | |
| Eun-Ji Lee, Ms. | Department of Chemistry, Seoul Womens University | |
| Hye-Lim Jeon, Ms. | Department of Chemistry, Seoul Womens University | |
| Hyun-Hwa Son, Ms. | Department of Chemistry, Seoul Womens University | |
| Sang-Jun Lee, Mr. | Rigong International Inc. | |
| Jae-Joon Lee, Mr. | Dong-il SHIMADZU Corp. | |
| Yong-Gyu Ham, Mr. | Dong-il SHIMADZU Corp. | |
| Un-Tak Song, Mr. | Dong-il SHIMADZU Corp. | |
| Woo-Sung Lee, Mr. | Dong-il SHIMADZU Corp. | |
| Hwang-Soo Kim, Mr. | Dong-il SHIMADZU Corp. | |

List of Participants from China

| Name | Organization | E-mail |
|-----------------------------|---|--------------------------------|
| Jin-Ming Lin, Prof. | Tsinghua University | jmlin@mail.tsinghua.edu.cn |
| Xinghua Xia, Prof. | Nanjing University | xhxia@nju.edu.cn |
| Xi Chen, Prof. | Xiamen University | xichen@xmu.edu.cn |
| Gongke Li, Prof. | Sun Yat-sen University | cesgkl@mail.sysu.edu.cn |
| Sufen Lin, Eng. | Research Center for Eco-Environmental Science, Chinese Academy | |
| Chengzhi Huang, Prof. | Southwest University | chengzhi@swu.edu.cn |
| Jianghua Wang, Prof. | Northeast University | jianhua@neju.edu.cn |
| Lehui Lu, Prof. | Changchun Institute of Applied Chemistry, CAS | lehuilu@yahoo.com |
| Hanfa Zou, Prof. | Dalian Institute of Chemical Physics, CAS | hanfazou@dicp.ac.cn |
| Yi Chen, Prof. | Institute of Chemistry, CAS | chenyi@iccas.ac.cn |
| Lan Zhang, Prof. | Fuzhou University | zlan@fzu.edu.cn |
| Hailong Wu, Prof. | Hunan University | hlwu@hnu.cn |
| Chengxiao Zhang, Prof. | Shaanxi Normal University | cxzhang@snnu.edu.cn |
| Yaqin Wang, Prof. | Shaanxi Normal University | |
| Yang Tian, Prof. | Tongji University | yangtian@mail.tongji.edu.cn |
| Bi-feng Liu, Prof. | Huazhong University of Science and Technology | bfliu@mail.hust.edu.cn |
| Mengsu(Michael) Yang, Prof. | City University of Hong Kong | bhmyang@cityu.edu.hk |
| Haifang Li, Prof. | Tsinghua University | lihaifang@mail.tsinghua.edu.cn |
| Zilin Chen, Prof. | Wuhan University | chenzl@whu.edu.cn |
| Yuki Hashi, Dr. | Shimadzu (Shanghai) Company | y-hashish@shimadzu.co.jp |
| Lin Zhen, Ms. | Tsinghua University | |
| Fang Li, Prof. | Huaqiao University | |
| Xiangying Sun, Prof. | Huaqiao University | |
| Huiting Lian, Prof. | Huaqiao University | |
| Chuanxiao Yang, Prof. | Huaqiao University | |
| Yuanfang Li, Prof. | Southwest University | |
| Xianming Hu, Prof. | Wuhan University | |
| Haibing Zhou, Prof. | Wuhan University | |
| Feng Luo, Prof. | Fujian Research Institute of Metric Science | |
| Takaya Hoshiida, Mr. | Shimadzu (Shanghai) Company | |
| Jia-Ping Li, Ms. | Shimadzu (Shanghai) Company | |
| Hong-Kai Wang, Ms. | Shimadzu (Shanghai) Company | |

List of Participants from Japan

| Name | Organization | E-mail |
|--------------------------|--|--|
| Hiroshi Nakamura, Prof. | Faculty of Pharmaceutical Science, Tokyo University of Science | nakamura@jsac.or.jp |
| Kei Toda, Prof. | Kumamoto University | todaye@sci.kumamoto-u.ac.jp |
| Osamu Niwa, Prof. | AIST | niwa.o@aist.go.jp |
| Hideaki Hisamoto, Prof. | Osaka Prefecture University | hisamoto@chem.osakafu-u.ac.jp |
| Kinichi Tsunoda, Prof. | Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University | tsunoda@chem-bio.gunma-u.ac.jp |
| Masami Shibukawa, Prof. | Saitama University | sibukawa@apc.saitama-u.ac.jp |
| Katsumi Uchiyama, Prof. | Tokyo Metropolitan University | uchiyama-katsumi@c.metro-u.ac.jp |
| Koichi Oguma, Prof. | Chiba University | koguma@faculty.chiba-u.jp |
| Hiroshi Sato, Prof. | Faculty of Pharmaceutical Science, Nagasaki International University | satoh@niu.ac.jp |
| Toshiyuki Hobo, Prof. | Tokyo Metropolitan University | yi25175@nifty.com |
| Hulie Zeng, Prof. | Tokyo Metropolitan University | zeng-hulie@tmu.ac.jp |
| Tsuneaki Maeda, Dr. | AIST | maeda-t@aist.go.jp |
| Ryozo Goto, Dr. | TOADKK | r-goto@toadkk.co.jp |
| Kazutoshi Sugita, Dr. | Mitsubishi Chemical Analytic | 6306378@cc.m-kagaku.co.jp |
| Makoto Ohashi, Mr. | SGE Japan Inc. | mohashi@sge.com |
| Masaaki Senda, Dr. | Senda Analytical Technologies Laboratory | sendas@crux.ocn.ne.jp |
| Takumi Takasuga, Dr. | Shimadzu Techno-Research Inc. | t_takasuga00@shimadzu-techno.co.jp |
| Ryoichi Ishimatsu, Prof. | Kyushu University | ishimatsu@cstf.kyushu-u.ac.jp |
| Hiroaki Nakagawa, Dr. | Hitach High-Tech. Corp. | nakagawa-hiroaki@naka.hitachi-hitec.com |
| Yoko Inoue, Ms. | Hitach High-Tech. Corp. | inoue-yoko@naka.hitachi-hitec.com |
| Yusuke Hosen, Mr. | Hitach High-Tech. Corp. | hosen-yusuke@naka.hitachi-hitec.com |
| Hideyuki Sakamoto, Mr. | Hitach High-Tech. Corp. | sakamoto-hideyuki@naka.hitachi-hitec.com |
| Shinya Tahara, Mr. | Kobayashi Pharmaceutical Co., Ltd. | s.tahara@kobayashi.co.jp |
| Yasuyuki Hasegawa, Mr. | Kobayashi Pharmaceutical Co., Ltd. | ya.hasegawa@kobayashi.co.jp |
| Daisuke Kozaki, Mr. | Hiroshima University | emerald.green.2-10@hotmail.co.jp |
| Weng Ying, Ms. | Tokyo Metroporitan University | weng-ying@ed.tmu.ac.jp |
| Hideki Wakayama, Mr. | Osaka Prefecture University | wakahide23@gmail.com |
| Shigenobu Tanaka, Mr. | Shimadzu Corp. | |
| Takashi Iwata, Mr. | Shimadzu Corp. | |

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PLENARY LECTURES

P.01

The Application of Monolithic and Mesoporous Materials in Analysis of Biological Samples.

Hanfa Zou. CAS Key Laboratory of Separation Science for Analytical Chemistry, National Chromatographic R&A Center Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

P.02

Development of Micro-Gas Chromatography System for On-Site Measurement.

Katsumi Uchiyama. Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo 192-0397, Japan, uchiyama-katsumi@tmu.ac.jp

P.03

Flow Field-Flow Fractionation: A New Pipeline to Proteomics.

Myeong Hee Moon. Department of Chemistry, Yonsei University, Seoul, 120-749, Korea, mhmoon@yonsei.ac.kr

P.04

SPME and GC-MS of Polycyclic Aromatic Hydrocarbons from Different Sources.

Yi Chen^{*1,2,3}, Yuan Wang¹, Zhenpeng Guo¹, ¹Key Lab of Analytical Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Email: chenyi@iccas.ac.cn, ²Beijing National Lab for Molecular Science, Beijing 100190, China, ³Beijing Center for Mass Spectrometry, Beijing 100190, China

P.05

Nano-structured Carbon Film for Direct Electron Transfer with Biomolecules.

Osamu Niwa^{1,2}, Hiroaki Inokuchi^{1,2}, Dai Kato¹, Akio Ueda^{1,3}, Tomoyuki Kamata¹, Shigeru Hirano⁴
¹National Institute of Advanced Industrial Science and Technology (AIST), Central 6, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8566, Japan, ²University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan, ³Tokyo Institute of Technology, 4259, Nagatsuta, Yokohama 226-8503 Japan, ⁴MES-Afty Corporation, 2-35-2 Hachioji Tokyo 192-0918, Japan niwa.o@aist.go.jp

P.06

Determination of E,E-farnesol in Makgeolli Using Stir Bar Sorptive Extraction Coupled with Gas Chromatography – Mass Spectrometry.

Jaeho Ha^{1*}, Yiru Wang^{1,2}, Hyejin Jang¹, Homoon Seog¹, and Xi Chen², ¹Food Analysis Center, Korea Food Research Institute, ²Department of Chemistry and the Key Laboratory of Analytical Sciences, Xiamen University

P.07

High-Throughput and Real-time Analysis of Cell Communication by Integrated Microfluidics.

Mengsu (Michael) Yang, Department of Biology and Chemistry, City University of Hong Kong, bhmyang@cityu.edu.hk

KEYNOTE LECTURES

L.01

Combinable PDMS Capillary (CPC) Sensor Array Towards the Development of Single Step and Multiple Biosensing Microdevices.

Hideaki Hisamoto, *Department of Applied Chemistry, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai-shi, Osaka 599-8531, Japan, hisamoto@chem.osakafu-u.ac.jp*

L.02

Interfacial Behavior of Biomolecules and Bioelectrochemical Analysis.

Xinghua Xia, *State Key Lab of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China, xhxia@nju.edu.cn*

L.03

A Novel Investigation Method of VOC Emission from Car Interior Components by μ -chamber.

Man-Goo Kim* and Ik-Hee Lee, *Department of Environmental Science, College of Natural Science, Kangwon National University, Kangwon, 200-701, Korea, mgkim@kangwon.ac.kr*

L.04

Biomass/cell Manipulation for Arsenic Analysis and Removal from Water Samples.

Ting Yang, Mingli Chen, **Jianhua Wang***, *Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China, jianhua@neju.edu.cn*

L.05

Atmospheric Isoprene and Formaldehyde Analyzers Utilizing Chemiluminescence Detection and Microchannel Scrubber.

Kei Toda, *Department of Chemistry, Kumamoto University, 2-39-1, Kurokami, Kumamoto 860-8555, Japan, today@sci.kumamoto-u.ac.jp*

L.06

Mass spectrometry-Based Hair Metabolomics in Biomarker Discovery of Hormonal-Dependent Diseases.

Man Ho Choi* and Bong Chul Chung, *Future Convergence Research Division, Korea Institute of Science and Technology, 39-1 Hawolkkok-dong, Seoul 136-791, Korea, mh_choi@kist.re.kr*

L.07

Application of GC-HRTOFMS for Environmental Analysis: A Comprehensive Screening and Identification Techniques for Trace Organohalogen Compounds in Environmental Matrices.

Takumi Takasuga^{1,2}, ¹*Shimadzu Techno Research, INC., 2-13, Nishinokyo-Sanjobocho, Nakagyo-ku, Kyoto, 604-8435, Japan, t_takasuga00@shimadzu-techno.co.jp*, ²*Center for Marine Environmental Studies (CMES), Ehime University, Matsuyama, Japan*

L.08

Determination of Carbamate Pesticides in Vegetables and Fruits by On-line GPC-LCMS System.

Yuki HASHI *¹, Feng JI¹, Feng-Yun PAN¹, Jin-Ming LIN², ¹*Shimadzu (China) Co., Ltd., Shimadzu Global COE for Application & Technical Development, Shanghai, 200052, P.R. China,* ²*The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China*

L.09

Liquid Chromatography with a Gas-Liquid Hybrid Stationary Phase.

Masami Shibukawa* and Hiroki Nakamura, *Division of Material Sciences, Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan, sibukawa@apc.saitama-u.ac.jp*

L.10

Hydrochar of Cabbage by Hydrothermal Carbonization Reaction and Its Sorption Capacity.

Eunsol Koh¹, **Sunyoung Bae**¹, Kyoung S. Ro², ¹ *Seoul Women's University, Department of Chemistry, Seoul, Korea. sbae@swu.ac.kr,* ² *USDA-ARS Coastal Plains, Soil, Water & Plant Research Center, Florence, SC, 29501, USA*

ORAL PRESENTATIONS

O.01

Preparation of Hydrogel Microarrays in Microchannels and Its Application for Cell Research.

Jin-Ming Lin, *Department of Chemistry, Tsinghua University, Beijing 100084, China, jmlin@mail.tsinghua.edu.cn*

O.02

Application of Electrospray Ionization Mass Spectrometry to the Determination of Inorganic Ions in Environmental Samples.

Kinichi Tsunoda¹, Hiroki Hotta², Kiichi Sato¹, Shota Kurihara¹, Rie Saito¹ and Kazuki Shimotori¹, ¹*Department of Chemistry and Chemical Biology, Gunma University, Kiryu 376-8515, Japan,* ²*Department of Chemical Education, Nara University of Education, Nara 630-8528, Japan*

O.03

Electrochemically Enhanced Solid-Phase Microextraction.

Feng LUO¹, Jing-Bin ZENG², **Xi CHEN***², ¹*Fujian Research Institute of Metric Science; Fuzhou 350003, China, luofeng6789@163.com,* ²*Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China, xichen@xmu.edu.cn*

O.04

Determination of Melamine and Its Analogues in Various Processed Foods by Using Tandem Mass Spectrometry.

Cheong-Tae Kim, *Food Safety Research Institute, NONGSHIM Co., Ltd., Korea*

O.05

On the Analytical Chemistry of Phosphate-Containing Anions.

Cheng Zhi Huang¹ and Xi Juan Zhao², ¹*Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Pharmaceutical Sciences,* ²*College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, China,* chengzhi@swu.edu.cn

O.06

Bi₂S₃ Nanodots as a Contrast Agent for *In Vivo* X-ray Computed Tomography Imaging.

Kelong Ai¹, Yanlan Liu^{1,2}, **Lehui Lu**^{*1}, ¹*State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China,* ²*Graduate School of the Chinese Academy of Sciences, Beijing, 100039, P.R.China*
lehui@ciac.jl.cn

O.07

Speciation of Vanadium using Difference in Rate of Complex Formation with Xylenol Orange.

Koichi Oguma, *Research Department, Nissan Arc, 1 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan,* k.oguma@nissan-arc.co.jp

O.08

A Ratiometric Fluorescent Biosensor for Intracellular Metal Ions Based on Inorganic-Organic Nanocomposites.

Yang Tian^{*}, Anwei Zhu, Qiang Qu, *Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, P. R. China,* yangtian@mail.tongji.edu.cn

O.09

Synthesis of Dual-Fluorescence Nanocomposites and Ratiometric Fluorescence Sensing for Hg²⁺.

Xiangying Sun^{*}, Fang Li, Chuanxiao Yang, Yibang Xu, *College of Material Science and Engineering, Huaqiao University, Xiamen, China,* sunxy@hqu.edu.cn

O.10

Analysis of Active Components in Chinese Herbs by LC/CE with MS and Electrochemical Detections.

Zilin Chen, *Wuhan University School of Pharmaceutical Sciences, Wuhan, 4320071, China,* chenzl@whu.edu.cn

O.11

Monitoring of Corticosteroids in cosmetic products manufactured in Korea.

Yun Sik Nam and **Kang-Bong Lee**^{*}, *Advanced Analysis Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryangri, Seoul 136-791, Republic of Korea*

O.12

Neuronal Analysis in vivo with Microfluidic Chip.

Bi-Feng Liu^{*} Jingjing Wang, Ying Wang, Wei Du, *Britton Chance Center for Biomedical Photonics, Wuhan National Laboratory for Optoelectronics, Department of Systems Biology, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China*

O.13

Current Eating Habits of Japanese and Their Effect on Fecal Odor.

Shinya Tahara*(1), Michika Sasaki (1), Koji Sakamoto (1), Yasuyuki Hasegawa (1), Tomoaki Kodama (2), Hiroshi Sato (3), 1) *KOBAYASHI Pharmaceutical Co., Ltd., Toyokawa, Ibaraki, Osaka 567-0057, Japan, Email: s.tahara@kobayashi.co.jp*, 2) *Department of Health and Nutrition* 3) *Department of Pharmacy, Nagasaki International University, Huis Ten Bosch, Sasebo, Nagasaki 859-3298, Japan, Email: satoh@niu.ac.jp*

O.14

Electrogenerated Chemiluminescence Biosensors for Proteins and Bacteria.

Cheng-Xiao ZHANG, *School of Chemistry and Chemical Engineering, Shaanxi Normal University, Key Laboratory of Analytical Chemistry for Life Science of Shaanxi Province, Xi'an, 710062, P. R. China, cxzhang@snnu.edu.cn*

O.15

Preliminary Study on Ion-Exclusion/Cation-Exchange Chromatography for Determining Simultaneously Radioactive Anions and Cations Released from Nuclear Power Plant.

Daisuke KOZAKI¹, Nobutake NAKATANI², Masanobu MORI³, Kazuhiko TANAKA¹, ¹*Graduate School for International Development and Cooperation, Hiroshima, University, 1-5-1, Kagamiyama, Higashi-hiroshima 739-8529*, ²*Faculty of Environmental Systems, Rakuno Gakuen University, 582, Bunkyo-dai-midorimachi, Ebetsu, Hokkaido 069-8501*, ³*Graduate School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma, 376-8515*

O.16

Hybrid Field-Assisted Solid-Liquid-Solid Dispersive Extraction for the Determination of Organochlorine Pesticides in Tobacco by Gas Chromatography.

Ting Zhou, Xiaohua Xiao, **Gongke Li***, *School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, China, cesgkl@mail.sysu.edu.cn*.

O.17

A Novel Sample Preparation Method by Rapid and Simple No-heating Saponification for the Determination of Cholesterol in Infant Formula.

Jang-Hyuk Ahn*, In-sik Jeong, Byung-Man Kwak, Seung-Hwan Jeong, Taehyung Yoon¹, Changyong Yoon¹, Jayoung Jeong¹, Jeongmin Park² and Jin-Man Kim², *Food Safety Center, Research and Development Institute, Namyang Dairy Co., Ltd., Gongju 314-914, Korea*, ¹*Nutrition and Functional Food Research Team, Korea Food and Drug Administration, Seoul 122-704, Korea*, ²*Department of Food Science and Biotechnology of Animal Resources, Konkuk University, Korea*

O.18

Urea Electrochemical Sensor Based on Molecularly Imprinted Chitosan Film Doped with CdS QDs.

Hui-Ting Lian, Yan-Ping Chen, Xiang-Ying Sun, and **Bin Liu***, *College of Material Science and Engineering, Huaqiao University, Xiamen 361-021, People's Republic of China, Email:*

bliu@hqu.edu.cn

O.19

A New Needle Packed with Poly(dimethylsiloxane) Having a Micro-bore Tunnel as Alternative Solid Phase Microextraction: Application for the Headspace Gas Chromatography and Mass Spectrometric Analysis of Volatile Aroma Active Compounds from Six Citrus Oils.

Hyun-Hwa Son and **Dong-Sun Lee***, *Department of Chemistry, Seoul Women's University, Seoul 139-774, Republic of Korea, dslee@swu.ac.kr*

O.20

Aspects of Recent Developments of Chemical Multiway Calibration Methodologies.

Hai-Long WU, *State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China, hlwu@hnu.cn*

POSTERS PRESENTATIONS

PT.01

Analysis of Volatile Flavor Compounds of Long-aged Doenjang by Automated HS-SPME-GC-MS.

Hye Young Seo*, Sun Young Lee, Ji Hee Yang, Kyung-Hyung Ku¹, Minseon Koo¹, *World Institute of Kimchi, ¹Korea Food Research Institute, Sunghnam-si 463-746, Korea*

PT.02

Changes of Free Sugar and Organic Acid of Kimchi During Fermentation with Different Ingredients.

Sung-Hee Park*, Ji-Hye Kim, Eung Soo Han, *World Institute of Kimchi, Korea*

PT.03

Identification and Quantification of S-allyl-L-cysteine in Heated Garlic Juice by HPLC with Ultraviolet and Mass Spectrometry Detection.

Sanghee Lee*, Miyoung Yoo, Dongbin Shin, *Korea Food Research Institute, Sunghnam-si 463-746, Korea*

PT.04

Analysis of *E*- and *Z*-Ajoene in Oil-Macerated Garlic by High-Performance Liquid Chromatography Method.

Miyoung Yoo*, Sanghee Lee, Dongbin Shin, *Korea Food Research Institute, Sunghnam-si 463-746, Korea*

PT.05

Rapid Method for the Determination of Capsorubin and Capsanthin in Red Pepper Powder Using Ultra High Performance Liquid Chromatography.

You-Shin SHIM*¹, Ki-Jin KIM¹, Dongwon SEO¹, Masahito ITO², Hiroaki NAKAGAWA², and Jaeho HA¹, *¹Food Analysis Center, Korea Food Research Institute, 516, Baekhyeon, Bundang, Seongnam, Gyeonggi, 463-746, Republic of Korea, ²Naka Division, Hitachi High-Technologies,*

Corporation, 882, Ishikawa-cho, Hitachinaka-shi, Ibaraki-ken, 312-8504, Japan

PT.06

Alternative Solid Phase Microextraction using a Hallow Needle Packed with Poly(dimethyl siloxane) for BTEX Analysis.

Sunyoung Bae, Hyun-Hwa Son, Hye Young Lee, Ye Jin Bang, **Dong-Sun Lee***, *Seoul Women's University, Department of Chemistry, Seoul, Korea.* dslee@swu.ac.kr

PT.07

Determination of Physicochemical Properties and Gas Chromatography of Mugwort Essential Oils: Preliminary Test for the Korean Standard on Oil of Mugwort (Sajabal ssuk), Korean Kanghwa Type (*Artemisia princeps* Pampan).

Eun-Ji Lee, Hyun-Hwa Son, Hye-Lim Jeon, and **Dong-Sun Lee***, *Department of Chemistry, Seoul Women's University, Seoul, Korea,* dslee@swu.ac.kr

PT.08

Analysis of Physicochemical Properties and Gas Chromatography of Citron (Yuza) Essential Oils: Preliminary Test for the Korean Standard on Oil of Citron (Yuza: Yuzu), Korean Koheung Type (*Citrus junos* Sieb. Ex Tanaka).

Hye-Lim Jeon¹, Hyun-Hwa Son¹, Eun-Ji Lee¹, Gyeong-Suk Jo² and **Dong-Sun Lee^{1*}**

¹*Department of Chemistry, Seoul Women's University, Seoul, Korea,* dslee@swu.ac.kr,

²*Jeollanamdo Agricultural Research and Extension Services, 206-7 Sanjeri, Sanpomyeon, Najusi 520-715, Republic of Korea*

PT.09

Gas Chromatography of Rose Essential Oils: A Round Robin Test for Resolution No 385-ISO/DIS 25157 on Oil of Rose, Chinese Kushui Type (*Rosa sertata* x *Rosa rugosa*).

Hyun-Hwa Son and **Dong-Sun Lee***, ¹ *Department of Chemistry, Seoul Women's University, Seoul, Korea,* dslee@swu.ac.kr

PT.10

Evaluation of Multiplexed Cytochrome P450 Metabolic Markers by Gas Chromatography-Mass Spectrometry Based Plasma Steroid Signatures.

Se Mi Kang^{*1,2}, Ju-Yeon Moon^{1,3}, Jongki Hong², Myeong Hee Moon³, Bong Chul Chung¹ and Man Ho Choi¹, ¹*Future Convergence Research Division, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Korea, Email: semi426@naver.com,*

²*Department of Basic Pharmaceutical Science, Kyung Hee University, Hoeigi-dong 1, Dongdaemun-gu, Seoul 130-701, Korea,* ³*Department of Chemistry, Yonsei University, 50 Yeonsei-ro, Seodaemun-gu, Seoul 120-749, Korea*

PT.11

Quantitative profiling of eicosanoids in plasma and urine by liquid chromatography-mass spectrometry in the high resolution selected-ion monitoring mode

Su Hyeon Lee^{*1,2}, Young Wan Ha¹, Won-Yong Lee², Bong Chul Chung¹ and Man-Ho Choi¹,

¹Future Convergence Research Division, KIST, 39-1 Hawolok-dong, Seoul 136-791, Korea, fomeandu@nate.com, ²Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seoul, 120-749, Korea

PT.12

Development of the HPLC method quantitating traces of vitamin B₁₂ and B₇ in complex matrices.
Joongmok Jung*, Inho Kim, Hyunseok Han, Taehwa Nah, Jonghoon Kim, *Young In Scientific Co., LTD. Seoul, Korea*

PT.13

Analyses of Immunoglobulin Pharmaceuticals using High Performance Liquid Chromatography.
Hiroaki Nakagawa*, Yusuke Hosen, Ayako Matsuzaki, Chihiro Yoshioka, Hiroshi Suzuki, Masaki Watanabe, Yoko Inoue, *Global Application Center, Hitachi High-Technologies Corporation, 11-1 Ishikawa-cho, Hitachinaka-shi, Ibaraki 3120057, Japan, nakagawa-hiroaki@naka.hitachi-hitec.Com.*

PT.14

Enzyme-linked Immunosorbent Assay Based on Temperature Responsive Filter.
Ying Weng, Hulin Zeng, Hizuru Nakajima, **Katsumi Uchiyama***, *Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University*

PT.15

High-Performance Liquid Chromatography Analysis of Biopharmaceuticals.
Yoko Inoue*, Yusuke Hosen, Ayako Matsuzaki, Chihiro Yoshioka, Hiroaki Nakagawa, Masahito Ito, *Global Application Center, Hitachi High-Technologies Corporation, 11-1 Ishikawa-cho, Hitachinaka-shi, Ibaraki 3120057, Japan. nakagawa-hiroaki@naka.hitachi-hitec.com*

PT.16

Preliminary Study on Ion-Exclusion/Cation-Exchange Chromatography for Determining Simultaneously Radioactive Anions and Cations Released from Nuclear Power Plant.
Daisuke KOZAKI*¹, Nobutake NAKATANI², Masanobu MORI³, Kazuhiko TANAKA¹, ¹*Graduate School for International Development and Cooperation, Hiroshima, University, 1-5-1, Kagamiyama, Higashi-hiroshima 739-8529*, ²*Faculty of Environmental Systems, Rakuno Gakuen University, 582, Bunkyo-dai-midorimachi, Ebetsu, Hokkaido 069-8501*, ³*Graduate School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515*

PT.17

Design and synthesis of fluorescent enzyme substrate monomer molecule and its application to hydrogel-based single step micro biosensing devices.
Hideki Wakayama*¹, Yoshinori Okamoto, Kunio Kawamura, Tatsuro Endo, Hideaki Hisamoto, *Department of Applied Chemistry, Graduate School of Engineering, OSAKA PREFECTURE UNIVERSITY, 1-1, Gakuen-cho, Naka-ku, Sakai-shi, Osaka, 599-8531, Japan, Email:Hisamoto@chem.osakafu-u.ac.jp*

PT.18

Measurement of Nitrous Oxide (N₂O) Released from Soil of the Vegetable Garden using GC/MS Method.

Kazutoshi SUGITA^{*1}, Yuusuke OOUCHI², Kimika KANESHIMA², Satoko TANAKA³, Shuji YOSHIZAWA³, Sumio GOTO², ¹Mitsubishi Chemical Analytech Co. Ltd., ²Azabu University, ³Meisei University

PT.19

Fluorometric Determination of Dopamine based on Calsein Blue – Fe(II) Complex and Its Application to Flow Analysis.

Ryoichi Ishimatsu^{*}, Daisuke Seto, Tomoharu Maki, Nobuaki Soh, Koji Nakano, Toshihiko Imato, Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Fukuoka, 819-0395, Japan. ishimatsu@csf.kyushu-u.ac.jp

PT.20

Development of Preventive Measure against Malodor Resulting from Composting Kitchen Scraps.

Hiroshi Sato^{*1}, Hitomi Shimomoto², Toshiyuki Hobo³, ¹Department of Pharmacy, Nagasaki, International University, Huis Ten Bosch, Sasebo, Nagasaki 859-3298, Japan, Email:satoh@niu.ac.jp, ²TOTOLtd., Kokurakita, Kitakyushu, Fukuoka 802-8601, Japan, ³Tokyo Metropolitan University, Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

PT.21

An Accurate Sample Introduction System for Capillary Electrophoresis

Hu-lie Zeng^{*}, Saori Ikeda, Hizuru Nakajama, Katsumi Uchiyama, Graduate school of urban environmental science, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji, Tokyo 192-0397, JAPAN, zeng-hulie@tmu.ac.jp

PT.22

Detection Lysozyme Based on Energy Transfer between Graphene Oxide and Rhodamine B.

Yong Chang^{*1}, Jia Li Xu¹, Yuan Fang Li¹, Cheng Zhi Huang², Detection lysozyme based on, ¹Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China, chengzhi@swu.edu, ²College of Pharmaceutical Sciences, Southwest University, Chongqing 400715, China

PT.23

Colorimetric Detection of ATP by Using Unmodified Au Nanoparticles and Melamine.

Ya Mei Yang^{*}, Min Le, Shu Jun Zhen, Yuan Fang Li, Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China, Liyf@swu.edu.cn

PT.24

Spectrofluorometric Detection of Phosphate on its Inhibition Effect on Copper Catalytic Reduction of Rhodamine Spirolactam in Basic Medium.

Hui Yang^{*1}, Lin Ling Zheng¹, Yuan Fang Li¹, Cheng Zhi Huang², ¹Education Ministry Key

Laboratory on Luminescence Real-Time Analysis, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China, chengzhi@swu.edu, ²College of Pharmaceutical Sciences, Southwest University, Chongqing 400715, China

PT.25

Facile Synthesis of Au Cubic Nanoparticles with Curcumin.

Xiao Xi Yang*, Cheng Zhi Huang, *Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Pharmaceutical Sciences, Chongqing 400715, China, chengzhi@swu.edu.cn*

PT.26

Peroxyntrous Acid Induced Chemiluminescence of Fluorescent Carbon Dots for Nitrite Sensing.

Zhen Lin, Wei Xue, Hui Chen, and **Jin-Ming Lin***, *Beijing Key Laboratory of Microanalysis and Instrumentation, Department of Chemistry, Tsinghua University, Beijing 100084, China*

PT.27

A pH Sensitive Self-Assembled Monolayer Film Based on Fluorescein Isothiocyanate.

Fang Li, **Xiang-Ying Sun*** and Bin Liu, *College of Material Science and Engineering, Huaqiao University, Fujian Xiamen 361-021, People's Republic of China, sunxy@hqu.edu.cn*

PT.28

Colorimetric Assay for Ag⁺ with ZnO/CdS@SiO₂ Core/Shell Nanostructures.

Chuanxiao Yang, **Xiangying Sun***, Bin Liu, *College of Material Science and Engineering, Huaqiao University, Xiamen, China, sunxy@hqu.edu.cn*

PT.29

Determination of Trace Inorganic and Organic Contaminants in Fuel Gas

Hai-Fang Li*, Jianmin Yang, Cuihua Gao, Meilan Li, Jin-Ming Lin*, *Department of Chemistry, Tsinghua University, Beijing, 100084, China, *Corresponding authors: lihaifang@mail.tsinghua.edu.cn, jmlin@mail.tsinghua.edu.cn*

PT.30

Examination of Application to Official Method of Surface Water Analysis by Flow Injection Method

Ryozo Goto*, *Japan Environmental Technology Association, 4-8-30-201 Kudan-minami, Chiyoda-ku, Tokyo 102-0074, Japan E-mail: r-goto@toadkk.co.jp*

PT.31

Preparation of organic polymer monoliths and its application in capillary electrochromatography

Lan Zhang*, Zongbao Chen, *Ministry of Education Key Laboratory of Analysis and Detection for Food Safety, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, Fujian, China, E-mail: zlan@fzu.edu.cn*

The Application of Monolithic and Mesoporous Materials in Analysis of Biological Samples

Hanfa Zou

CAS Key Laboratory of Separation Science for Analytical Chemistry, National Chromatographic R&A Center Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Sample preparation has been playing an important role in the analysis of complex samples. Mesoporous materials as the promising adsorbents have gained increasing research interest in sample preparations due to their desirable characteristics of high surface area, large pore volume, tunable mesoporous channels with well defined pore-size distribution, controllable wall composition, as well as modifiable surface properties. The recent advances of mesoporous materials in sample preparation with emphases on the size selective enrichment of peptides/proteins, specific capture of post-translational peptides/proteins and enzymatic reactor for protein digestion will be discussed. On the other hand, the organic inorganic hybrid monolithic columns have been attracting great attention in separation sciences. A one pot process for the preparation of organic silica hybrid capillary monolithic columns by concurrently using organic monomers and alkoxy silanes was developed. Different types of organic-silica hybrid capillary monolithic columns with hydrophobic, hydrophilic, ion exchange functionality and chiral selectors have been fabricated, respectively, by this one pot process using different types of organic monomers. Furthermore, the polyhedral oligomeric silsesquioxane reagents were proposed as the cross linkers for preparation of hybrid monolithic capillary column via thermal free radical copolymerization with different types of organic monomers. The synthesized hybrid monoliths possessed the merits of organic polymer-based monoliths and silica based monoliths with good mechanical and pH stabilities and high column efficiencies. The performances of these organic-silica monolithic columns were investigated by capillary liquid chromatography separation and micro-extraction of the biological samples.

Development of Micro-Gas Chromatography System for On-Site Measurement

Katsumi Uchiyama

*Department of Applied Chemistry, Graduate School of Urban Environmental Sciences,
Tokyo Metropolitan University, Tokyo 192-0397, Japan, uchiyama-katsumi@tmu.ac.jp*

We have developed a portable gas chromatography(GC) system for on site environmental measurement by the support of JST program. In order to realized the system, we have developed following elemental technologies at first, 1) micro chip sample injector for pico - nano liter amount of liquid sample injection, 2) on chip GC column unit, 3) small and high sensitive detection devices and 4) GC utilities. By the organic integration of these technologies, we have succesfully realized on site GC system for the first time. The target performance of the GC system was as follows:

Samples analysed: environmentally huzardous substances (PCBs, pesticides), Sample injection: ink-jet introduction, Sample amount: few ~ dozend micro liter, Detection limit: 0.2 pg (on site ECD detector) and 20 pg (for Phosphorous, Sulfur detector), Analytical time: 1~several min., Reproducibility: less than 1%, Size: 250 × 250 × 150 mm (max), Weight: less than 5 kg, Electric power supply: Transportable battery. The performance of the colmn, which was developed with silicon technology, was as follows. The column with 5% phenyl 95 % dimethylpolysiloxane stationary phase showed about 36,000 theroetical plate (TP) and 4,200 HETP/m, and WAX stationary phase showed about 11,000 TP and 1,285 HETP/m. Ink jet injector for the on chip capillary colum was developed for the first time. The injector could introduce several pico liter to several tens nanoliter liquid sample directly onto the colum unit without any splitting. The injector enabled reproducible sample introduction under high pressure. Portabel ECD detector and atomic emission detector (AED) were developed. Detection limit of the ECD detector was about 0.04 pg (S/N=10, gamma-BHC). Detection limit of AED with coaxial eletrodes for sulfur was about 8 pgS/sec (S/N=3) and for phosphorous was 12 pgP/sec (S/N=3). The micro GC system developed has world smallest AED, nano-injector and an on chip column unit with highest performance. From 2010, the project was moving to new stage. Recent progress for the projects and some topics for sample pretreatment method will be also presented. The work was carried out by the successfull collaboration with Shimadzu Co. (K. Komori, M. Ueda, T. Nishimoto, M. Kanai, M. Nishino, Y. Takemori, S. Matsuoka), Fuji electronics Co. (M. Shinoda, N. Seino), Hirosaki University (T. Mineta), Tokyo metropolitan (K. Mizuishi) and Tokyo metropolitan university (T. Nakagama, H. Zeng) under the finacial support by JST.

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Flow Field-Flow Fractionation: A New Pipeline to Proteomics

Myeong Hee Moon

*Department of Chemistry, Yonsei University, Seoul, 120-749, Korea,
mhmoon@yonsei.ac.kr*

This presentation shows the combination of flow field-flow fractionation (FIFFF) and nanoflow liquid chromatography – electrospray ionization-tandem mass spectrometry (nLC-ESI-MS-MS) that can be readily utilized for the proteomics and lipidomics study. For the study of biological macromolecules, it often requires a comprehensive approach including high performance separation/isolation methods, mass spectrometry (MS), and bioinformatics. While MS has been rapidly evolved to high resolution analytical method, a high performance separation/isolation of proteome sample is still required in proteomics prior to MS analysis due to the complexity of proteome. FIFFF is an elution technique that can be utilized for pre-fractionating biomolecules such as proteins, cells, lipoproteins, and subcellular species by sizes. Introduced are the recent studies on the use of FIFFF as an alternative pre-analytical method for fractionating proteome followed by shotgun proteomic analysis of collected species after digestion or extraction using nLC-ESI-MS-MS. For the size fractionation of membrane proteins, glycosylated or phosphorylated proteins, FIFFF techniques such as hollow fiber FIFFF (HF5), frit inlet asymmetrical FIFFF (FI-AF4), and the isoelectric focusing-asymmetrical FIFFF (IEF-AF4) which is an on-line non-gel based two-dimensional (pI & hydrodynamic diameter) protein separation devices are utilized. This presentation also shows a potential utility of multiplexed HF5 and nLC-ESI-MS-MS for the lipidomics especially for the systematic profiling of various phospholipids (PLs) in lipoproteins from human blood plasma. Semi-preparative HF5 is utilized for the size fractionation of high density lipoproteins (HDL) and low density lipoproteins (LDL) from human plasma from coronary artery disease, and followed by the shotgun lipidomic analysis of various kinds of lipoproteins and lysolipoproteins for the biomarker development.

SPME and GC-MS of Polycyclic Aromatic Hydrocarbons from Different Sources

Yi Chen*^{1,2,3}, Yuan Wang¹, Zhenpeng Guo¹

¹Key Lab of Analytical Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Email: chenyi@iccas.ac.cn

²Beijing National Lab for Molecular Science, Beijing 100190, China

³Beijing Center for Mass Spectrometry, Beijing 100190, China

Polycyclic Aromatic Hydrocarbons (PAHs) have more than 200 derivatives, which can be found in any a place with organic productions and wastes, and are crucial pollutants in environments and various foods [1,2]. Quite many of PAHs are carcinogenic, teratogenic and/or mutagenic, of which benzo[α]pyrene and benzo[α]anthracene are the most famous. Their analysis and identification are hence of great importance and have impacted on the analytical chemistry for not a short time. The difficulty lies in the finding of trace PAHs, which depends on the pretreatment of various samples. During recent years, solid-phase micron-extraction (SPME) has been developing very fast and is becoming a powerful tool in combination with high performance separation techniques such as gas chromatography (GC) coupled with identifying instruments like mass spectrometer (MS). At present, SPME can be performed on a monolithic capillary[3], cold fiber[4] or metal needle [5] coated with various materials such gold clusters [6], carbon nanotubers [7] and graphene [8], where the graphene coating is the most attractive since it offers the ideal π - π attraction with PAHs. In this presentation, oxidized graphene (OG) is used to coat the SPME needles. Different approaches have been studied and tested first with standard PAHs, of which punctuation needles were demonstrated to be facile for the preparation of OG-based SPME, able to give a recovery of > 90%. In combination with GC-MS, the new SPME was used to extract and analyze PAHs in various samples such as wastewaters, burned smokes, and airs near by gas stations, over bituminous streets, in doors and close to paper printings (such as news papers, books, journals and so forth). It is greatly surprising that the printings, especially the new books, news papers and journals, emit all strong PAHs, suggesting that readers should pay a high attention to keep way the printings during reading.

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Nano-structured Carbon Film for Direct Electron Transfer with Biomolecules

Osamu Niwa^{1,2} Hiroaki Inokuchi^{1,2}, Dai Kato¹, Akio Ueda^{1,3}, Tomoyuki Kamata¹, Shigeru Hirono⁴

¹*National Institute of Advanced Industrial Science and Technology (AIST), Central 6, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8566, Japan*

²*University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*

³*Tokyo Institute of Technology, 4259, Nagatsuta, Yokohama 226-8503 Japan*

⁴*MES-Afty Corporation, 2-35-2 Hachioji Tokyo 192-0918, Japan niwa.o@aist.go.jp*

Nano-size structured carbon materials such as carbon nanotube and mesoporous carbon have been studied to increase the amounts of immobilized enzymes or direct access of electrons from/to enzyme redox center due to their large reaction area. However, these materials are powder or fiber shapes which should be used by modifying these materials on the solid electrodes. In contrast, carbon film electrode can be easily formed on various substrates including glass or plastic and mass producible. We have developed a new carbon film electrode material by using electron cyclotron resonance (ECR) sputtering method. The film has nano-crystalline structure consisting of sp² and sp³ bonds [1]. The film shows wide potential window and low adsorption of biomolecules since it has extremely smooth surface (Average roughness:0.07 nm) [2, 3]. We have been applied the film for detecting biomolecules such as DNA and DNA methylation[4]. By utilizing this film, we recently fabricated nano-thorn-like surface structures to realize efficient direct electron transfer (DET) with an enzyme[5], which is very important for various enzyme biosensors and for anodes or cathodes used in biofuel cells. The nano-thorn-like structure was fabricated by using UV/ozone treatment (UV: 185 and 254 nm) without a mask, and the obtained nano-spines are typically 2-3.5 nm high as confirmed by atomic force microscopy (AFM) measurements. With X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM), we found that the thorn-like structure could be formed by employing significantly different etching rates depending on nm order differences in the local sp³ content of the nanocarbon film. The size and density of the thorn-like structure can be varied by changing the ratio of sp³ and sp² bonds. With electrochemical characterization, the nano-spine carbon film had an increased surface area, a larger amount of surface oxide and improved electrochemical activity compared with the original carbon film. With physically adsorbed bilirubin oxidase on a nano-thorn-like carbon surface, the DET catalytic current amplification was 30 times greater than that obtained with the original carbon film with a flat surface, suggesting that DET was accelerated by the formation of surface nano-structure. Similar response was also obtained when we modified cytochrome C on hydrophobic nano-thorn-like carbon film.

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Determination of E,E-farnesol in Makgeolli Using Stir Bar Sorptive Extraction Coupled with Gas Chromatography – Mass Spectrometry

Jaeho Ha¹ * , Yiru Wang^{1,2}, Hyejin Jang¹, Homoon Seog¹, and Xi Chen²

¹*Food Analysis Center, Korea Food Research Institute*

²*Department of Chemistry and the Key Laboratory of Analytical Sciences, Xiamen University*

In this paper, we analyzed the volatile and semi-volatile compounds, including E,E-farnesol in Makgeolli which is a traditional type of Korean fermented rice wines. Forty-one compounds including alcohols, 1-butanol-3-methyl acetate, E,E-farnesol, stearol, and phytane, were separated and quantified by dynamic headspace sampling (DHS) and stir bar sorptive extraction (SBSE) coupled with gas chromatography-mass spectrometry. E,E-farnesol, a known anti-tumor agent, was detected by the SBSE method in Makgeolli. SBSE has been found to be an effective method for analyzing E,E-farnesol levels in Makgeolli. The experimental parameters related to the extraction efficiency of the SBSE method, such as ethanol concentration and filtration, were studied and optimized. The linear dynamic range of the SBSE method for E,E-farnesol ranged from 0.05 to 500 ng/mL with $R^2 = 0.9974$. The limit of detection and limit of quantification of the SBSE method were 0.02 and 0.05 ng/mL, respectively. The relative standard deviation of intra- and inter-day reproducibility was less than 5.4% and 9.9%, respectively.

High-Throughput and Real-time Analysis of Cell Communication by Integrated Microfluidics

Mengsu (Michael) Yang

Department of Biology and Chemistry, City University of Hong Kong,
bhmyang@cityu.edu.hk

Our research interest has been focusing on developing microfluidic device as a tool in studying cellular communication and performing high-throughput bioassays [1-14]. Microfluidic chips with cell localization and cell array formation structures have been developed within microfluidic networks where continuous and discrete concentration gradients were generated by controlled laminar mixing and fluid distribution. In this lecture, I will present some of our recent work on microfluidic formation of single cell array for parallel analysis of ion channel activation and inhibition, and the development of a microfluidic platform to study suspension cell-cell communication under microvalve actuated mechanical stimulation. We have designed a microfluidic device consisting of parallel, independent channels with cell-docking structures for the formation of an array of individual cells. The microfluidic cell array was used to quantify single cell responses and the distribution of response patterns of calcium channels among under the effects of specific activator and inhibitor molecules for a population of individual cells. The results demonstrate that it is possible to acquire single cell features in multichannels simultaneously with passive structural control, which provides an opportunity for high-throughput single cell response analysis in a microfluidic chip. We have also developed a microfluidic device for on-chip monitoring of suspension cell-cell communication. A deformable PDMS membrane was developed as a compressive component to perform cell entrapment and exert different modes of mechanical stimulation. The trapped cells could be triggered to release mediators by mechanical stimulation. Calcium oscillations were evoked in the recipient cells by the released mediators. Different mechanical stimulation and flow environment were also employed to study their impact on the behavior of cell-cell communication, where both the duration and intensity of intracellular calcium responses increased in persistent stimulation and decreased in flowing environment. This microfluidic device may open up new avenues for real-time monitoring of suspension cell-cell communication, which propagates via gap-junction independent mechanism, with multiple variables under control.

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Combinable PDMS Capillary (CPC) Sensor Array Towards the Development of Single Step and Multiple Biosensing Microdevices

Hideaki Hisamoto

*Department of Applied Chemistry, Osaka Prefecture University
1-1 Gakuen-cho, Naka-ku, Sakai-shi, Osaka 599-8531, Japan
hisamoto@chem.osakafu-u.ac.jp*

Here we report a novel capillary-type sensor array called, Combinable PDMS Capillary (CPC) sensor array, allowing single step and multiple bioanalysis by simply introducing a sample solution by capillary action, followed by spontaneous mixing and reactions for fluorescence readout. The developed CPC sensor can eliminate the complicated step-by-step operations required for some conventional bioassays, leading to the realization of "Sample-in & Signal-out" type biosensing.¹⁻³ Since the CPC is fabricated by combining "Convex"-shaped PDMS plate immobilizing an insoluble membrane containing analytical reagents and "Concave"-shaped PDMS plate immobilizing a soluble membrane containing other kind of analytical reagents, it is very useful especially for "single-step" enzyme inhibitor assay which has been difficult to demonstrate by either conventional assay or commercially available capillary-based assay, because enzyme inhibitor assay requires both enzyme and fluorescent substrates which can react each other during the immobilization procedure. Here, various bioassays using CPCs involving enzyme inhibitor assay, multiassay of serum components will be presented in detail.

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Interfacial Behavior of Biomolecules and Bioelectrochemical Analysis

Xinghua Xia

State Key Lab of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China, xhxia@nju.edu.cn

Micro/nanotechnologies are promising for the construction of functional biointerfaces for bioelectronic devices and biosensors. Recent reports have shown that nanomaterials could be ideal electron mediators or ideal nano-interfaces for biomolecules due to their unique properties. Application of nanomaterials in microtechnology reveals an interesting field of bioanalytical chemistry. We are recently focusing on the construction of micro/nanotechnology-based functional biointerfaces for electrocatalysis and direct electron transfer of model biomolecules such as hydrogen peroxide, glucose, glucose oxidase and heme proteins. The nanostructured interfaces including 2D films of SAM, and 3D macroporous structures of Graphene, Prussian blue, silica, and noble metals of Au, Pt and hybrid composites have been designed and successfully synthesized. Systematical studies on the thermodynamics and kinetics of electrocatalysis and the assembly of model biomolecules on the functional biointerfaces have been carried out with the help of scanning electrochemical microscopic, electrochemical and in situ spectroscopic techniques. Results evidently demonstrate that the studied materials show considerable catalytic activities and their functional interfaces provide biocompatible microenvironments for retaining the bioactivity and structure of immobilized biomolecules. In addition, for better understanding the performance of biosensors, the influence of interfacial electric field induced by surface protonation/deprotonation and external electric field on the orientation, bioactivity and electron communication of the biomolecules at electrode surfaces have been systematically studied. Results show that the interfacial electric field manipulates the orientation and structure of the immobilized biomolecules and affects the performance of constructed biosensors as well. Understanding of the fundamentals of nanochannel properties is essential for exploring the potential application of nanochannel based devices. To this issue to be addressed, nanochannel arrays based on porous anodic alumina membranes with controlled pore diameter and pore-length aspect ratio have been fabricated. Influence of nanochannel diameter and pore-to-length ratio on the electroosmotic and electrophoretic properties of the nanochannels has been studied in detail. The observed abnormal diffusion through the nanochannels would enable us to understand the biological phenomena. In addition, based on the abnormal diffusion properties through the nanochannels, a proper electrochemical probe ferricyanide was suggested. Due to the steric inhibition and electrostatic repulsion effect, ferricyanide ion diffusion through the nanochannels will be specifically modulated by the morpholino-DNA hybridization, therefore, a sensitive label-free DNA detection system was proposed.

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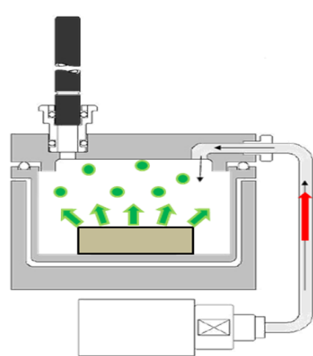
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A Novel Investigation Method of VOC Emission from Car Interior Components by μ -chamber

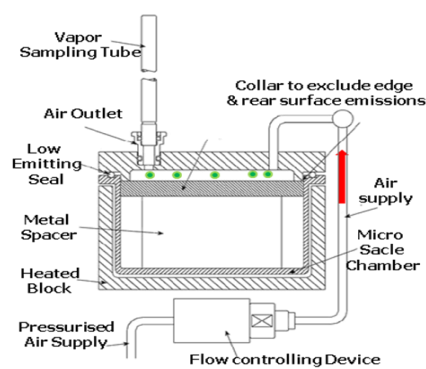
Man-Goo Kim* and Ik-Hee Lee

Department of Environmental Science, College of Natural Science, Kangwon National University, Kangwon, 200-701, Korea, mgkim@kangwon.ac.kr

Volatile organic chemicals (VOCs) levels in car cabin air have much attention and regulated in recent years. A significant proportion of the chemicals found in car cabin air are released from the interior trim components¹). It is therefore important to identify and measure chemical emissions from car interior trim components and to reduce or eliminate them wherever practical. Various module and multi-layer components with and without solvent based and organic coating within the micro chamber were evaluated. The micro-chamber lid eliminates ingress of emissions from cut edge and the rear surface effectively. This novel method is being developed as part of ISO 12219-32) and applied to investigation of manufacturing steps of causing VOC emission, and searching VOC problem materials (layer) in multi-layer components. Adhesive was The relationship of micro-chamber method and static chamber method were compared and discussed.



Bulk emission test



Surface emission test

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Biomass/cell Manipulation for Arsenic Analysis and Removal from Water Samples

Ting Yang, Mingli Chen, Jianhua Wang*

Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China, jianhuaqrz@mail.neu.edu.cn

Bacillus subtilis is a spore forming bacterium that takes up both inorganic As(III) and As(V). At low pH the binding capacity for the two arsenic species is the same and is too large to be just membrane-bound on the bacteria. Incubating the bacteria with Fe(III) causes iron uptake (up to ~0.6% by weight), and some of the iron attaches to the cell membrane as hydrous ferric oxide (HFO) with additional HFO as a separate phase. Remarkably, 30% of the bacteria cells remain viable after treatment by a large amount of Fe(III). At pH 3, upon metallation, As(III) binding capacity by the ferrated bacteria becomes ~0, while that for As(V) increases more than three times, offering an unusual high selectivity for As(V) against As(III). At pH 10 both arsenic forms are sorbed, the As(V) sorption capacity of the ferrated bacteria is at least of 11 times higher than that of the native bacteria. At pH 8 (close to the pH of most natural water samples), the arsenic binding capacity per mole iron for the ferrated bacteria is greater than those so far reported for any iron containing sorbent. The ferrated bacteria treated with high concentrations of iron can adsorb on a molar basis more arsenic than the iron they contain. Besides, we found that live HeLa cells also take up arsenic (As(V) and As(III)), where both surface and intracellular accumulation are involved. Interestingly, while both As(V) and As(III) were taken up at high pH, at low pH, As(V) was taken up with a 40:1 selectivity over As(III). Based on the extremely high selectivity for As(V) against As(III) on the above cases, speciation of inorganic arsenic in water samples is readily feasible.

Atmospheric Isoprene and Formaldehyde Analyzers Utilizing Chemiluminescence Detection and Microchannel Scrubber

Kei Toda

*Department of Chemistry, Kumamoto University, 2-39-1, Kurokami, Kumamoto
860-8555, Japan, todakei@sci.kumamoto-u.ac.jp*

Atmospheric chemistry is becoming more complicated and detailed analyses are mandatory to understand their effects and mechanisms. In this half decade, photochemical pollutions were significantly observed in rural and suburb area of west Japan; they were not in big cities in contrast to the typical photochemical smog. Reason of the mystery is thought as coming of the oxidants from Chinese Continent. This is true but there might be another reason. We thought there was interaction between continental oxidants and local chemicals especially biogenic organic compounds (BVOCs) to multiply the oxidants. The most abundant BVOCs is isoprene and it reacts with oxidants to produce HCHO. Thus we have developed instruments for analysis of isoprene and HCHO in low ppbvs. Isoprene was measured by single column trapping/separation – chemiluminescence detection (SCTS-CL)¹; isoprene was collected in a silica gel column for 3 min and desorbed to react with ozone produced by electric discharge. Isoprene could be measured every 10 min with limit of detection of 0.15 ppbv. Micro Gas Analysis System (μ GAS)² developed before was modified to measure HCHO in trace level. Gaseous HCHO was collected in a microchannel scrubber device and fluorescence was monitored continuously after reaction with acetyl acetone. The both isoprene and HCHO were analyzed for two years in a forest area and useful variation data were successfully obtained by the novel two devices.

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Mass spectrometry-Based Hair Metabolomics in Biomarker Discovery of Hormonal-Dependent Diseases

Man Ho Choi* and Bong Chul Chung

Future Convergence Research Division, Korea Institute of Science and Technology, 39-1 Hawolkkok-dong, Seoul 136-791, Korea, mh_choi@kist.re.kr

The objective of hair metabolomics is to investigate alteration of lipid hormones in hair samples obtained from patients with many diseases using mass spectrometry based analytical techniques. Due to the metabolic perturbation in hair reflects the conditions of diseases, the level of diverse lipid molecules were evaluated. In the present studies, metabolite profiling in combination with or without multivariate data analysis was therefore introduced to quantify changes in hair metabolic patterns for mining biomarkers in and evaluating drug efficacies. The hair samples were extracted with optimized conditions depends on the characteristics of analytes and analyzed by gas or liquid chromatography-mass spectrometry (GC-MS or LC-MS). Altered hair steroid levels could indicate disease development as well as drug effects due to its direct action or stimulatory effect on local enzyme activity. This presentation will demonstrate that the described MS based hair metabolomics is potentially useful diagnostic tools and provide an effective means of biomarker ‘mining’.

**Application of GC-HRTOFMS for Environmental Analysis:
A Comprehensive Screening and Identification Techniques for Trace
Organohalogen Compounds in Environmental Matrices**

Takumi Takasuga^{1,2}

¹*Shimadzu Techno Research, INC., 2-13, Nishinokyo-Sanjobocho, Nakagyo-ku, Kyoto
604-8435, Japan, t_takasuga00@shimadzu-techno.co.jp*

²*Center for Marine Environmental Studies (CMES), Ehime University, Matsuyama,
Japan*

The application of gas chromatography/high resolution time-of-flight mass spectrometry (GC-HR-TOFMS) for environmental analysis was evaluated. HR-TOFMS has high sensitivity as low as sub-picogram levels with high resolution. This can also provide full exact mass spectrum information and accuracy of exact mass measurement are within around 5ppm. Furthermore 2-dimesional MAP data assignment, individual exact mass spectrum and exact mass chromatography data processing can be used for screening analysis of suspected compounds as one of the new techniques with only one injection. Additionally it is possible to identify unknown interfering compounds in routine dioxin analysis. Semi quantification data for POPs analysis by isotope dilution method with GC-HRTOFMS was compared with conventional GC-HRMS SIM data on biological samples. Comprehensive analytical methodology for the investigation of organohalogen compounds in environmental samples were evaluated by GC-HRTOFMS, for example, chlorinated PAHs and chlorinated carbazol in contaminated site soil, PCNs in a trans former oil observed interferences of PCB analysis by GCECD, chlorinated pesticides and it's degradation products and flame retardant in river water and sediment, POPs, PCDEs and halogenated natural products in marine mammals. These results suggest that GC-HR-TOFMS is a useful technique for full characterization and profiling of chemical components in a whole range of sample types with selectivity, specificity, increased sensitivity and easily accurate data interpretation for getting data of highest reliability. Further possible application is as a data bank of HR-TOFMS data, Mass Spectrum with GC-MS information for many kinds of important sample.

Determination of Carbamate Pesticides in Vegetables and Fruits by On-line GPC-LC/MS System

Yuki HASHI *¹, Feng JI¹, Feng-Yun PAN¹, Jin-Ming LIN²

¹Shimadzu (China) Co., Ltd., Shimadzu Global COE for Application & Technical Development, Shanghai, 200052, P.R. China

²The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

Pesticides such as carbamate are now commonly used for crop protection which leads to unneglectable threat on both environment and public health. Various national standards/regulations have been established for the maximum concentration of pesticides residue limits (MRLs) in vegetables and fruits. Therefore it is necessary to develop special method of identification and quantification of carbamate pesticides. As non-volatile pesticides, carbamates show low UV absorbance and no fluorescence. Due to the special properties, it is almost impossible to analyze carbamates pesticides by conventional detection method such as GC and HPLC without derivation process. In this regard, LC/MS is getting popular to analyze these carbamates pesticides. GPC is widely used for sample preparation of residual pesticides analysis. Since this technique includes evaporation for solvent of GPC fraction which may cause poor recovery of residual pesticides due to volatility. Moreover this procedure is time-consuming. In order to improve the recovery and shorten the preparation time, we have developed on-line GPC-LC/MS system. Two high pressure 6-port valves were employed to hyphenate GPC and LC/MS system. One valve functions for fractionation of pesticides with sample loop and the other one is working for concentration of pesticides with solid phase extraction column. Since THF for GPC solvent caused poor recovery of pesticides in the concentration step, the fractionated pesticides were diluted by pure water 19 times automatically before concentration step. Therefore, recovery of pesticides was improved. In this paper, we will discuss on system performance of on-line GPC-LC/MS for determination of carbamates pesticides. The absolute recoveries, evaluated at three fortification levels (0.01, 0.05 and 0.1 $\mu\text{g ml}^{-1}$), ranged from 32 to 128%, with relative standard deviations (RSDs) from 1 to 8%. All the limits of detection (LODs) were in the range of 0.001–0.005 $\mu\text{g ml}^{-1}$ and, in any case, lower than maximum residue limits (MRLs) established by Japan and Chinese legislations. Besides, the total analysis only takes 25 min. The proposed new method can be applied to the determination of carbamates pesticides in vegetable and fruits samples.

Liquid Chromatography with a Gas-Liquid Hybrid Stationary Phase

Masami Shibukawa* and Hiroki Nakamura

Division of Material Sciences, Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan
sibukawa@apc.saitama-u.ac.jp

Water confined in hydrophobic nano-space has attracted considerable interest because its properties could vary considerably from those in a bulk phase. It is commonly believed that the structure and dynamics of water are modified by the presence of hydrophobic surfaces, both by a change of hydrogen bonding and by modification of the molecular motion. Reversed-phase liquid chromatography (RPLC) constitutes one of the most important means of separating chemicals in solution and its retention process with aqueous mobile phases is considered to be driven predominantly by the change in structure of water in the hydrophobic pores. We have clarified that there exists interfacial water functioning as the stationary phase in the pores of alkyl-bonded silica particles and solute compounds can differentiate it from the bulk water [1, 2]. It has been demonstrated that liquid water is forced out of the hydrophobic pores when the pressure on the RPLC columns filled with water is released. This phenomenon is a natural consequence of the existence of capillary pressure in the pores of hydrophobic materials unwetted with water. The remaining pore space is occupied by the gas phase of water formed as a result of the extreme change in structure of water in hydrophobic nano-space. The fact that this phenomenon causes rather drastic retention losses indicates that, in aqueous systems, it is not the alkyl bonded layer but the interface between the bonded layer and water or the interfacial water formed on the hydrophobic surface that has a key role in retention. The gas phase of water is steadily fixed in the pores of the packing materials so that it can act as the stationary phase, leading to establishment of a liquid–gas chromatographic system. The possibility and usefulness of liquid-gas chromatography for separation of volatile compounds have already been discussed theoretically and experimentally [3, 4]. More importantly, the gas-liquid hybrid stationary phase consisting of the gas phase and the interfacial water has a great potential as a new separation medium for manipulation of retention and separation selectivity in RPLC with aqueous mobile phase since the structure and the amount of the interfacial water can be changed by controlling temperature and pressure. In this paper, change in retention and separation selectivity with pressure and temperature and usefulness of the RPLC with the gas-liquid hybrid stationary phase are discussed.

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Hydrochar of Cabbage by Hydrothermal Carbonization Reaction and Its Sorption Capacity

Eunsol Koh¹, Sunyoung Bae^{1*}, Kyoung S. Ro²

¹ *Seoul Women's University, Department of Chemistry, Seoul, Korea. sbae@swu.ac.kr*

² *USDA-ARS Coastal Plains, Soil, Water & Plant Research Center, Florence, SC, 29501, USA*

Hydrothermal carbonization (HTC) is a novel thermal conversion process that can convert biomass into useful products. HTC is a wet process conducted at relatively low temperature under autogenous pressures as a method to convert carbohydrates into a carbonaceous residue referred to as hydrochar. This process has a great advantage that wet feedstock can be thermally treated without extra drying pretreatment. The objectives of this study were to evaluate the feasibility of carbonization with cabbage and the distinctive physical and chemical property of the produced hydrochar, and evaluate the sorption capacity of heavy metals. Based on the previous study, hydrochar was produced at 150 °C and 220 °C for 30 min, 1.5 hr, and 2 hr in a tubular microreactor with cabbage. The physicochemical characteristics were identified using iodine number, FT-IR, and SEM analyses. To improve the sorption capacity of biochar, the activation process was conducted using potassium hydroxide solution. The sorption of zinc and lead was performed on the hydrochar and the activated hydrochar. The effect of pH was also investigated in the range of pH 5 to pH 8. The sorption isotherm results show that Zn sorption was favorable, spontaneous and increase in the pH ranges while Pb was independent of pH tested.

Preparation of Hydrogel Microarrays in Microchannels and Its application for Cell Research

Jin-Ming Lin

*Department of Chemistry, Tsinghua University, Beijing 100084, China
jmlin@mail.tsinghua.edu.cn*

In this work, a microfluidic approach for anticancer drug analysis based on hydrogel encapsulated cells was developed. The coupling of photolithography with microfluidic chip realizes the fabrication of three dimensional hydrogel microstructures in the microchannels with controlled position and shape by using a fluorescence microscope. By using this approach, human hepatoma HepG2 cells and human lung epithelial A549 cells were simultaneously immobilized inside three-dimensional hydrogel microstructures on a same array, and they were identified with different shapes. Microarrays of hydrogel encapsulated many kinds of living cells could also be fabricated in a microchannel, which offered the potential for high-throughput assays. In addition, the prepolymer composition and crosslinking parameters that influenced cell viability inside photocrosslinked hydrogels were investigated. By optimizing these conditions, the cell viabilities were nearly reached up to 100%. For the long-term culture of the encapsulated cells, the majority of these cells could keep viable for at least three days, which were able to carry out cell-based assays. In addition, two anticancer drugs were used to stimulate HepG2 and A549 cells encapsulated inside hydrogel microstructures. The variation of two intracellular redox parameters containing glutathione and reactive oxygen species was investigated. The results showed that these two drugs exhibited distinct effects on intercellular redox state. It is indicated that the selectivity of these drugs in inducing cell apoptosis. This established platform provides a simple, fast and high-throughput method for monitoring the effect of anticancer drugs on tumor cells, which has an important application in fundamental biomedical research.

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Application of Electrospray Ionization Mass Spectrometry to the Determination of Inorganic Ions in Environmental Samples

Kinichi Tsunoda¹, Hiroki Hotta², Kiichi Sato¹, Shota Kurihara¹,
Rie Saito¹ and Kazuki Shimotori¹

¹*Department of Chemistry and Chemical Biology, Gunma University, Kiryu 376-8515, Japan:*

²*Department of Chemical Education, Nara University of Education, Nara 630-8528, Japan.*

Electrospray ionization mass spectrometry (ESIMS) is one of powerful tools for detecting metal-organic ligand complexes because of its soft ionization. Thus, we have been interested in its application to speciation analysis for trace elements. In particular, it has been applied to identify the chemical forms of Al in some Al-accumulating plant samples. During such studies, we have found that ESIMS may also have the great potentialities for determining trace inorganic ions such as metal ions and halide ions. In this paper, therefore, discussed is the application of ESIMS for the determination of trace inorganic ions in environmental samples such as biological, soil and water samples [1, 2]. Metal ions could be detected by ESIMS in the negative ion mode as monovalent negative ions of their aminopolycarboxylic acid (APC) complexes, e.g., [Al(edta)]⁻, [Pb(Hedta)]⁻, where excess amounts of the APC agents were added to sample solutions. Among several APCs studied, we chose diaminocyclohexane tetraacetic acid (CyDTA) as the best chelating agent because of higher stabilities and higher sensitivities of the complexes. However, the ionization efficiency of these metal complexes was strongly interfered with the presence of other salts, e.g., NaCl, KNO₃. Therefore, a size exclusion column (G-10) was used for the on-line separation of metal-APC complexes from other matrix salts. This method was successfully applied to the quantitative analyses for Al, Ni, Cu, Zn and Pb in the biological certified reference materials, Olive Leaves (BCR-062) and Plankton (BCR-414). Analytical results obtained by the present method were in good agreement with the certified values. The detection limits of the present methods for these elements were several to several ten nM levels. This approach was extended to determine ultra-traces of halide ion (F⁻, Cl⁻, Br⁻, I⁻) by the formation of the ternary complex of group 13 element (Al, Ga, or In), halide and NTA (nitrilo triacetic acid). We found that [AlF(nta)]⁻ is the most sensitive for fluoride and [InCl(nta)]⁻, [InBr(nta)]⁻, and [InI(nta)]⁻ for chloride, bromide, and iodide, respectively. Their detection limits are about 10 nM. In particular, the [AlF(nta)]⁻ method shows two orders of magnitude better sensitivity than the F⁻-ISE method and is one of the most sensitive methods for fluoride ion at present.

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Electrochemically Enhanced Solid-Phase Microextraction

Feng LUO¹, Jing-Bin ZENG², Xi CHEN^{*2}

¹*Fujian Research Institute of Metric Science; Fuzhou 350003, China, luofeng6789@163.com*

²*Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China, xichen@xmu.edu.cn*

We proposed an electrochemically enhanced solid-phase microextraction (EE-SPME) method, which applies an electrochemical approach using multi-walled carbon nanotubes (MWCNTs)/Nafion composite coating as a working electrode, to enhance the extraction of the selected analytes. For example, a suitable negative or positive potential is selected and applied to enhance the extraction of cationic and anionic compounds in aqueous solutions. Compared to the direct SPME mode (DI-SPME) (without applying potential), the EE-SPME presented more effective and selective extraction of target analytes primarily via complementary charge interaction. The potentials in terms of magnitude and polarity can be easily altered from the electrochemistry analyzer and used for the extraction of corresponding ionic species without the need to modify fiber coating, which demonstrates the simplicity, versatility and flexibility of the EE-SPME method.

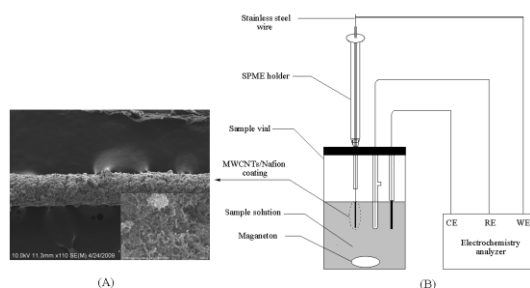


Figure 1. (A) Scanning electron micrographs of the MWCNTs/Nafion fiber coating; and (B) Schematic of the proposed MWCNTs/Nafion EE-SPME device.

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Determination of Melamine and Its Analogues in Various Processed Foods by Using Tandem Mass Spectrometry

Cheong-Tae Kim

Food Safety Research Institute, NONGSHIM Co., Ltd

After illicit addition of melamine to pet feed has caused serious death of pets, US-FDA published the bulletin method about determination of melamine and its analogues from milk and related products. The governments in many countries had to prepare appropriate measures to strengthen the quarantine. Economically motivated adulteration is becoming a new key target of scientist's efforts to protect and promote public health. When it comes to reasonable prediction against those adulteration, even though it might be challenging, crucial key to implement new analysis method should be easy to handle as well as being came out accurate result in advance. Recently, new analysis techniques are being magnified as one of way for trade barrier. Especially, determination of melamine and related compounds precisely from processed foods has been quite difficult. The bulletin method using GC/MS is not suitable way to determine all of them from various types of foods with complex matrices. In some cases, when those compounds were analyzed by using GC/MS method, the ammeline and/or ammelide could be detected from processed foods rather than detection of melamine and/or cyanuric acid. Unfortunately, those results were proved to be false. Furthermore, there have been no reported results on residues of ammeline and ammelide without melamine and/or cyanuric acid from foods and foodstuff yet. Therefore, development of determination method for melamine and related compounds has been conducted. The tandem mass spectrometry method was suitable for determination of melamine and its analogues from process foods with complex matrices. Prior to analyzing them using GC/MS/MS simultaneously, derivatization step was needed, however, hydrophilic interaction column mode and LC/MS/MS could be employed to analyze melamine and related compounds simultaneously without derivatization step of those food samples. These new methods using tandem mass spectrometry would be applied to protect economical gains from adulterations effectively.

On the Analytical Chemistry of Phosphate-Containing Anions

Cheng Zhi Huang¹ and Xi Juan Zhao²

¹*Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Pharmaceutical Sciences,*

²*College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China, chengzhi@swu.edu.cn*

Phosphate-containing anions such as pyrophosphate (PPi), polyphosphate, and various nucleotides including (p)ppGpp, which compose a big family of anions, possess significant biological functions. For example, PPi and ATP are associated with many metabolic reactions and bioenergetic processes. GTP is known to play important roles in the synthesis of RNA and (p)ppGpp, while (p)ppGpp is an important regulatory factor to facilitate the resilience of bacteria and plants to stress. Using the strong coordination ability of phosphate with transition-metal-ions, we have developed some new reagents for selective detection of these phosphate-containing anions [1, 2]. The hypocrellin A-Zn(II) complex can be applied to the highly selective recognition of PPi. [1] One imidazolium derivative has been synthesized and its complex with Zn(II) displays a ratiometric fluorescence response to guanosine phosphates, and ppGpp has the best response. Based on the complexation of PPi and Fe³⁺, a new method of colorimetric detection of ppGpp is proposed with good selectivity against other nucleotides by inhibiting the appearance of bluish-green color of ABTS radical cation. In fact, real-time detection of a certain phosphate-containing anion is still tough owing to the interference induced by other ones. We are convinced that in the near future, more molecules or materials would be designed for selective and real-time detection of one phosphate-containing anion, which are helpful to understand the role of the big family of anions in life sciences.

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Bi₂S₃ Nanodots as a Contrast Agent for In Vivo X-ray Computed Tomography Imaging

Kelong Ai¹, Yanlan Liu^{1,2}, Lehui Lu*¹

¹*State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China.*

²*Graduate School of the Chinese Academy of Sciences, Beijing, 100039, P.R.China
lehuilu@ciac.jl.cn*

X-ray computed tomography (CT) is regarded as one of most powerful diagnostic imaging techniques due to its many advantages that include cost effectiveness, deep tissue penetration, and high resolution. Currently, the only CT contrast agents approved for clinical use are small iodinated molecules. These small iodinated molecules, nevertheless, typically suffer from short circulation time, potential renal toxicity and iodine hypersensitivity reaction. Engineering nanoparticulate CT contrast agents that comprise high atomic number (high-Z) metal elements have been proved to be a powerful strategy to address these issues. Compared to small iodinated molecules, these nanoparticles have the long circulation times, high contrast densities, and a functional surface; thus they are well-suited for in vivo angiography or target detection. Among the currently available Au-, Pt-, Ta- or Bi-based nanomaterials, Bi₂S₃ nanostructures hold great promise for CT contrast agents because Bi possesses the largest X-ray attenuation coefficient. Nevertheless, the exploration of Bi₂S₃-based nanoparticulate CT contrast agents is still in its infancy; this can be attributed primarily to the challenge in controlling its synthesis and surface modification. We developed a facile strategy for producing oleic acid coated Bi₂S₃ nanodots (OA-Bi₂S₃) using commercially available bismuth neodecanoate as the precursor. Distinct from the traditional strategies, the proposed method allows the large-scale manufacture of Bi₂S₃ nanodots with a narrow size distribution and excellent monodispersity. Furthermore, the surface of Bi₂S₃ nanodots can be readily modified with poly(vinylpyrrolidone) (PVP) through a facile ligand exchange method. Small-animal experiments demonstrate that the yielded PVP-Bi₂S₃ nanodots can provide much higher contrast efficacy with respect to a clinical iodinate agent, no adverse effects to organs, and extensive in vivo circulation time. Thus, PVP-Bi₂S₃ nanodots have great potential for improving the capabilities of angiography and tumor targeted imaging in the detection of liver metastases.

Speciation of Vanadium using Difference in Rate of Complex Formation with Xylenol Orange

Koichi Oguma

Research Department, Nissan Arc, 1 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan, k.oguma@nissan-arc.co.jp

Vanadium can exist in oxidation states from II to V in aqueous solution. However, most analytical methods have concentrated on its determination in the states IV and V, as these are the most common forms encountered in inorganic and biological systems. The present paper will describe a flow injection method for the simultaneous determination of V (IV) and V (V) based on the difference in the rate of complex formation of V (IV) and V (V) with xylenol orange (XO) under acidic conditions. A 90- μ L volume of the 0.02 M H₂SO₄ solution containing V (IV) and V (V) was injected into the carrier stream (0.02 M H₂SO₄, 1.1 mL/min) and merged with the 5 x 10⁻⁴ M XO solution (1.3 mL/min). V (IV) and V (V) reacted with XO in the first reaction coil and the absorbance (A₁) of the formed V (IV/V)-XO complexes was measured at 530 nm in the first flow cell attached in the spectrophotometric detector. The sample zone was then merged with the 0.2 M formate buffer solution (pH 3.5, 0.7 mL/min) and passed through the second reaction coil, followed by the measurement of the absorbance (A₂) of V (IV/V)-XO complexes at 530 nm in the second flow cell. Hence, two peaks were obtained per injection and the concentrations of V (IV) and V (V) were calculated by solving the following simultaneous equations.

$$A_1 = (\alpha_{IV} [V (IV)] + \beta_{IV}) + (\alpha_V [V (V)] + \beta_V) \quad (1)$$

$$A_2 = (\gamma_{IV} [V (IV)] + \delta_{IV}) + (\gamma_V [V (V)] + \delta_V) \quad (2)$$

Here, the constants, α, β, γ and δ , were obtainable by construction of the each calibration graph for V (IV) and V (V). The complex formation reaction of V (V) with XO under acidic conditions was much faster than that of V (IV) under the same conditions. The detection limit calculated as 3 σ of noise signals was 0.01 ppm for vanadium in both oxidation states. The relative standard deviations for V (IV) and V (V) were 1.6 and 2.4 %, respectively. The sample through put was found to be about 19 h⁻¹. The effects of foreign ions and applicability of the present method to real samples will be discussed.

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A Ratiometric Fluorescent Biosensor for Intracellular Metal Ions Based on Inorganic-Organic Nanocomposites

Yang Tian*, Anwei Zhu, Qiang Qu

Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, P. R. China, yangtian@mail.tongji.edu.cn

The integration of unique electronic and optical characteristic of inorganic nanomaterials such as gold nanostructures, carbon nanotubes, semiconductor nanoparticles, and so on, with highly specific recognition elements of organic molecules or biomolecules has generated a large amount of new strategies for bioanalysis and bioimaging. In our recent work, we designed several novel inorganic-organic fluorescence probes for biosensing and in vivo imaging of metal ions with high selectivity and long photostability. Water-soluble inorganic quantum dots, such as carbon quantum dots (CQDs), CdSe quantum dots, with carboxylic groups were fabricated as a fluorophore, while selected copper ion (Cu^{2+}) as a target model, an amine-TPEA was first synthesized for specific receptor of Cu^{2+} . Copper, after iron and zinc, is the third most abundant essential trace element in the human body. It also serves as an essential cofactor for a variety of enzymes, including cytochrome c oxidase, and Cu/Zn superoxide dismutase, in all living organisms. However, excessive amounts of copper can lead to eczema, kidney disease, and damage to the central nervous system. Thus, a reliable and stable method for monitoring intracellular Cu^{2+} can help understand its complex contributions to physiological functions and disease states. Fluorescence bioimaging and biosensing with developed selectivity, sensitivity, and resolution provide an attractive approach to achieve this goal. Herein, we first integrate quantum dots with a specific organic molecule for Cu^{2+} and thus develop a selective, sensitive, and photostable strategy for biosensing and in vivo imaging of cellular Cu^{2+} . The inorganic-organic fluorescence probe can monitor Cu^{2+} with a broad linear range with high selectivity. Meanwhile, the nanoconjugated probe shows good cell-permeability, low cytotoxicity, and long-term photostability. As expected, the real-time imaging and biosensing of cellular Cu^{2+} have been successfully achieved in living cells, indicating the excellent cell membrane permeability of this probe.

Synthesis of Dual-Fluorescence Nanocomposites and Ratiometric Fluorescence Sensing for Hg^{2+}

Xiangying Sun*, Fang Li, Chuanxiao Yang, Yibang Xu

*College of Material Science and Engineering, Huaqiao University, Xiamen, China,
sunxy@hqu.edu.cn*

To date, most of the traditional fluorescence probes use single fluorescence intensity as a response signal. However, the analysis of single fluorescent signal is interfered by environmental factors, such as photobleaching, the optical length and intensity of excitation light, the concentration and stability of probes, and so on. The ratiometric fluorescence sensing can effectively eliminate these uncertain environmental effects by using another fluorescence signal as a reference[1-2]. Quantum dots (QDs) have unique optical properties such as photostability, broad excitation spectra and tunable emission spectra, which make it a superior fluorescence material to prepare ratiometric fluorescence probes[3]. In this study, CdS QDs modified by chitosan (CS) were first cross-linked with sodium tripolyphosphate to prepare blue fluorescence CdS@CS nanomicrospheres. The synthesized CdS@CS nanomicrospheres had much better luminescence properties than free CdS QDs, exhibited high quantum yields and narrow full-width at half-maximum. And then, dual-fluorescence nanocomposites with tunable emission were synthesized, in which negatively charged TGA-CdTe QDs with different emission wavelength had electrostatic interaction with positively charged CdS@CS nanomicrospheres. The fluorescence intensity ratio of the dual emission can be tuned by altering the molar ratio of CdTe/CdS@CS or exciting wavelength. The nanocomposites exhibited good photobleaching and pH stability comparing with the pure CdTe QDs. The influences of different metal ions on the fluorescent intensity of dual-fluorescence nanocomposites were investigated. Results showed that the emission contributed by CdTe QDs was found to exhibit maximum quenching in the presence of Hg^{2+} and no significant quenching in the presence of other ions, whereas the intensity of emission by CdS@CS nanomicrospheres was kept constant in all cases. Consequently, the dual-fluorescence nanocomposites may be used as a novel ratiometric and colorimetric fluorescence probe for the detection of trace Hg^{2+} with a detection limit (3SD/k) of 5.6 nM. The method presented here is simple, rapid, inexpensive, sensitive and suitable for practical application.

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Analysis of Active Components in Chinese Herbs by LC/CE with MS and Electrochemical Detections

Zilin Chen

*Wuhan University School of Pharmaceutical Sciences, Wuhan, 4320071, China,
chenzl@whu.edu.cn*

In this presentation, some new approaches for analysis of active components in several Chinese medicines by liquid chromatographic and capillary electrophoretic separations with mass spectrometric and electrochemical detections will be presented. *Catharanthus roseus* is an important dicotyledonous medicinal plant that contains various anticancer components, such as vinblastine and its monomeric precursors (vindoline and catharanthine). We have developed a CE-MS analytical method for analysis of active components in *Catharanthus roseus* [1]. Figure 1 shows the typical total ion chromatogram of three major components (Peak identification: 1 vinblastine; 2 catharanthine; 3 vindoline) in *Catharanthus roseus* extract by CE-MS. Bavachin, bavachinin, bakuchiol and isobavachalcone are typical flavonoid components in *Fructus Psoraleae*. Orientin and isorientin are isomeric flavonoid components in *Lophatherum gracile* Brongn. We have developed analytical methods for analysis of these components by LC-MS and ECD detections. High sensitivity of ECD over 10-100 times higher than UV has been achieved [1]. Figure 2 shows the typical chromatogram of analysis of four flavonoid components in *Fructus Psoraleae* by LC-ECD.

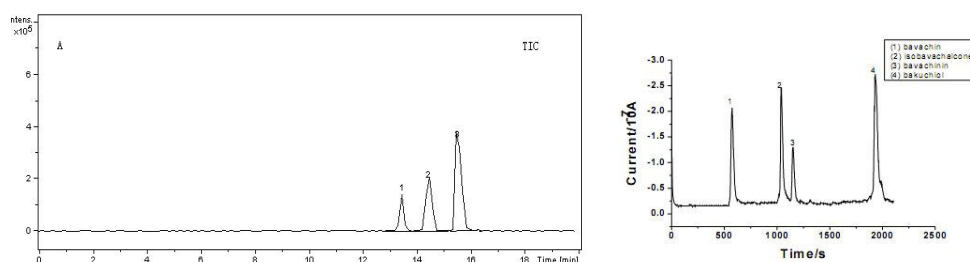


Figure 1 (Left) Typical total ion chromatogram of three major components in *Catharanthus roseus* extract by CE-MS.

Figure 2 (Right) Typical chromatogram of analysis of four flavonoid components in *Fructus Psoraleae* by LC-ECD

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Monitoring of Corticosteroids in cosmetic products manufactured in Korea

Yun Sik Nam and Kang-Bong Lee*

*Advanced Analysis Center
Korea Institute of Science and Technology
P.O. Box 131, Cheongryangri, Seoul 136-791, Republic of Korea*

Some cosmetic products manufactured in Korea have been suspected to contain anti-inflammatory corticosteroids such as prednisolone, hydrocortisone, betamethasone, dexamethasone and triamcinolone acetonide for the treatment of eczema, seborrhea and psoriasis without indication on the label of cosmetic products. Due to their severe side effects such as permanent skin atopy, these corticosteroids have to be monitored in cosmetic products from a forensic point of view. Cosmetic product samples of manufacturers charged by consumers have been collected in local and online markets of Korea, and those corticosteroids contained in cosmetic samples were analyzed by HPLC-UV and LC-MS/MS with diagnostic ion and multiple reaction monitoring. Linearity was studied with 0.1~10 µg/mL range in all corticosteroids. Good correlation coefficients ($r^2 \geq 0.997$) were found and their limits of quantitation were 4.68~7.97 ng/g at each corticosteroids. At three different concentrations spanning the linear dynamic ranges, mean recoveries were 97.2~113.5% and precisions (RSD) for intra-day and inter-day analysis were less than 8.9%. Also, accuracy (Bias %) were less than 11.8%. The results showed that the 0.76~0.94 µg/g levels of prednisolone were detected in four cosmetic products and triamcinolone acetonide was monitored with the concentration of the range of 11.5~272 µg/g in nine samples. This fact reveals that some manufacturers have arbitrarily added these corticosteroids in their cosmetic products to advertise spuriously the treatment effect for skin atopy. Thus, these cosmetic products have to be monitored exhaustively, and removed from the market.

Neuronal Analysis in vivo with Microfluidic Chip

Bi-Feng Liu* Jingjing Wang, Ying Wang, Wei Du

Britton Chance Center for Biomedical Photonics, Wuhan National Laboratory for Optoelectronics, Department of Systems Biology, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

The behavior of an animal is closely related to its inner neural activity. To explore the neuronal activities of live *C. elegans* in response to the changing environments, chemical stimulations are usually conducted to output certain stimulus to animals [1]. Recently, microfluidic technology has drawn increasing attentions of researchers in studying the neuronal activities of *C. elegans* [2], due to advantages of ease of fabrication, good transparency, flexible fluid control and size compatibility. Here, we demonstrate a microfluidic system that allowed stable immobilization of young adult *C. elegans* for neuronal analysis upon chemical stimulations. A comb-shaped microvalve was developed for enhanced immobilization of *C. elegans*, especially at the tapered head area of the animal due to multiple force-bearing points, with minimal movement in the z-plane and negligible influence on the activities of the animal during long-term immobilization. Chemical stimuli were delivered to the head of the animal by rapid interface shifting of laminar flows and neuronal activities could then be monitored by in vivo Ca²⁺ imaging. We combined a single or a multiple T-shaped drug delivery system with this microvalve-based immobilization and investigated neuronal responses of the ASH neurons and their adaptations to high osmotic shock. We expect this new method to open up a new avenue for neuronal studies of *C. elegans* as well as high-throughput mutant screening and drug discovery.

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Current Eating Habits of Japanese and Their Effect on Fecal Odor

Shinya Tahara*(1), Michika Sasaki (1), Koji Sakamoto (1), Yasuyuki Hasegawa (1),
Tomoaki Kodama (2), Hiroshi Sato (3)

1) *KOBAYASHI Pharmaceutical Co., Ltd., Toyokawa, Ibaraki, Osaka 567-0057, Japan, Email: s.tahara@kobayashi.co.jp*

2) *Department of Health and Nutrition* 3) *Department of Pharmacy, Nagasaki International University, Huis Ten Bosch, Sasebo, Nagasaki 859-3298, Japan, Email: sato@niu.ac.jp*

Nowadays, the eating habits of Japanese people are changing considerably. For instance, the amount of garlic imported from overseas has been increasing yearly and many ethnic foods with various spices and herbs are now widely known and becoming popular among Japanese people. This study was carried out with the purpose of analyzing the composition of fecal odor and how it changes depending on the food consumed.

Six males aged 24 to 30 were used as subjects in this experiment. Their meals were strictly controlled and they were asked to ingest two types of sample daily meal, each type for one week (Table 1). The sample gas was collected in a 100 L sampling bag with an apparatus especially designed for this experiment and analyzed by GC, GC/MS, TDS (Thermal Desorption Spectrometry) and sensory evaluation.

The result indicates that the consumption of food containing a large amount of meat (modern meal) contributes to the increase in the concentration of sulfur compounds in feces (Fig.1). Furthermore, according to the analysis by TDS, allyl methyl sulfide, which probably resulted from garlic ingestion, was detected only from the gas collected after the ingestion of the modern meal.

Table1 Sample daily meals

| | Ingredients | | | Nutrients | | |
|------------------|---|--|--|-----------------|-------------|--------------------|
| | Breakfast | Lunch | Dinner | Protein [g/day] | Fat [g/day] | Calorie [kcal/day] |
| Traditional meal | rice·pickled plum·seaweed·vegetable juice | rice·root vegetable s·potatoes·egg·fish·pork·seaweed | rice·fish·octopus·seaweed·vegetable s·miso·sesame·yogurt | 76 | 57 | 2267 |
| Modern meal | bread·chicken·beef·egg·cheese | noodles·garlic·pork·Chinese chive·spring onion·bean sprout | rice·beef·pork·chicken·garlic·egg·vegetable s·spring onion | 112 | 152 | 2828 |

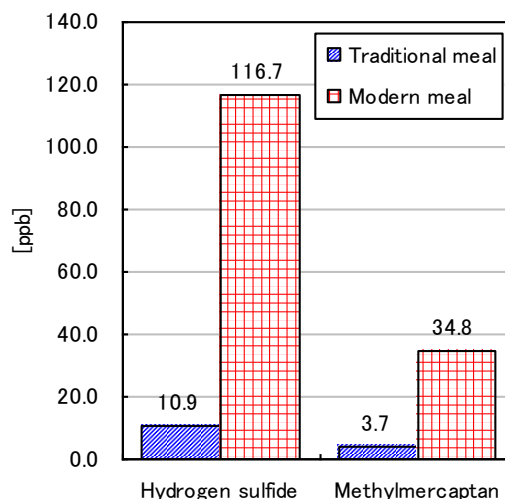


Fig. 1 Comparison of concentrations of hydrogen sulfide and methylmercaptan

Keywords: Fecal odor, Hydrogen sulfide, Methyl mercaptan, Odor intensity, Meal

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Electrogenerated Chemiluminescence Biosensors for Proteins and Bacteria

Cheng-Xiao ZHANG

*School of Chemistry and Chemical Engineering, Shaanxi Normal University,
Key Laboratory of Analytical Chemistry for Life Science of Shaanxi Province,
Xi'an, 710062, P. R. China, cxzhang@snnu.edu.cn*

Electrogenerated chemiluminescence (ECL) is a method of generating light by using electrochemical reactions to produce highly reactive species at the surface of an electrode that can produce excited states in energetic electron transfer reactions. It combines the advantages of both electrochemical and chemiluminescent methods, such as highly sensitive, easy to control and operate with inexpensive equipment, and exceedingly selective due to the use of the biological recognition element in conjunction with specific ECL label and coreactant. In recent ten years, ECL research papers each year have increased from ~120 in 2000 to ~500 in 2010. In this report, the recent development of ECL and its application in biosensing, mainly including organic compound ECL in organic media, ECL of semiconductor nanoparticles, ECL biosensing/biosensors, and ECL combination technologies such as HPLS-ECL, CE-ECL, ECL imaging will be briefly presented. Our Lab has developed a series of ECL biosensors for the highly sensitive detection of DNA, proteins, bacteria, small biologic active molecules and metal ions. In this report, design of ECL biosensors, including synthesis of the ECL probes consisting of molecular recognition elements (such as hairpin DNA, aptamer and lectins) and ECL signal compound such as ruthenium complex, novel immobilization methods and amplification strategies using nanomaterials and dendrimer for multi-label and ECL probe carrier will be extensively presented. The set-up of ECL imaging and its application in detection of cells are also discussed.

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**Preliminary Study on Ion-Exclusion/Cation-Exchange Chromatography
for Determining Simultaneously Radioactive Anions and Cations
Released from Nuclear Power Plant**

Daisuke KOZAKI,¹ Nobutake NAKATANI,² Masanobu MORI,³
Kazuhiko TANAKA¹

¹*Graduate School for International Development and Cooperation, Hiroshima University, 1-5-1, Kagamiyama, Higashi-hiroshima 739-8529*

²*Faculty of Environmental Systems, Rakuno Gakuen University, 582, Bunkyo-dai-midorimachi, Ebetsu, Hokkaido 069-8501*

³*Graduate School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515*

The Fukushima 1st Nuclear Power Plant located in Fukushima Prefecture of Japan suffered severe damage from the earthquake on March 11, 2011. A large amounts of radioactive substances has been released into the surrounding environments by the accident. Therefore, the monitoring of the radioactive substances is one of the most important tasks for evaluating the impact to the environments. By the nuclear fission reaction of ^{235}U , many fission products are released. In these fission products, ^{131}I , ^{90}Sr and ^{137}Cs are recognized to be strongly carcinogenic radioactive substances. In this study, to determine simultaneously the radioactive ions such as I^- , Sr^{2+} , and Cs^+ , the ion-exclusion/cation-exchange chromatography (IEC/CEC) with conductivity detection on a polymethacrylate-based weakly acidic cation-exchange resin column [Tanaka et al., *J. Chromatogr. A*, 804 (1998) 179; *ibid*, 884 (2000) 167] was studied preliminarily using aqueous eluent consisting of sulfosalicylic acid, crown ether and methanol. As a result, under the optimized chromatographic conditions (0.8 mM sulfosalicylic acid, 3 mM crown ether and 30 % methanol at 0.6 mL/min), the high resolution and simultaneous separation of the radioactive ions such as I^- , Sr^{2+} , and Cs^+ from the common anions such SO_4^{2-} , Cl^- , NO_3^- and the cations such as Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} was achieved in ca.30 min. This simultaneous separation mechanism is based on the ion-exclusion effect for the anions and the cation-exchange effect for the cations. The analytical performances tests including calibration graph, detection limit, reproducibility and recovery were carried out under the optimized ion chromatographic conditions. In future work, the radioactivity detectors to monitor selectively β -ray for ^{137}Cs , ^{131}I , ^{90}Sr and γ -ray for ^{137}Cs , ^{131}I are introduced instead of the conductivity detector for applying practically to the several Fukushima's environmental samples.

Hybrid Field-Assisted Solid-Liquid-Solid Dispersive Extraction for the Determination of Organochlorine Pesticides in Tobacco by Gas Chromatography

Ting Zhou, Xiaohua Xiao, Gongke Li*

School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, China, cesgkl@mail.sysu.edu.cn.

In this paper, a novel one-step sample preparation technique termed hybrid field-assisted solid-liquid-solid dispersive extraction (HFASLSDE) was developed. A simple glass system equipped with an air-cooled condenser was designed as an extraction vessel. The HFASLSDE technique was a three-phase dispersive extraction approach. Target analytes were extracted from sample into the extraction solvent enhanced by microwave and ultrasonic irradiation, meanwhile the interfering matrix components are absorbed by dispersing sorbent. No cleanup step preceded chromatographic analysis. The efficiency of the novel HFASLSDE approach was demonstrated in the determination of organochlorine pesticides (OCPs) residues in tobacco with gas chromatography-electron capture detector (GC-ECD). Various operation conditions were studied systematically. Under the optimized conditions, the detection limits of OCPs were in the range of 0.4-0.9 $\mu\text{g/L}$. The recoveries of OCPs were in the range of 70.2-118.2% with relative standard deviations less than 9.6% except for the lowest fortification level. Due to the effect of the hybrid field, HFASLSDE showed significant predominance compared with other extraction techniques. And the dispersing sorbent with good cleanup ability used in this study was also found to be a microwave absorption medium, which could heat the non-polar extraction solvent under microwave irradiation. Different microstructures of tobacco samples before and after extractions demonstrated that the mechanism of HFASLSDE was based on an explosion at the cell level. According to the results, HFASLSDE was proved to be a simple and effective method in the determination of pesticides residues in samples and could potentially be extended to other non-polar target analytes such as pyrethroid insecticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in complex matrix.

A Novel Sample Preparation Method by Rapid and Simple No-heating Saponification for the Determination of Cholesterol in Infant Formula

Dr. Jang-Hyuk Ahn, In-sik Jeong, Byung-Man Kwak, Seung-Hwan Jeong, Taehyung Yoon¹, Changyong Yoon¹, Jayoung Jeong¹, Jeongmin Park² and Jin-Man Kim^{2*}

Food Safety Center, Research and Development Institute, Namyang Dairy Co., Ltd., Gongju 314-914, Korea

¹*Nutrition and Functional Food Research Team, Korea Food and Drug Administration, Seoul 122-704, Korea*

²*Department of Food Science and Biotechnology of Animal Resources, Konkuk University, Korea*

Two methods with no-heating saponification processing were developed by rapid and easy sample preparation for the determination of cholesterol in infant formula. First method was developed for GC(Gas Chromatography) and second method was developed for HPLC(High Performance Liquid Chromatography). The cholesterol determination methods were investigated on the basis of microextraction and no-heating saponification. For the first method, the cholesterol was instrumentally separated using a gas chromatography with a flame ionization detector (GC-FID). Easily extracted cholesterol containing layer by ethyl ether from 1 g infant formula was then saponified with KOH in methanol solution. The extraction and saponification process were simply occurred in the centrifuge tube and the test results for certified reference materials were profitable to the certification of SRM 1849. For the second method, sample pretreatment method to separate cholesterol by HPLC-UVD was developed. 1 g infant formula sample in 50 mL centrifuge tube was mixed with distilled water and isopropyl alcohol plus $(\text{NH}_4)_2\text{SO}_4$ to extract cholesterol efficiently. Then, NaCl, KOH and bonded silica NH_2 were added to the extracted solution with simultaneous clean-up and the solution was induced phase separation and force lipophilic compounds into the upper isopropyl alcohol layer. Thus, analysis time for cholesterol in infant formula could be reduced. Those methods are respected to be implemented in laboratories to reduce inspection time and cost to 20% level from the existing official method. The results for recoveries were in the range of 90~110% and RSDs were below 5%. Two methods by GC and HPLC could be widely used in a routine laboratory providing increased sample treat capacity and reducing time and cost.

Urea Electrochemical Sensor Based on Molecularly Imprinted Chitosan Film Doped with CdS QDs

Hui-Ting Lian, Yan-Ping Chen, Xiang-Ying Sun, and Bin Liu*

College of Material Science and Engineering, Huaqiao University, Xiamen 361-021, People's Republic of China, Email: bliu@hqu.edu.cn

Molecularly imprinted polymers (MIP) [1] are reported as the promising direct recognition elements in sensing fields currently. However, the low sensitivity caused by slow mass transfer process becomes bottleneck for the development of the MIP electrochemical sensor. Hoping to solve that, various nano particles which possessed the outstanding conductivity were introduced [2]. Herein, an improved MIP sensor based on the chitosan (CS) imprinted film doping CdS quantum dots (QDs) was developed going through constant potential electrodeposition and the elution of template molecule urea. Electrochemical impedance spectra (EIS) in Fig.1 showed the conductivity promoting of the proposed sensor, and other test results also indicated the sensitivity enhancing along with the specific recognition remaining compared to MIP sensor without CdS QDs.

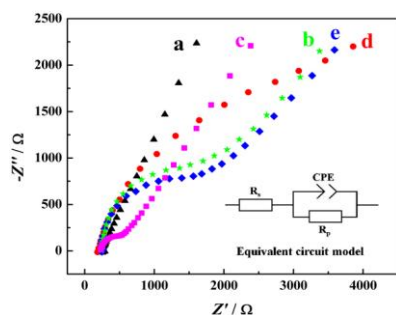


Figure 1. EIS of bare Au (a), CdS QDs-urea-CS/Au (b), CdS QDs-MIP/Au (c), urea-CS/Au (d) and MIP/Au (e) in 1.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.01 M KCl. The inset was the equivalent circuit model for the system.

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A New Needle Packed with Poly(dimethylsiloxane) Having a Micro-bore Tunnel as Alternative Solid Phase Microextraction

-Application for the Headspace Gas Chromatography and Mass Spectrometric Analysis of Volatile Aroma Active Compounds from Six Citrus Oils-

Hyun-Hwa Son and Dong-Sun Lee*

Department of Chemistry, Seoul Women's University, 139-77 Korea dslee@swu.ac.kr

In this study, a prototype stainless steel needle (Hamilton 90022, 22 gauge bevel tip, 51 mm length) packed with poly(dimethylsiloxane) (0.413 mm O.D., 10 mm length) having a micro-bore (0.2 mm I.D.) tunnel was prepared as a new in-needle solid phase microextraction (SPME) device. This needle with a barrel and a plunger is then inserted and exposed into the headspace over the sample. Headspace sampling can be speeded up by compression and aspiration of the plunger through the barrel (Hamilton 1001N, 1 mL) using a reciprocal pump. After the extraction, the needle was then inserted directly to the heated injection port of the gas chromatograph (GC) for the thermal desorption and the simultaneous injection to the GC column. The procedure has been optimized along with the validation of method performance. The methodology has been applied for the analysis of volatile aroma active compounds from six kinds of citrus peel essential oils by GC/MS. The proposed method showed excellent linearity, reproducibility, and low detection limit. This solventless technique is simple to operate, inexpensive to fabricate, and provides a facile means for collecting and introducing volatile aroma active compounds from essential oils. The main advantages of this in-needle SPME technique were the significantly higher extraction speed and the practical merits of a durable stainless steel needle compared to those of easy to fragile SPME fiber.

Aspects of Recent Developments of Chemical Multiway Calibration Methodologies

Hai-Long WU

*State Key Laboratory of Chemo/Biosensing and Chemometrics,
College of Chemistry and Chemical Engineering, Hunan University,
Changsha 410082, China, hlwu@hnu.cn*

Multiway calibration methodologies are gaining more and more attention in the field of analytical chemistry. Multivariate calibration (two-way calibration, first-order calibration) methods including PCR and PLS have been widely applied, for instance, in on-site real-time analysis and on-line monitoring and control coupled with near-infrared spectroscopy. Three-way calibration (second-order calibration) methods have many advantages: 1) It is a smart and green quantitative analysis strategy based on “mathematical separation” for complex chemical systems when combined with advanced instruments capable of generating multidimensional arrays, such as EEMs, HPLC-DAD and LC-MS; 2) It enables one to quantify the component(s) of analytical interest even in the presence of unknown interferences not included in the calibration samples, which has been known as “second-order advantage”. It makes the final goal of analytical chemistry achievable even without the aid of complicated separation procedures. Some multiway calibration algorithms based on the alternating (weighted) least-squares principle have been introduced in the past decades. These methods especially three-way calibration can be used to resolve different problems of qualitative and quantitative analysis in complex chemical systems. They have been applied to simultaneous or direct determinations of multiple components of analytical interest in many fields such as food, environmental, biomedical, pharmaceutical sciences. The main points on successful applications of these chemometric methods combined with analytical instruments have been also summarized.

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Analysis of Volatile Flavor Compounds of Long-aged Doenjang by Automated HS-SPME-GC-MS

Hye Young Seo*, Sun Young Lee, Ji Hee Yang, Kyung-Hyung Ku¹, Minseon Koo¹

World Institute of Kimchi, Korea, 1Korea Food Research Institute

A method for automatic analysis of volatile flavor compounds in Doenjang (Korean soybean paste) by headspace-solid phase micro-extraction-gas chromatography-mass spectrometric (HS-SPME-GC-MS) method was established. The different fibers and capillary columns were tested and their effectiveness compared in order to optimize solute extraction and separation. The HS-SPME sampling conditions were properly tuned in order to maximize solute adsorption. The optimized method was applied to the investigation of long-aged Doenjang for 1, 2 and 3 years and their flavor profiles were evaluated. The major volatile flavor compounds were benzacetaldehyde, 3-methyl butanoic acid, benzaldehyde, butanoic acid, 1-octen-3-ol, and acetic acid in fermented Doenjang for one year. Compositions of these major volatile compounds in long-aged Doenjang for 2 and 3 years were changed. Contents of benzaldehyde, benzacetaldehyde and 3-methyl butanoic acid were increased during fermentation. Established HS-SPME-GC-MS method could be used for determination of volatile indicator in Doenjang and similar products.

Changes of Free Sugar and Organic Acid of Kimchi During Fermentation with Different Ingredients

Sung-Hee Park, Ji-Hye Kim, Eung Soo Han

World Institute of Kimchi

The changes of the content of organic acids and free sugar of the various ingredients added to Kimchis. The control Kimchi was made of salted cabbage with green onion, garlic, ginger and red pepper and sample Kimchis were made without garlic or red pepper and fermented for 9 days at 20°C. Changes of pH, total acidity, salt content, free sugar content and free amino acid content were measured and compared with the control Kimchi and salted cabbage. Organic acids identified were lactic, succinic, fumaric and malic acid. It was found that lactic and succinic acid were relatively high among the organic acid. The content of lactic acid was increased over 20 times from a little amount at the initial period. Free sugars identified were mannitol, fructose and glucose. Total sugar content decreased until 8th day fermentation at 20°C. The mannitol was increased in palatable period in contrast with those of other free sugars.

Identification and Quantification of S-allyl-L-cysteine in Heated Garlic Juice by HPLC with Ultraviolet and Mass Spectrometry Detection

Sanghee Lee*, Miyoung Yoo, Dongbin Shin

Korea Food Research Institute, Sungnam-si 463-746, Korea

The paper presents a new HPLC method for the identification and quantification of S-allyl-L-cysteine (SAC) that is the most important bioactive compounds present in heated garlic juice (HGJ) using liquid chromatography combined with ultraviolet (LC-UV) method and mass spectrometry detection (LC-MS/MS) method, based on a dansyl chloride derivatization step. The method validation included selectivity, linearity, precision, accuracy, and sensitivity. The linear correlation coefficients (r) were always higher than 0.998. Intra- and inter-day precision for SAC at three concentrations demonstrated a relative standard deviation (RSD) of less than 15.3% for both methods. The limit of quantification (LOQ) was $0.71\mu\text{g g}^{-1}$ and $0.07\mu\text{g g}^{-1}$ for UV and MS methods, respectively. There were statistically indistinguishable between the SAC contents determined by using the UV and MS detection in real HGJ samples. The herein described both methods were proposed to be a useful tool for determination of correct SAC content of garlic preparations for quality control.

Analysis of *E*- and *Z*-Ajoene in Oil-Macerated Garlic by High-Performance Liquid Chromatography Method

Miyoung Yoo*, Sanghee Lee, Dongbin Shin

Korea Food Research Institute, Sunghnam-si 463-746, Korea

High-performance liquid chromatography (HPLC) method for determination of ajoene isomers in garlic oil products was optimized and validated. *E*- and *Z*- ajoene were extracted with ethyl acetate and followed by the sensitive and selective determination of two isomers in a single run using normal phase HPLC equipped with silica gel column. The mobile phase was *n*-hexane and 2-propanol (85/15, V/V) with an isocratic condition as a flow rate of 1.0 mL/min and 240 nm of HPLC ultra visible detector. All calibration curves of *E*- and *Z*- ajoene in oil-macerated garlic showed good linearity ($r=0.998$). Overall, intra- and inter-day were in the range of 0.12-2.30% and 2.84-5.26%, respectively. Recovery was in range of 87.17-98.53% for *E*-ajoene and 85.16-99.23% for *Z*-ajoene. The validated method was applied to determine contents of ajoene in macerate garlic juices prepared with various vegetable oil. There were no any matrix effects in all chromatograms. The proposed method may be useful for quality control and evaluation of garlic oil products.

**Rapid Method for the Determination of Capsorubin and Capsanthin in
Red pepper powder Using Ultra High Performance Liquid
Chromatography**

You-Shin SHIM¹, Ki-Jin KIM¹, Dongwon SEO¹, Masahito ITO², Hiroaki NAKAGAWA²,
and Jaeho HA¹

¹*Food Analysis Center, Korea Food Research Institute, 516, Baekhyeon, Bundang,
Seongnam, Gyeonggi, 463-746, Republic of Korea*

²*Naka Division, Hitachi High-Technologies, Corporation, 882, Ishikawa-cho,
Hitachinaka-shi, Ibaraki-ken, 312-8504, Japan*

A rapid and novel ultra high performance liquid chromatography (u-HPLC) method for the determination of capsorubin and capsanthin in red pepper powder was validated in terms of its precision, accuracy, and linearity. The u-HPLC separation was performed on a reversed phase C18 column (particle size 2 μm , i.d. 2 mm, length 100mm), followed by photo diode array detector. The recovery of capsorubin was more than 72.12 % and the limit of detection and limit of quantification of the u-HPLC analysis were 0.043 and 0.129 mg/kg, respectively. The intra- and inter-day precision was less than 9.45 %. The recovery of capsanthin was more than 75.45 %, and the limits of detection and the limits of quantification were 0.101 and 0.306 mg/kg, respectively. All calibration curves had good linearity ($r^2 = 0.99$) within the test ranges. It seemed that the novel rapid, method coupled to u-HPLC can provide significant improvements in the speed, sensitivity and resolution.

Alternative Solid Phase Microextraction using a Hollow Needle packed with Polydimethyl siloxane for BTEX Analysis

Sunyoung Bae, Hyun-Hwa Son, Hye Young Lee, Ye Jin Bang, Dong-Sun Lee*

Department of Chemistry, Seoul Women's University, Seoul, Korea. dslee@swu.ac.kr

Soil can be easily contaminated by organic pollutants, in particular benzene, toluene, ethyl benzene and xylenes (BTEX) via uncontrolled spills, industrial waste or the misuse of pesticides and herbicides. The analysis of different volatile organic compounds in soils such as BTEX has been widely conducted using solid phase microextraction (SPME) which is a rapid, selective, and solvent-free technique. In this study, the quantitative determination of BTEX in soils was performed by headspace-SPME (HS-SPME) using a new in-needle SPME device coupled to GC-FID. This alternative SPME device was prepared using a stainless steel needle (Hamilton 90022, 22 gauge bevel tip, 51 mm length) packed with polydimethyl siloxane (0.413 mm O.D x 10 mm L) having a micro-bore (0.2 mm I.D.) tunnel. This needle attached to a syringe was then exposed to the headspace over the soil sample. The in-needle SPME technique is expected to improve extraction time, extraction efficiency, cost effectiveness, durability of a steel needle compared to conventional SPME fiber, and to enhance its utilization in various areas.

Determination of Physicochemical Properties and Gas Chromatography of Mugwort Essential Oils:

Preliminary Test for the Korean Standard on Oil of Mugwort (Sajabal ssuk),
Korean Kanhwa Type (*Artemisia princeps* Pampan)

Eun-Ji Lee, Hyun-Hwa Son, Hye-Lim Jeon, and Dong-Sun Lee*

Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea
dslee@swu.ac.kr

In this work, preliminary determinations of the physicochemical properties and aroma constituents of the mugwort (Sajabalssuk, wormwood) essential oil, Korean Kanhwa type (*Artemisia princeps* Pampan) belonging to Asteraceae by GC-FID were conducted for the Korean Standard. Major aroma constituents (over 5%) by GC-FID were cineol, terpine-4-ol, and borneol. α -Terpineol, camphor, eugenol, thujene, thujone, bornyl acetate, α -pinene, β -pinene, α -terpinene, γ -terpinene, terpinolene, sabinene hydrate, β -caryophyllene and caryophyllene oxide were also detected as its minor components. Sajabalssuk oil has characteristic mint-like herbaceous odor and greenish yellow color. Its relative density at 20 °C was 0.881~0.941, refractive index at 20 °C: 1.466~1.467 and optical rotation at 25 °C: $-5^{\circ}87' \sim -5^{\circ}90'$, respectively. Its acid value, ester value, and flash point (Abel closed cup method- Stanhope-SETA model 34000+34200) at 1001 hPa were 0.4 ~ 0.6, 0.00 ~ 5.68 and 51 °C, respectively.

Analysis of Physicochemical Properties and Gas Chromatography of Citron (Yuza) Essential Oils:

Preliminary Test for the Korean Standard on Oil of Citron (Yuza: Yuzu),
Korean Koheung Type (*Citrus junos* Sieb. Ex Tanaka)

Hye-Lim Jeon¹, Hyun-Hwa Son¹, Eun-Ji Lee¹, Gyeong-Suk Jo² and
Dong-Sun Lee^{1*}

¹*Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea
dslee@swu.ac.kr*

²*Jeollanamdo Agricultural Research and Extension Services, 206-7 Sanjeri,
Sanpomyeon, Najusi 520-715, Republic of Korea*

Preliminary analyses of the physicochemical properties and aroma constituents of the citron (Yuza: Yuzu) essential oil, Korean Koheung type (*Citrus junos* Sieb. ex Tanaka) by GC-FID were conducted for the Korean Standard. Major aroma constituents (over 5%) by GC-FID were D-limonene and γ -terpinene. Whereas α -pinene, β -pinene, β -myrcene, α -phellandrene, α -terpinene, terpinolene, linalool, p-mentha-dien-ol, α -terpineol, β -elemene, β -caryophyllene, α -caryophyllene and farnesene were its minor components. Yuza oil has sweet floral and lemon-like scent and pale yellow or greenish yellow color. Its relative density at 20 °C was 0.830~0.848, refractive index at 20 °C: 1.474~1.476 and optical rotation at 25 °C: +88°10' ~ +91°00', respectively. Its acid value, ester value, carbonyl value, and flash point (Abel closed cup method- Stanhope-SETA model 34000+34200) at 1001 hPa were 0.2 ~ 0.8, 0 ~ 12, 0.05~ 0.67 and 50 °C, respectively.

Gas Chromatography of Rose Essential Oils:

A Round Robin Test for Resolution No 385-ISO/DIS 25157 on Oil of Rose, Chinese

Kushui Type (*Rosa sertata* x *Rosa rugosa*)

Hyun-Hwa Son and Dong-Sun Lee*

*Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea
dslee@swu.ac.kr*

Analysis of the aroma constituents present in the rose essential oil of Chinese Kushui type (*Rosa sertata* x *Rosa rugosa*) by GC-FID and GC-MS was performed independently as an expert for the inter-laboratory round robin test to verify reproducibility according to the decision of the preliminary meeting of ISO/TC-54 (Shanghai, Sep. 14-15, 2010). Total 179 peaks (using SPB-1 apolar column), 165 peaks (using DB-624 intermediate polar column), and 162 peaks (using Supelco wax polar column) were detected by GC-FID, respectively. Major constituents (over 5%) by GC-FID were citronellol and geraniol. Whereas citronellol, geraniol, citronellyl acetate, (Z,Z)-farnesol, nerol and linalool were their predominant components by GC/MS. Our results were generally consistent with Chinese data (ISO/DIS 25175), however, a peak of β -phenethyl alcohol separated by using PEG(wax) column was found at the quite different retention time (about 61 min by GC-FID). Comparative analysis was conducted using Bulgarian rose (*Rosa damascena* Miller) oil and perfume. Bulgarian rose oil showed rich amounts of characteristic aroma constituents.

Evaluation of Multiplexed Cytochrome P450 Metabolic Markers by Gas Chromatography-Mass Spectrometry Based Plasma Steroid Signatures

Se Mi Kang*^{1,2}, Ju-Yeon Moon^{1,3}, Jongki Hong², Myeong Hee Moon³, Bong Chul Chung¹ and Man Ho Choi¹

¹*Future Convergence Research Division, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Korea, Email: semi426@naver.com*

²*Department of Basic Pharmaceutical Science, Kyung Hee University, Hoeigi-dong 1, Dongdaemun-gu, Seoul 130-701, Korea*

³*Department of Chemistry, Yonsei University, 50 Yeonsei-ro, Seodaemun-gu, Seoul 120-749, Korea*

The human cytochrome P450s (CYPs) enzymes are responsible for the detoxication of drugs, and the synthesis and metabolism of endogenous compounds such as steroids. The quantitative evaluation of CYP-mediated hydroxy steroids is needed to elucidate activities of steroid-metabolizing CYPs by drugs, leading to clinically significant drug-drug interaction that can cause unanticipated adverse reactions or therapeutic failures. A quantitative analysis by gas chromatography-mass spectrometry in the selected-ion monitoring (GC-SIM/MS) have been achieved for multiplexed CYP assay with plasma steroids including 26 androgens, 8 estrogens, 6 corticoids and 5 progestines. The plasma samples (0.4 mL) were diluted with 2.6 mL acetate buffer (0.2 M, pH 5.2) and 100 μ L of aqueous 0.2% ascorbic acid and purified by solid-phase extraction of Oasis HLB cartridge. All 45 steroids monitored had a good linearity ($r^2 > 0.99$) in a dynamic range, and the precision (% CV) and accuracy (% bias) of the assay were 7.5 ~ 22.2% and 88.2 ~ 127.4% at three different concentrations. The validated multiplexed CYP enzyme assay may be a useful tool for assessing the drug efficacy/metabolism as well as the cross-validation of the pharmacogenomics-based CYP biomarkers.

Quantitative profiling of eicosanoids in plasma and urine by liquid chromatography-mass spectrometry in the high resolution selected-ion monitoring mode

Su Hyeon Lee*^{1,2}, Young Wan Ha¹, Won-Yong Lee², Bong Chul Chung¹ and Man-Ho Choi¹

¹*Future Convergence Research Division, KIST, 39-1 Hawolkkok-dong, Seoul 136-791, Korea, fomeandu@nate.com*

²*Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seoul, 120-749, Korea*

Eicosanoids as the metabolites of arachidonic acid, a 20-carbon polyunsaturated fatty acid, are rapidly biosynthesized and degraded in regulating vascular function, inflammation, hypertension and other pathologies. A validated quantitative analysis of 30 eicosanoids, such as 18 prostaglandins (PGs), 4 leukotrienes (LTs), 2 thromboxanes (TXs) and 6 hydroxyeicosatetraenoic acids (HETEs), have been developed with liquid chromatography-quadrupole/time-of-flight-mass spectrometry (LC-QTOF-MS). This sensitive and selective method was achieved in negative ionization of the high-resolution selected-ion monitoring (HR/SIM) mode. All eicosanoids were purified by solid-phase extraction of Oasis MAX and were separated through an 1.9 μm particle C18 column (50 \times 2.1 mm) at a flow rate of 0.25 mL/min. The gradient elution consisted of 0.1 % formic acid in 95 % water (solvent A) and 0.1 % formic acid in 95 % acetonitrile (solvent B) was used with 55 min run. The LC-HR/SIM-MS based eicosanoids analysis was found to be linear ranged from 0.9922 to 0.9999, while the detection limits ranged from 5 to 500 ng/mL in both plasma and urine samples. The 3 PGs, 5 HETEs and 1 LT in control plasma and 6 PGs, 2 LTs and 1 HETE in control urine were detected within dynamic ranges. The devised method could be applicable into the clinical diseases related on inflammation.

**Development of the HPLC method quantitating traces of vitamin B₁₂
and B₇ in complex matrices**

Joongmok Jung, Inho Kim, Hyunseok Han, Taehwa Nah, Jonghoon Kim

Young In Scientific Co., LTD. Seoul, Korea

Vitamins are vital nutrients for all life, but the required amounts are diverse depending on the kind of vitamins. Because the problem occurs in states of not only deficiency but also excess in intake of vitamins, it is important to exactly quantitate those in foods or vitamin supplements. Especially, it is more important to determine the contents of vitamins that are needed to body by small amount, such as vitamin B₁₂ (cyanocobalamin) or B₇ (biotin). But the quantitation analysis of the vitamins is not an easy work, because those exist tinily in complex and excessive matrices. To detect these vitamin B₁₂ and B₇, special methods are used in analyses, such as microbiological assay, immune-affinity column method and two-dimensional(2D) LC method. In this development, the improved 2D LC method was set up and it broke the previous limit of quantitation. Agilent Infinity 1260 LC instrument with Max-Light Cartridge Cell(60mm-path flow cell) was used in the experiment. Also the method was applied by the three-columns system that consists of pretreatmental, focusing and analytical column. This improved 2D LC method lowered the LOQ of vitamin B₁₂ and B₇ up to 50ppt and 2ppb, it means that the sensitivity is increased at least 10 times higher than conventional methods. Also some real food samples such as milk, beef, vitamins supplement were pretreated by KFDA method and analyzed by the improved 2D LC method. Because the results were reproducible and sensitive near to the LOQ, it was approved this method was suitable to determine the contents of vitamin B₁₂ and B₇ in various food samples.

Analyses of Immunoglobulin Pharmaceuticals using High Performance Liquid Chromatography

Hiroaki Nakagawa*, Yusuke Hosen, Ayako Matsuzaki, Chihiro Yoshioka, Hiroshi Suzuki,
Masaki Watanabe, Yoko Inoue

*Global Application Center, Hitachi High-Technologies Corporation, 11-1 Ishikawa-cho,
Hitachinaka-shi, Ibaraki 3120057, Japan. nakagawa-hiroaki@naka.hitachi-hitec.com*

The use of antibody-pharmaceuticals has expanded enormously for cancer therapy in these years. Immunoglobulins are proteins, which makes control of post-translational modifications, such as a glycan and protein folding, of great importance. However, no standard approved quality control analyses for these glycans exist, with a variety of methods being tried for each product. In this presentation, the following three methods for the quality control of proteins will be introduced. Peptide fingerprint analysis is one popular method for the quality control of proteins. Bovine serum albumin and immunoglobulin are digested by trypsin and then analyzed on a LaChrom C18 column using the Chromaster HPLC system. Good separation and reproducibility can be obtained. Glycan structure may affect bioactivity of proteins, so glycans need to be examined for variations. A post-column method using phosphoric acid and phenylhydrazine can detect glycans on a peptide. We will present glycopeptide mapping using this method. In both of these analyses, chromatograms are changed by glyco-related enzymes. These analyses are promising for quality control and production management of antibody-biopharmaceuticals.

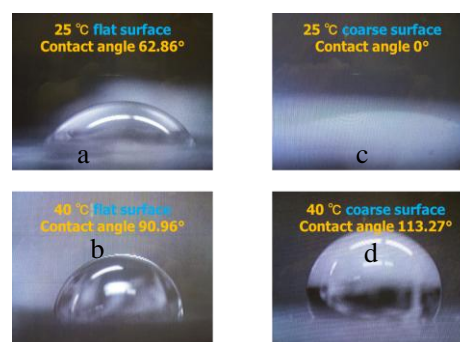
Enzyme-linked Immunosorbent Assay Based on Temperature Responsive Filter

Ying Weng, Hulin Zeng, Hizuru Nakajima, Katsumi Uchiyama*

Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University

A miniaturized enzyme-linked immunosorbent assay (ELISA) on a chip was designed, fabricated and performed for immunological detection with anti-human immunogen A (IgA) sandwich assay system. The chip contained temperature responsive valve which was fabricated with a smart polymer N-isopropylacrylamide. The chemical valve allowed the user to carry out an immunological assay with simplified washing, pouring and loading process. The principle of the valve was based on the switching function that can change the hydrophilicity to the hydrophobicity controlled by the (surrounding) temperature. To enhance the assay sensitivity, the antibody was adsorbed on the surface of polystyrene micro beads aiming at increase of total surface area used for antigen-antibody reaction for ELISA.

Figure 1 shows the pictures of droplets on the surface of temperature responsive polymer fabricated on flat glass (Fig.1 (a), (b)) and on porous glass (Fig. 1 (c), (d)) changing surrounding temperature.



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High-Performance Liquid Chromatography Analysis of Biopharmaceuticals

Yoko Inoue*, Yusuke Hosen, Ayako Matsuzaki, Chihiro Yoshioka, Hiroaki Nakagawa,
Masahito Ito

*Global Application Center, Hitachi High-Technologies Corporation, 11-1 Ishikawa-cho,
Hitachinaka-shi, Ibaraki 3120057, Japan. nakagawa-hiroaki@naka.hitachi-hitec.com*

Recently, the production of biopharmaceuticals, such as immunoglobulins and erythropoietin, has increased greatly. As the majority of these biopharmaceuticals are proteins, the control of post-translational modifications, such as a glycan and protein folding, is crucial. No standard method for the quality control analysis for these proteins has yet been agreed upon, with a variety of methods being tried for each product. In this presentation, we will present and discuss three methods currently used for the quality control of proteins. One popular method for the quality control of proteins is peptide fingerprint analysis. In this method, bovine serum albumin and immunoglobulin are digested by trypsin prior to analysis on a LaChrom C18 column using the Chromaster HPLC system. Good separation and reproducibility have been observed using this technique. As glycan structure can affect the bioactivity of proteins, variations in glycans need to be examined. A post-column method using phosphoric acid and phenylhydrazine is able to detect glycans on a peptide, and we will explain how this method can be used for glycopeptide mapping. Finally, the analysis of amino acid components is necessary to obtain basic data for proteins as they are polymers of amino acids. We will present the L-8900 amino acid analyzer which combines good reproducibility with ease of operation.

**Preliminary Study on Ion-Exclusion/Cation-Exchange Chromatography
for Determining Simultaneously Radioactive Anions and Cations
Released from Nuclear Power Plant**

Daisuke KOZAKI,¹ Nobutake NAKATANI², Masanobu MORI³,
Kazuhiko TANAKA¹

¹*Graduate School for International Development and Cooperation, Hiroshima
University, 1-5-1, Kagamiyama, Higashi-hiroshima 739-8529*

²*Faculty of Environmental Systems, Rakuno Gakuen University, 582,
Bunkyo-dai-midorimachi, Ebetsu, Hokkaido 069-8501*

³*Graduate School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma
376-8515*

The Fukushima 1st Nuclear Power Plant located in Fukushima Prefecture of Japan suffered severe damage from the earthquake on March 11, 2011. A large amounts of radioactive substances has been released into the surrounding environments by the accident. Therefore, the monitoring of the radioactive substances is one of the most important tasks for evaluating the impact to the environments. By the nuclear fission reaction of ^{235}U , many fission products are released. In these fission products, ^{131}I , ^{90}Sr and ^{137}Cs are recognized to be strongly carcinogenic radioactive substances. In this study, to determine simultaneously the radioactive ions such as I^- , Sr^{2+} , and Cs^+ , the ion-exclusion/cation-exchange chromatography (IEC/CEC) with conductivity detection on a polymethacrylate-based weakly acidic cation-exchange resin column [Tanaka et al., *J. Chromatogr. A*, 804 (1998) 179; *ibid*, 884 (2000) 167] was studied preliminarily using aqueous eluent consisting of sulfosalicylic acid, crown ether and methanol. As a result, under the optimized chromatographic conditions (0.8 mM sulfosalicylic acid, 3 mM crown ether and 30 % methanol at 0.6 mL/min), the high resolution and simultaneous separation of the radioactive ions such as I^- , Sr^{2+} , and Cs^+ from the common anions such SO_4^{2-} , Cl^- , NO_3^- and the cations such as Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} was achieved in ca.30 min. This simultaneous separation mechanism is based on the ion-exclusion effect for the anions and the cation-exchange effect for the cations. The analytical performances tests including calibration graph, detection limit, reproducibility and recovery were carried out under the optimized ion chromatographic conditions. In future work, the radioactivity detectors to monitor selectively γ -ray for ^{137}Cs , ^{131}I , ^{90}Sr and β -ray for ^{137}Cs , ^{131}I are introduced instead of the conductivity detector for applying practically to the several Fukushima's environmental samples.

Design and synthesis of fluorescent enzyme substrate monomer molecule and its application to hydrogel-based single step micro biosensing devices

Hideki Wakayama*¹, Yoshinori Okamoto, Kunio Kawamura, Tatsuro Endo, Hideaki Hisamoto

Department of Applied Chemistry, Graduate School of Engineering, OSAKA PREFECTURE UNIVERSITY, 1-1, Gakuen-cho, Naka-ku, Sakai-shi, Osaka, 599-8531, Japan, Email: hisamoto@chem.osakafu-u.ac.jp

Recently, microdevices using hydrogels have reported to demonstrate various bioassays involving enzyme reaction or immuno reaction. However, most of these reports still involve the complicated operation step of premixing fluorescent substrate before measurement.¹ Furthermore, especially for immunoassay, requirement of complicated operation steps is still a problem.² Here, we report design and synthesis of fluorescent enzyme substrate monomer molecule, which is immobilizable to hydrogel by copolymerization. This monomer molecule is expected to make various bioassays using micro flow channel be simplified into single step bioassays. First, we have designed and synthesized a fluorescent enzyme substrate monomer molecule for alkaline phosphatase (ALP) (Figure 1). We investigated the fundamental characteristics of this molecule, and confirmed that the fluorescence intensity changed after enzyme reaction according to ALP concentration and the substrate is immobilizable to hydrogel by copolymerization. Next, we prepared a pH sensing and an enzyme activity sensing micro devices using hydrogels immobilizing the synthesized molecules. We confirmed that the fluorescence intensity changed upon pH and enzyme concentration changes, respectively. These results indicated that the synthesized molecule was useful for single step pH sensing and enzyme activity sensing using micro hydrogels.

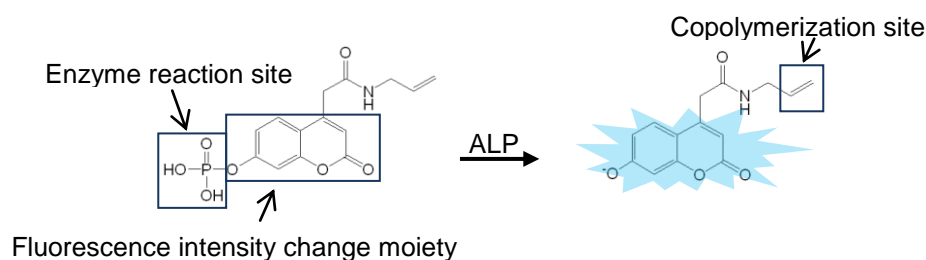


Figure 1. Molecular design concept of an enzyme substrate molecule for ALP

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Measurement of Nitrous Oxide (N₂O) Released from Soil of the Vegetable Garden using GC/MS Method

Kazutoshi SUGITA¹, Yuusuke OOUCHI², Kimika KANESHIMA², Satoko TANAKA³,
Shuji YOSHIKAWA³, Sumio GOTO²

¹*Mitsubishi Chemical Analytech Co. Ltd.*, ²*Azabu University*, ³*Meisei University*

The N₂O is known as global warming gas and ozone-depletion gas and it is one of the most important environmental pollutant of the world. The density of atmospheric N₂O is smaller than carbon dioxide, but the coefficient of global warming effect is very big with approximately 300. It was known that combustion process, nitrogenous fertilizer, a chemical substance manufacturing process and organic biodegradation are the emission sources of N₂O. And, it is considered that the emission of N₂O participated with microbe will grow big in the future. In this study, therefore, we examined a method of measurement for the low-concentration N₂O using general GC/MS with PLOT column to examine emission behavior of N₂O in environment. And we applied this method to the flux measurement of N₂O released from the soil of vegetable garden.

Fluorometric Determination of Dopamine based on Calcein Blue – Fe(II) Complex and Its Application to Flow Analysis

Ryoichi Ishimatsu, Daisuke Seto, Tomoharu Maki, Nobuaki Soh, Koji Nakano, Toshihiko Imato

Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Fukuoka, 819-0395, Japan. ishimatsu@cstf.kyushu-u.ac.jp

Dopamine is one of the neurotransmitters to adjust homeostasis, and it is known that excess or deficiency of dopamine causes various kinds of symptoms. HPLC, immunoassay, and electrochemical methods for the determination of dopamine have been widely used. We have recently developed a simple and convenient method for the detection of dopamine using a fluorescent probe, a calcein blue (CB)-Fe(II) complex, based on the following findings. Namely, fluorescence spectra of CB has a maximum at 430 nm, and its fluorescence intensity is almost quenched by an addition of equimolar of Fe(II) due to formation of a CB-Fe(II) complex. While fluorescent intensity recovers after an addition of dopamine by formation of a new complex between Fe(II) and dopamine through a ligand exchange reaction. In this paper, we will present our method for the determination of dopamine and its application to flow analysis.

Experimental

Aqueous solutions of CB and FeCl₂ were mixed and pH was adjusted to 7.4 by a 0.1 M phosphate buffer solution to obtain an aqueous solution of 0.5 M CB-Fe(II). After various concentrations of dopamine solutions were added to the CB-Fe(II) solution, fluorescence spectra of the resulting solutions were measured (ex = 340 nm).

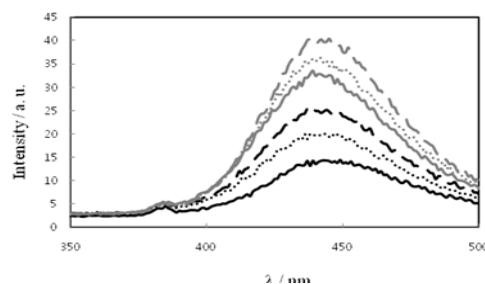


Figure 1. Fluorescence spectra of 0.5 μ M CB-Fe(II) upon an addition of different concentrations of dopamine (0, 0.1, 0.2, 0.3, 0.4, and 0.5 mM from the bottom).

Figure 1 shows fluorescence spectra of the 0.5 M CB-Fe(II) solutions added with dopamine solution at six different concentrations. The maximum of the fluorescent intensity appears at 430 nm. The fluorescent intensity of the 0.5 M CB solution was about 120 a.u. and was quenched to 15 a.u. by addition of equimolar of Fe(II). As can be seen from Fig. 1, the fluorescent intensity is recovered with increasing the concentration of dopamine added, and a good liner relationship between the fluorescence intensity and the concentration of dopamine is obtained. This indicates that Fe(II) liberates from the CB complex and forms the dopamine-Fe(II) complex by the ligand exchange reaction. We will present the application of this method to flow analysis of dopamine.

Development of Preventive Measure against Malodor Resulting from Composting Kitchen Scraps

Hiroshi Sato*¹, Hitomi Shimomoto², Toshiyuki Hobo³

¹Department of Pharmacy, Nagasaki International University, Huis Ten Bosch, Sasebo, Nagasaki 859-3298, Japan, Email: sato@niu.ac.jp

²TOTOLtd., Kokurakita, Kitakyushu, Fukuoka 802-8601, Japan

³Tokyo Metropolitan University, Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

Though the use of composting devices is becoming common in the society; houses however, some problems such as malodor emission, exhaust of fine particles, and infection occurring from close contact with a large number of bacteria and fungi should be considered. These problems in the case when composting devices are placed indoors were examined, and an effective preventive measure against the emission of malodorous compounds was developed by controlling the pH of the fermenting mixture in the device. When composting devices are in operation (under aerobic condition), the concentrations of ammonia, amine, and methyl mercaptan were observed to be high. On the other hand, when the devices were not in operation (anaerobic condition), the concentration of sulfur-containing compounds was high compared with that of nitrogen-containing compounds. Since ammonia, amine and methyl mercaptan are major malodorous compounds, operating composting devices under an aerobic condition and controlling nitrogen-containing compounds could lower the amount of malodor emitted by the devices during operation. In our experiment, buffering with potassium hydrogen phosphate was effective for controlling the pH of fermenting mixture in the devices to between 6.7 and 7.5 during the composting process and ammonia emission was well controlled, as shown in Figure 1. To investigate, the performance of the composting devices, long-term observation and evaluation were also conducted. Results showed that there was no difference in the performance between the compost with and without the buffer solution. The similar result was obtained in an experiment performed with a traditional composter, which proves that buffering with potassium hydrogen phosphate is highly effective for preventing the emission of malodor from composting kitchen scraps.

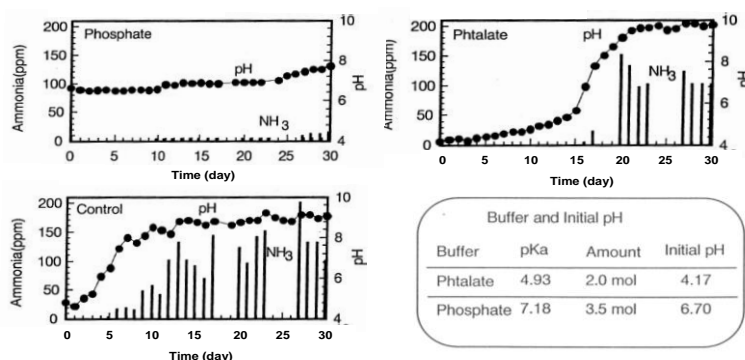


Fig.1 Relationship between pH control of compost and amount of ammonia diffusion

Reference:

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An Accurate Sample Introduction System for Capillary Electrophoresis

Hu-lie Zeng*, Saori Ikeda, Hizuru Nakajama, Katsumi Uchiyama

*Graduate school of urban environmental science, Tokyo Metropolitan University, 1-1
Minamiohsawa, Hachioji, Tokyo 192-0397, JAPAN, zeng-hulie@tmu.ac.jp*

An accurate sample introduction system based on ink-jet technology was designed and built up for capillary electrophoresis (CE) analysis. The ink-jet sample introduction system could inject accurate volume of the liquid sample without any discrimination and uncertainty, which is prior to the classic electrokinetic sample introduction or hydrodynamic introduction. The accurate sample introduction system consisted with an exact sample loading position controlling part adjusted by a three dimensional stage, and a movable reservoir switching the loading and separating status of CE. The volume of the injected droplet can be controlled by the driving voltage and waveform for piezoelectric (PZT) chip, which is the driver for the ink-jet microchip. Then the injected volume to the capillary could be calculated by the number of droplets. The repeatability and the reproductively of the sample introduction system was evaluated through the analysis of pigments. The well linear relationships were obtained between the concentration and the peak area or peak height of the pigments.

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Detection Lysozyme Based on Energy Transfer between Graphene Oxide and Rhodamine B

Yong Chang¹, Jia Li Xu¹, Yuan Fang Li¹, Cheng Zhi Huang²

¹Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China, chengzhi@swu.edu.cn

²College of Pharmaceutical Sciences, Southwest University, Chongqing 400715, China

Lysozyme, also called muramidase or petidoglycan N-acetylmuramoyl-hydrolase, has lytic activity on the cell wall of Gram-positive bacteria so it is widely applied in pharmaceutical and food industries due to its antimicrobially, antiphlogosis and antiviral. Meanwhile, the content of lysozyme in vivo can be a useful indicator of some diseases, for example, meningitis, rheumatoid arthritis, leukemia and kidney problems.^[1] Therefore, detection of lysozyme has attracted more and more attention. New, rapid, cheap and effective methods have been under investigation.

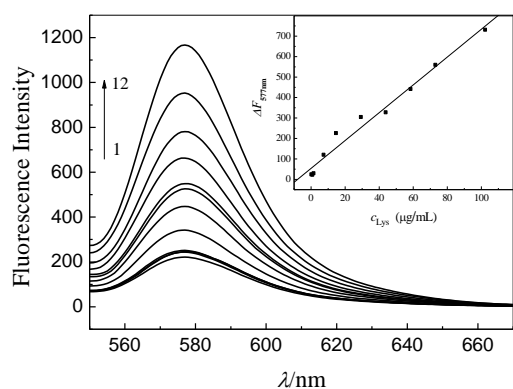


Fig. 1 Fluorescence spectra of the solution with different concentrations of lysozyme. c_{GO} , 0.10 mg/mL; c_{RhB} , 1.5×10^{-7} mol/L; B-R buffer pH, 9.9; 25°C ; Curves 1-11, RhB+GO+Lys; Curve 12, RhB. c_{Lys} (Curve 1-11, $\mu\text{g/mL}$): 0, 0.15, 0.73, 1.46, 7.30, 14.6, 29.2, 43.8, 58.4, 73.0, 102.2.

of lysozyme in the range of 0.146~102.2 $\mu\text{g/mL}$ with linear equation $F = 59.49 + 6.37c$ ($\mu\text{g/mL}$) and correlation coefficient 0.988 (Fig. 1).

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In this study, a rapid and convenient spectrophotometric method of lysozyme was proposed. When rhodamine B approaching to graphene oxide, its fluorescence gets quenched owing to the long range resonance energy transfer (LrRET).^[2] With lysozyme added, however, lysozyme could be adsorbed on graphene oxide by electrostatic interaction, the fluorescence of rhodamine B gets recovered owing to the hydrophobic, stacking and hydrogen binding, that results in the separation of rhodamine B from graphene oxide.^[3] Under optimal conditions, a linear relationship was found between the fluorescence recovery and the concentration

Colorimetric Detection of ATP by Using Unmodified Au Nanoparticles and Melamine

Ya Mei Yang, Min Le, Shu Jun Zhen, Yuan Fang Li

Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China, Liyf@swu.edu.cn

Adenosine Triphosphate (ATP) is present in all living organisms, which plays a critical role in regulating cellular metabolism and biochemical pathways, and it is the most important energy currency for biological processes. Therefore, ATP determination is very important for studying cell physiological activity as well as food quality control¹. In this contribution, we proposed a new colorimetric assay of ATP using melamine and citrate-capped Au nanoparticles (Au NPs). It was reported that Au NPs could self-assemble in present of melamine through electrostatic interactions. The aggregates of Au NPs resulted in a new band at the long-wavelength, and the color of Au NPs changed from red to blue². Upon addition of ATP, ATP molecules could compete with melamine to adsorb on the surface of the Au NPs, consequently, the aggregates of Au NPs re-dispersed, and the long-wavelength band disappeared. Meanwhile, the color of the solution turned into red again (Fig. 1). Based on this phenomenon, we presented a simple and label-free colorimetric method for the determination of ATP using Au NPs as a colorimetric probe.

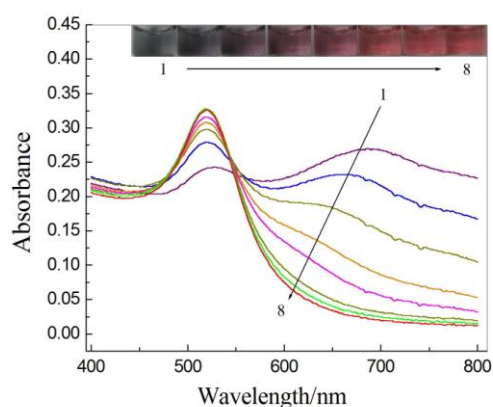


Figure.1 Absorption spectra of melamine-Au NPs mixture in the present of different concentrations of ATP. Insert pictures displays the color change of Au NPs corresponding to the curves 1 to 8.

c_{ATP} (curve 1-8, $\times 10^{-7}$ mol/L), 0, 0.6, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8 from 1 to 8

Reference:

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Spectrofluorometric Detection of Phosphate on its Inhibition Effect on Copper Catalytic Reduction of Rhodamine Spirolactam in Basic Medium

Hui Yang¹, Lin Ling Zheng¹, Yuan Fang Li¹, Cheng Zhi Huang²

¹Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China, chengzhi@swu.edu.cn

²College of Pharmaceutical Sciences, Southwest University, Chongqing 400715, China

Anions play important roles in a varieties of chemical and biological processes.¹ Among the environment pollutants, phosphate ion (Pi) is particularly considerable, as it plays a key role in the eutrophication processes ranging from information processing to effectively trace the phosphorus load in bodies of water.² As yet, reported detection methods of Pi involves in spectrophotometry,³ electrochemical analysis,⁴ and enzymatic biosensing.⁵

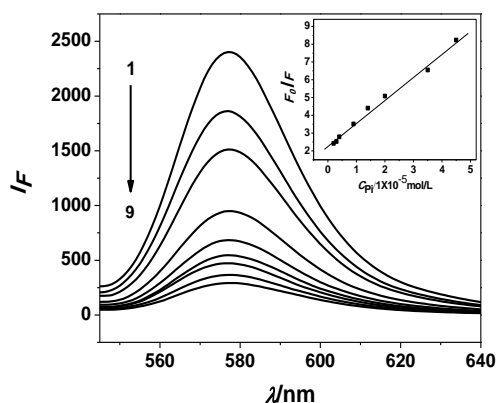


Fig. 1 Fluorescence spectra of the system in the presence of different concentration of phosphate. The linear equation is $F_0/F = 2.2 + 1.3 c$. pH 7.4; c_{RBh} , 5.3×10^{-7} mol/L; $c_{Cu^{2+}}$, 5.5×10^{-5} mol/L; c_{Pi} (Curves 1-9, $\mu\text{mol/L}$), 0, 0.7, 5.0, 9.0, 14, 20, 35, 45; c_{NaCl} , 0.05 mol/L.

In this contribution, a simple fluorescent method of Pi was developed. Rhodamine spirolactam (RBh), a non-fluorescent dye, can be hydrolyzed to form rhodamine B (RhB) in the presence of Cu^{2+} , yielding strong fluorescence emission. Since Cu^{2+} can coordinate with Pi intensively in neutral conditions, the catalysis gets inhibited, and thus the fluorescence emission greatly reduced. With that, we established an analytical method for quantitative detection of Pi. Under the optimization conditions, phosphate in the linear range of 3.0×10^{-6} - 4.5×10^{-5} mol/L could be detected with the correlation coefficient of 0.9938. The detection limit is 1.6×10^{-7} mol/L (3σ). This method has been

successfully applied to the detection of Pi in very complicated matrixes, such as artificial wetlands system with the recovery from 93.0% to 108.0% and the RSD lower than 6.0%.

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Facile Synthesis of Au Cubic Nanoparticles with Curcumin

Xiao Xi Yang, Cheng Zhi Huang

Education Ministry Key Laboratory on Luminescence Real-Time Analysis, College of Pharmaceutical Sciences, Chongqing 400715, China, chengzhi@swu.edu.cn

Curcumin is extracted from footof curcuma longa. It has strong anti-inflammatory, antiseptic and anticancer properties.¹ More importantly, it has been applied in many areas owing to its low toxicity.² The phenolic hydroxyl group and enolic structure assign the curcumin reducible. Herein, we synthesized Au nanoparticles³ with curcumin with the purpose that the Au nanoparticles coated with curcumin can have the antiseptic or anti-inflammatory properties. Our present synthesis did not involve in the use of any seeds. The reaction directly starts off the reflux of curcumin and chlorauric acid in aqueous medium by keeping the mixture boiling. The resulting substrate is amaranth, which has the plasmon absorption characterized at 535 nm, and take the shape of cubic as displayed by the scanning electron microscopy (SEM) imaging. The prepared Au nanoparticles are stable more than two weeks, indicating that curcumin acts as both reducing agent and stabilizer. Further experiments will focus on its application in antiseptic or anti-inflammatory properties.

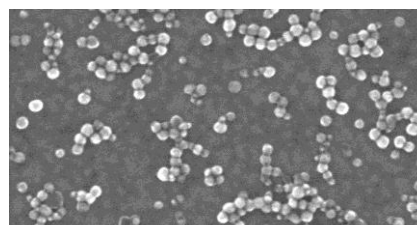
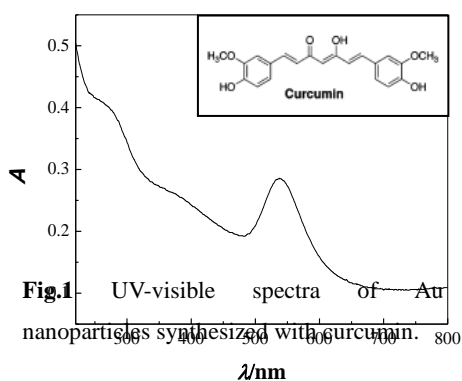


Fig.2 The scanning electron microscopy image of Au nanoparticles

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Peroxynitrous Acid Induced Chemiluminescence of Fluorescent Carbon Dots for Nitrite Sensing

Zhen Lin, Wei Xue, Hui Chen, and Jin-Ming Lin*

Beijing Key Laboratory of Microanalysis and Instrumentation, Department of Chemistry, Tsinghua University, Beijing 100084, China

Nitrite widely exists in environment and is used as preservatives for food. However, nitrite is an essential precursor for the formation of carcinogenic N-nitrosamine. Therefore, it is of significant importance to detect the nitrite in environment and in food. Photoluminescent carbon nanoparticles (carbon dots) are a new class of fluorescent carbon material with higher photoactivity, lower toxicity and cheaper cost compared with heavy-metal contained quantum dots.^{1,2} On-line mixing of nitrite and acidified hydrogen peroxide produced peroxynitrous acid.³ In this work, chemiluminescent (CL) property of the carbon dots in the presence of peroxynitrous acid was studied. The CL intensity was increased linearly with nitrite concentration in the range of 1.0×10^{-7} to 1.0×10^{-5} M and the detection limit was 5.3×10^{-8} M (S/N=3). This method has been successfully applied to the determination of nitrite in pond water, river water and pure milk with the recoveries in the range of 98-108 %. The CL mechanism of the peroxynitrous acid-carbon dots system was investigated by the CL, UV-vis and electron paramagnetic resonance (EPR) spectra. The electron-transfer annihilation of hole-injected and electron-injected carbon dots could mainly account for the CL emission, which sheds new light on the optical properties of the carbon dots.

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A pH Sensitive Self-Assembled Monolayer Film Based on Fluorescein Isothiocyanate

Fang Li, Xiang-Ying Sun* and Bin Liu

*College of Material Science and Engineering, Huaqiao University, Fujian Xiamen
361-021, People's Republic of China, sunxy@hqu.edu.cn*

Self-assembled monolayers (SAMs) offer the possibility to immobilize fluorescent molecule on a variety of substrates, and monitor their interactions with compounds in the relational solution [1-3]. We obtain a fluorescent film bearing fluorescein isothiocyanate (FITC) as a fluorophore through this way. First, a monolayer of 3-amino-propyltriethoxysilane was attached to the quartz substrate, and then it was immersed in a FITC solution in alcohol. Self-assembled monolayers of FITC was prepared. And a simple and sensitive method for the determination of pH was developed. It was found that the FITC SAMs responds to the change of environmental pH over the range of 1.1~5.1. This method possessed short response time ($\leq 2\text{min}$) and good reversibility (RSD=0.91%, n=6) for the PBS buffer solution of pH=4.00. Furthermore, the film can be re-used again if necessary. This work was supported by the National Natural Science Foundation of China (grant nos 21175049 and 20955001), Natural Science Foundation of Fujian Province (grant no 2011J01049).

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Colorimetric Assay for Ag⁺ with ZnO/CdS@SiO₂ Core/Shell Nanostructures

Chuanxiao Yang, Xiangying Sun*, Bin Liu

*College of Material Science and Engineering, Huaqiao University, Xiamen, China,
sunxy@hqu.edu.cn*

Nanomaterials with dual emission are widely applied in the fields of bioluminescence, dual labeling and detection[1,2]. In this paper, water-soluble ZnO/CdS quantum dots (QDs) capped by tripolyphosphate was synthesized in an alkaline medium and at 100°C temperature, where the S²⁻ was got from thiourea. And then, mesoporous ZnO/CdS@SiO₂ Core/shell nanostructures (pore size: 3.6nm) were synthesized, in which aqueous solution of ZnO/CdS QDs was directly added to a clean glass reaction vessel containing anhydrous ethanol and ammonium hydroxide and TEOS. ZnO/CdS@SiO₂ QDs could emit intense blue fluorescence with an emission peak at 481 nm under ultraviolet lamp irradiation. However, the ZnO/CdS@SiO₂ QDs could emit red fluorescence with a new emission peak at 595nm in the presence of Ag⁺. The results indicated that blue fluorescence intensities of ZnO/CdS@SiO₂ QDs were decreasing, and the red fluorescence intensities were increasing with increasing concentration of Ag⁺. For this reason, the ZnO/CdS@SiO₂ Core/Shell nanostructures may be used as a novel colorimetric fluorescence probe for the detection of trace Ag⁺ with a detection limit 40 nM. The method is simple, rapid and sensitive. This work was supported by the National Natural Science Foundation of China (grant nos 21175049 and 20955001), Natural Science Foundation of Fujian Province (grant no 2011J01049), Fundamental Research Funds for the Central Universities (No. JB-ZR1118).

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Determination of Trace Inorganic and Organic Contaminants in Fuel Gas

Hai-Fang Li*, Jianmin Yang, Cuihua Gao, Meilan Li, Jin-Ming Lin*

Department of Chemistry, Tsinghua University, Beijing, 100084, China.

**Corresponding authors: lihaifang@mail.tsinghua.edu.cn, jmlin@mail.tsinghua.edu.cn*

The presence of the damaging minor inorganic and organic contaminants in fuel gas generally causes corrosion and deposition to the power plants of equipments [1]. Many minor inorganic elements including Na, K, V, Pb, Zn, Ca, Ba, Mn, Al, P, S, Cl, NO_x, NH₃ and a varied of minor organic compositions of butadiene, styrene, naphthalene, indene, cyclopentane and BTX in fuel gas play important roles for the damaging effects. Due to the trace amounts and complexity of these contaminants in fuel gas, it is challenging to rapidly sampling and accurately determine these contaminants [2]. The high sensitive capillary electrophoresis (CE) method coupled with head-column field-amplified sample stacking (HC-FASS) technique has been developed for rapid analysis of trace inorganic contaminants in fuel gas. Different background electrolyte additives were employed for separation and indirect UV detection of cations and anions, respectively. The FASS preconcentration improved the sensitivities by 200-700 times with the lower detection limits at ng/mL levels. The reliable and efficient gas-liquid absorption setup was constructed for collection of inorganic targets from real liquefied petroleum gas (LPG). The CE results presented that multi ions including NH₄⁺, K⁺, Ca²⁺, Na⁺, Mn²⁺, Zn²⁺, Ba²⁺, Cl⁻, NO₂⁻, SO₄²⁻, and NO₃⁻ were found in the LPG absorption solution. The GC-MS analysis method was developed for determination of organic contaminants. Under optimized conditions, ten organic targets including butadiene, cyclopentane, styrene, indene, naphthalene, benzene, toluene, and xylene (m-, p- and o-) could be sensitively analyzed with detection limits at ng/mL levels. The gas-solid absorption sampling method based on graphitized carbon black (GCB) solid phase extraction (GCB-SPE) was applied for organics collection from LPG [3]. When the gas passed through the GCB column, the organics were absorbed on the GCB absorption column. The collection and preconcentration were integrated into one step. The collected samples were analyzed by the developed GC-MS method. The toluene, p-xylene, m-xylene, o-xylene, styrene, and naphthalene were found in the LPG.

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Examination of application to official method of surface water analysis by flow injection method

Ryozo Goto*

*Japan Environmental Technology Association, 4-8-30-201 Kudan-minami, Chiyoda-ku,
Tokyo 102-0074, Japan E-mail:r-goto@toadkk.co.jp*

1. Introduction

Recently, a variety of aqueous environment problems have been actualized. In such, the water quality monitoring is increased in importance more and more. Introducing a highly accurate, efficient analysis into water analyses on the other hand becomes possible, because the environmental analysis and the monitoring technique have improved. From such a background, the Ministry of the Environment executed "Official analysis method investigation that lay the matching with the international standard of the water analyses method ". The investigation was done about "Flow analysis" and "Fluorescent dissolved oxygen measurement" intended for the environmental sample. Here, it reports on the flow analysis.

2. Outline of examination

The utility of the test method based on JIS (Japan Industrial Standard) K 0170-2(2011) was confirmed for the nitrate nitrogen and the nitrite nitrogen by the flow analysis.

The examination does the following item.

- a) A basic performance is confirmed by using the standard solution.
- b) The flow analysis method is compared by using the environmental water sample with the official method.

3. Sampling and test method

The sample gathered from 10 places in the Kanto area (6 samples in river water, 2 samples in marshes and 2 samples in sea water) was used for the examination. After the sample had been filtered with the filter of 0.45 microns, it distributed it to each laboratory. The calibration curve, repeatability, and the detection limit in the standard solution were calculated by using the test method described in JIS K 0170-2. Moreover, repeatability, the average value, and the minimum limit of determination were calculated by using the gathered sample. And analytical value using each method compared with official method of analysis.

4. Result

Both nitrate ions and nitrite ions had a high correlation between JIS K 0102(official method in Japan, Absorptiometry or Ion chromatography) and JIS K 0170-2 in a real sample. And detection limit (DL) of NO₃-N is 0.02-0.06mg/L, DL of NO₂-N is

0.001-0.005mg/L. It has been understood that this methods of analysis are very high sensitivities.

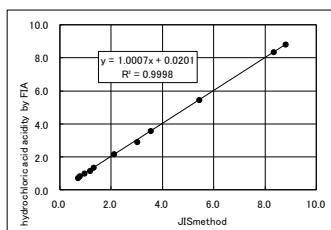


Fig. Relationship between hydrochloric acid

5. Summary

As for the flow analysis, it has been understood that there is especially no problem compared with the absorptiometry described in JIS K 0102. And it was proven that it was a very useful method from the viewpoint of the automation and the conserved reagent. It was admitted that there was no difference between the methods in JIS K 0170-2 (4 methods) but there was an utility enough at the same time.

Key words: Flow analysis, Environment surface water analysis, compared the official method, JIS K0170 , JIS K 0102 , Nitrate-nitrogen, Nitrite-nitrogen

Preparation of organic polymer monoliths and its application in capillary electrochromatography

Lan Zhang*, Zongbao Chen

Ministry of Education Key Laboratory of Analysis and Detection for Food Safety, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, Fujian, China, E-mail: zlan@fzu.edu.cn

In this work, some types of monolithic columns were prepared. Firstly, a porous polymethacrylate ester-based monolithic column was designed by mean of in situ co-polymerizing lauryl methacrylate (LMA), ethylene dimethacrylate (EDMA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) in a ternary porogenic solvent including cyclohexanol, 1,4-butanediol and water. Secondly, in order to improve the column efficiency, the lauryl methacrylate monolithic column was prepared by a novel controlled/"living" radical polymerization. Lastly, a hydrophilic monolithic column was prepared in capillaries by in situ polymerization of acrylamide (AA), glycidyl methacrylate (GMA), and N, N'-methylenebisacrylamide (MBAA) in the presence of dodecanol, toluene and DMSO as porogens. the monolithic column was modified by 0.1 mol/L ammonia water for opening epoxide groups of glycidyl methacrylate. In addition, these self-made monolithic columns were investigated by capillary electro- chromatography (CEC). They showed a very good performance in CEC for some small molecules including flavanoids, stimulants, alkaloids and so on. The retention behavior and separation mechanism were systematically studied in our experiments. As a stationary phase, the organic polymer monoliths might be a promising alternative for separation medium in CEC.

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