2015 China-Japan-Korea Symposium on Analytical Chemistry

Program and Abstracts

October 13 – 15, 2015

Haeundae Grand Hotel, Busan, Korea

2015 China-Japan-Korea Symposium on Analytical Chemistry

October 13 – 15, 2015
Haeundae Grand Hotel, Busan, Korea

Organized by

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

Supported by

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Message from Chairman

You are cordially invited to participate in the 2015 China-Japan-Korea Symposium on Analytical Chemistry (CJK 2015), to be held in Haeundae Grand Hotel, Busan, Korea on October13-15, 2015. The Conference should provide a forum for the analytical scientists to discuss their recent progress, to exchange the ideas and experiences on a broad range of analytical sciences, and to promote international cooperation and friendship.

A number of fruitful discussions and suggestions are expected during the conference. Outstanding analytical scientists from Korea, China and Japan are to be invited to present plenary and keynote lectures on a broad range of topics for the opening of China-Japan-Korea Symposium on Analytical Chemistry.

In this opportunity the organization committee appreciates to Dr. Yong-Kon Park, the president of Korea Food Research Institute, and several sponsors, Professor Jin-Ming Lin of China and Professor Hiroshi Sato of Japan 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 extended our friendship. We are looking forward to welcoming you to beautiful Busan in the autumn of 2015.

Professor Jaeho HA, Ph.D.

Chair of the Organizing Committee of 2015 CJK Symposium.

ORGANIZING COMMITTEE

Chairperson : Dr. Jaeho Ha
Food Analysis Center
Korea Food Research Institute
1201-62, Anyangpangyo-ro, Bundang-gu, Seongnam, Gyeonggi, 463-746, Korea
jhkfri@kfri.re.kr, Tel: +82-31-780-9127, Fax: +82-31-780-9280

Korea University of Science and Technology
217 Gajeong-ro Yuseong-gu, Daejeon, Korea

Co-Chair: Prof. Jin-Ming Lin
Tsinghua University, CHINA

Co-Chair: Prof. Hiroshi Sato
Nagasaki International University, JAPAN

COMMITTEE MEMBERS

KOREA

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Prof. Seong Ho Kang
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Seoul National University

Dr. Jang-Hyuk Ahn
KOTITI Testing & Research Institute

Prof. Yong-Moon Lee
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Dr. Haewon Jang
Korea Food Research Institute

Mr. Dongwon Seo
Korea Food Research Institute

Dr. Tae-Gyu Nam
Korea Food Research Institute

Ms. Jooyoung Lee
Korea Food Research Institute

Ms. Jisu Park
Korea Food Research Institute

CHINA

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Chinese Academy of Sciences

Prof. Jin-Ming Lin
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Prof. Yi Chen
Chinese Academy of Sciences

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Dr. Tsuneaki Maeda
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Prof. Kazuichi Hayakawa
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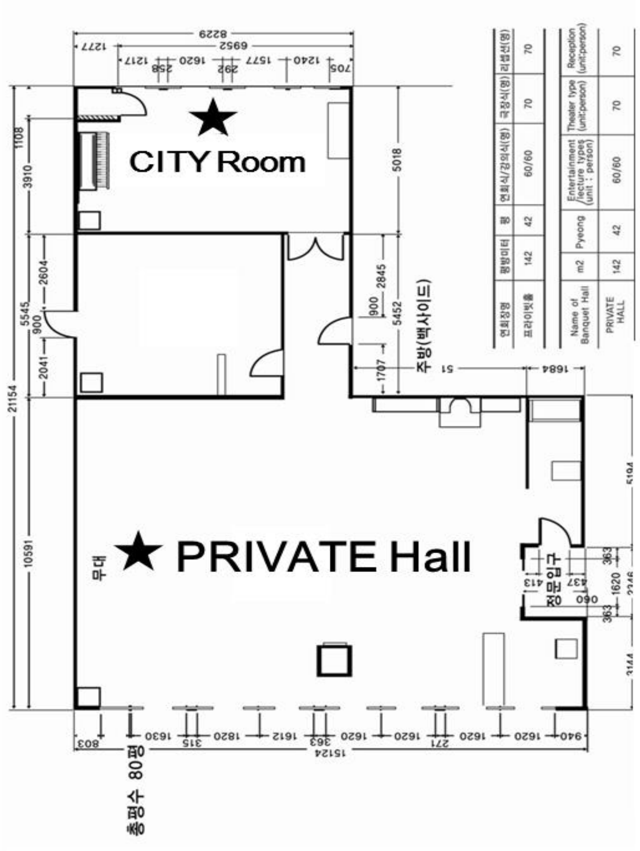
Lecture Rooms Floor Plan



연회장명	평방미터	평	연회식/강의식(명)	극장식(명)	리셉션(명)
프라이빗홀	142	42	60/60	70	70

Name of Banquet Hall	m2	Pyeong	Entertainment /lecture types (unit : person)	Theater type (unit:person)	Reception (unit:person)
PRIVATE HALL	142	42	60/60	70	70

2015 CJK SCIENTIFIC PROGRAMME

TUESDAY, OCTOBER 13th, Hotel Lobby	
13:30 - 18:00	Registration

WEDNESDAY, OCTOBER 14th, SKY Hall	
OPENING CEREMONY	
08:00 - 08:30	Opening Ceremony **Prof. Jaeho Ha**, Korea Food Research Institute, Korea
Session 1, PLENARY LECTURES	Chairperson : Prof. Seong Ho Kang
08:30 - 09:00	Study of DNA/Small Molecule Interaction by Dual Polarization Interferometry **Prof. Xiurong Yang**, Chinese Academy of Sciences, China
09:00 - 09:30	Inkjet-printed analytical devices made from paper **Prof. Daniel Citterio**, Keio University, Japan
09:30 - 10:00	Determination of trans fatty acids in daily consumed foods using a silver ion cartridge solid phase extraction method coupled with GCXGC-TOFMS **Prof. Jaeho Ha**, Korea Food Research Institute, Korea
10:00 - 10:30	Generation of Droplets of Liquid for Mass Spectrometry **Prof. Jin-Ming Lin**, Tsinghua University, China
10:20 - 10:50	**Coffee Break**
Session 2, KEYNOTE LECTURES	Chairperson : Prof. Joon Myong Song
10:50 - 11:10	Gold-containing Nanocarriers/Nanocomposites for Anti-bacterial Applications **Prof. Jian-Hua Wang**, Northeastern University, China
11:10 - 11:30	Simultaneous and selective determination of inorganic nitrogen species in seawater samples **Prof. Kazuaki Ito**, Kinki University, Japan
11:30 - 11:50	Odor variation on the car air conditioning evaporator according to the feeding nutrients **Prof. Man-Goo Kim**, Kangwon National University, Korea
11:50 - 13:00	**Luncheon, EMERALD Hall, 6th Floor**
Session 3, KEYNOTE LECTURES	Chairperson : Prof. Jian-Hua -Wang
13:00 - 13:20	Development of on-line SFE-SFC system and its application **Dr. Yuki Hashi**, Shimadzu (China) Co., Ltd., China
13:20 - 13:40	Quantitative on-line Concentration and Reaction for Capillary Electrophoresis with Inkjet Sample Introduction **Prof. Katsumi Uchiyama**, Tokyo Metropolitan University, Japan
13:40 - 14:00	Introduction of 2016 CJK Symposium in China **Prof. Chunhua Ma**, Wuyi University, China
14:00 - 14:20	Detection of Benzo[a]pyrene-induced Breast Cancer Stem Cells Using Quantum dot-based High-content Assay **Prof. Joon Myong Song**, Seoul National University, Korea

14:20 - 14:40	**Coffee Break**

Session 4, KEYNOTE LECTURES Chairperson : Prof. Jang-Hyuk Ahn

14:40 - 15:00	Micro ion extractor for transferring inorganic and organic trace anions from a single drop of whole blood **Prof. Kei Toda**, Kumamoto University, Japan
15:00 - 15:20	The research of sample preparation method based on metal organic frameworks **Prof. Gongke Li**, Sun Yat-sen University, China
15:20 - 15:40	LC-MS/MS analysis of sphingolipid metabolites in mice during acute exercise stress **Prof. Yong-Moon Lee**, Chungbuk National University, Korea
15:40 - 16:00	Microfluidic Chips towards Cell Signaling Analysis **Prof. Bi-Feng Liu**, Huazhong University, China
16:00 - 17:00	**Poster Presentations**

Session 5, KEYNOTE LECTURES & ORAL PRESENTATIONS

Chairperson : Prof. Yi Chen

17:00 - 17:20	Determination of Important Volatile Compounds from Aqueous Matrix **Prof. Sunyoung Bae**, Seoul Women's University, Korea
17:20 - 17:35	Electrochemical study on electron transfer across DNA base pairs **Prof. Jifeng Liu**, Tianjin University, China
17:35 - 17:50	Antioxidant Activity of Volatile Compounds Isolated from Broccoli (Brassica oleracea L.) sprouts by GC and GC-MS **Dr. Hae Won Jang**, Korea Food Research Institute, Korea
17:50 - 18:05	Analytical Applications of Higher-order Calibration Methods Based on Alternating Multilinear Decomposition Algorithms **Prof. Hai-Long Wu**, Hunan University, China
18:30 - 21:00	**Banquet, EMERALD Hall, 6th Floor**

WEDNESDAY, OCTOBER 14th, PRIVATE Hall

Session 1, KEYNOTE LECTURES Chairperson : Prof. Shin-Ichi Ohira

10:50 - 11:10	The synthesis of fluorescent graphitic carbon nitride nanomaterials and their application in fluorescence sensing **Prof. Xi Chen**, Xiamen University, China
11:10 - 11:30	Sputtered nanocarbon film electrodes for bioelectroanalysis **Prof. Dai Kato**, National Institute of Advanced Industrial Science and Technology (AIST), Japan
11:30 - 11:50	Break diffraction-limited barrier with wavelength-modulation fluorescence-free nanoscopy **Prof. Seong Ho Kang**, Kyunghee University, Korea
11:50 - 13:00	**Luncheon, EMERALD Hall, 6th Floor**

Session 2, KEYNOTE LECTURES Chairperson : Prof. Xi Chen

13:00 - 13:20	Novel Solid Phase Microextraction and Capillary Electrochromatographic Column for Pharmceutical Analysis **Prof. Zilin Chen**, Wuhan University, China
13:20 - 13:40	Discrimination technique using fragmentless ionization mass spectrometry and multivariate analysis for food analysis **Prof. Takahisa Tsugoshi**, National Institute of Advanced Industrial Science and Technology (AIST), Japan
13:40 - 14:00	Fast Analysis by Microextraction Coupled to Ambient Mass Spectrometry **Prof. Huwei Liu**, Peking University, China
14:00 - 14:20	Determination of copper content in processed food by ICP **Dr. Jang-Hyuk Ahn**, KOTITI Testing & Research Institute, Korea
14:20 - 14:40	**Coffee Break**
Session 3, KEYNOTE LECTURES	Chairperson : Prof. Hailong Wu
14:40 - 15:00	Lysine surface modified Fe3O4@SiO2@TiO2 microspheres-based preconcentration and photocatalysis for in situ selective determination of nanomolar dissolved organic and inorganic phosphorus in seawater **Prof. Shunxing Li**, Minnan Normal University, China
15:00 - 15:20	Electrochemical and optical monitoring of enzyme reaction on compact disc-type microchip **Prof. Toshihiko Imato**, Kyushu University, Japan
15:20 - 15:40	Strategy toward the ultrafast separation **Prof. Yi Chen**, Chinese Academy of Sciences, China
15:40 - 16:00	Polycyclic Aromatic Hydrocarbons, Nitropolycyclic Aromatic Hydro- carbons and Inorganic Ions in Snow Layers at Murodo, Tateyama, Japan **Prof. Kazuichi Hayakawa**, Kanazawa University, Japan
16:00 - 17:00	**Poster Presentations**
Session 4, ORAL PRESENTATIONS	Chairperson : Prof. Shunxing Li
17:00 - 17:15	Application of novel nanomaterials in the phosphopeptide enrichment **Prof. Yu Bai**, Peking University, China
17:15 - 17:30	Water Quality Monitoring of Drainage River in Kuantan, Malaysia by using Ion-exclusion/Ion-exchange Chromatography **Dr. Daisuke Kosaki**, University Malaysia Pahang , Japan
17:30 - 17:45	Preparation and Application of Microextraction Probe for Enrichment of Organics from Aqueous Matrices **Dr. Hai-fang Li**, Tsinghua University, China
18:30 - 21:00	**Banquet, EMERALD Hall, 6th Floor**

THURSDAY, OCTOBER 15th, PRIVATE Hall

Session 1, ORAL PRESENTATIONS	Chairperson : Yu Bai
09:00 - 09:15	Multifunctional fluorescent optical sensors for bioanalysis **Prof. Yanqing Tian**, South University, China
09:15 - 09:30	Facile preparation of a novel benyl imidazolium ionic liquids hybrid monolithic column for residue analysis of nitrogen-heterocyclic pesticides by CEC

	Prof. Xiaoping Wu, Fuzhou University, China
09:30 - 09:45	Electrodialytic Matrix Isolation and Preconcentration for Ionic Solutes **Prof. Shin-Ichi Ohira**, Kumamoto University, Japan
09:45 - 10:00	Electrothermal vaporization or atomization on tungsten coil for analytical atomic spectrometry **Prof. Xiandeng Hou**, Sichuan University, China
10:00 - 10:15	Determination of silicate, borate and carbonate ions in natural waters using ion-exclusion chromatography coupled with charged aerosol detector **Prof. Nobutake Nakatani**, Rakuno Gakuen University, Japan
10:30 – 11:00	**Closing Ceremony** (Young Scientists & Best Posters Awards)

THURSDAY, OCTOBER 15th, CITY Room

Session 1, ORAL PRESENTATIONS	Chairperson : Prof. Kei Toda
09:00 - 09:15	Development of a Hybrid Pyrolyzer for Gas Chromatography **Prof. Naoki Oguri**, Japan Analytical Industry Co., Ltd., Japan
09:15 - 09:30	New strategies for the functionalization of polymer monolith and applications to separation and preconcentration of organic compounds **Prof. Qiong Jia**, Jilin University, China
09:30 - 09:45	Determination of arsenic species in food by LC-ICP-MS **Dr. Cheong-Tae Kim**, NONGSHIM CO., LTD., Korea
09:45 - 10:00	Functionalized Gold-Nanomaterials Fluorescence Probe for Cyanide Detection **Prof. Shaomin Shuang**, Shanxi University, China
10:00 - 10:15	Hairpin DNA Template-based Copper Nanoparticles for the Detection of NAD+ **Prof. Jianzhong Lu**, Fudan University, China
10:30 – 11:00	**Closing Ceremony** (Young Scientists & Best Posters Awards), **PRIVATE Hall**

List of Participants from Korea

Name	Organization	E-mail
Jaeho Ha, Dr.	Korea Food Research Institute	jhkfri@kfri.re.kr
Haewon Jang, Dr.	Korea Food Research Institute	hwjkfri@kfri.re.kr
Jinbong Hwang, Dr.	Korea Food Research Institute	hwangjb@kfri.re.kr
Dongwon Seo, Mr.	Korea Food Research Institute	dwseo@kfri.re.kr
Tae-Gyu Nam, Dr.	Korea Food Research Institute	ntg97@kfri.re.kr
Jooyoung Lee, Ms.	Korea Food Research Institute	jylee@kfri.re.kr
Jisu Park, Ms.	Korea Food Research Institute	goo819@kfri.re.kr
Seong Ho Kang, Prof.	Kyunghee University	shkang@khu.ac.kr
Moonhee Park, Ms.	Kyunghee University	moonhee@khu.ac.kr
Sujin An, Ms.	Kyunghee University	tnwls8210276@naver.com
ChangHee Kang, Prof.	Jeju National University	changhee@jejunu.ac.kr
Jung-Min Song, Dr.	Jeju National University	songjm@jejunu.ac.kr
Jun-Oh Bu, Mr.	Jeju National University	uaeveros@jejunu.ac.kr
YongMoon Lee, Prof.	Chungbuk National University	ymleefn@hanmail.net
HwaMi Lee, Dr.	Gyeongin Regional Food and Drug Administration	lhm9904@naver.com
JaeYoung Shim, Dr.	Busan Regional Korea Food and Drug Administration	shilvi0321@gmail.com
Sunyoung Bae, Prof.	Seoul Women's University	sbae@swu.ac.kr
Soomi Park, Ms.	Seoul Women's University	aclsoom2@naver.com
Soyoung Lee, Ms.	Seoul Women's University	kitty_sy@naver.com
Yura Hwang, Ms.	Seoul Women's University	yura4931@naver.com
Dong-Sun Lee, Prof.	Seoul Women's University	dslee@swu.ac.kr
Joon Myong Song, Prof.	Seoul National University	jmsong@snu.ac.kr
Jieun Ki, Ms.	Seoul National University	jieunki@snu.ac.kr
Gee Woo Nam, Ms.	Seoul National University	nameraser@snu.ac.kr
Baskaran Purushothaman	Seoul National University	baskaran@snu.ac.kr
Hee Ju, Ms.	Seoul National University	juhee9079@snu.ac.kr
Jang-Hyuk Ahn, Dr.	KOTITI	ahn5470@hanmail.net
Cheong-Tae Kim, Dr.	NONGSIM CO., LTD	kctmass@hanmail.net
Man-Goo Kim, Prof.	Kangwon National University	mgkim@kangwon.ac.kr
Yunje Kim, Prof.	Korea Institute of Science and Technology	yjkim@kist.re.kr
Ho Soo Lim, Dr.	Food and Drug Safety	hslim70@korea.kr
Yunsuk Kim, Dr.	K-water Institute	yunskim@kwater.or.kr
Wonjin Yoon, Mr.	Korea Food Research Institute	Yoon.Won-jin@kfri.re.kr

Name	Organization	E-mail
Haejin Wang, Ms.	Korea Food Research Institute	Sarah15232477@gmail.com
Jangho Lee, Mr.	Korea Food Research Institute	penguini@daum.net
So Young Kim, Ms	Korea Food Research Institute	07419@kfri.re.kr
Eun-Joo Park, Ms	Korea Food Research Institute	07727@ kfri.re.kr
Ahmad Rois Mansur, Mr.	Korea Food Research Institute	rais.ahmad07@yahoo.com

List of Participants from China

Name	Organization	E-mail
Xiurong Yang, Prof.	Chinese Academy of Sciences	xryang@ciac.ac.cn
Jin-Ming Lin, Prof.	Tsinghua University	jmlin@mail.tsinghua.edu.cn
Jian-Hua Wang, Prof.	Northeastern University	jianhuajrz@mail.neu.edu.cn
Xi Chen, Prof.	Xiamen University	xichen@xmu.edu.cn
Yuki Hashi, Dr.	Shimadzu China	y-hashi@shimadzu.co.jp
Zilin Chen, Prof.	Wuhan University	chenzl@whu.edu.cn
Chunhua Ma, Prof.	Wuyi University	chma@wuyiu.edu.cn
Huwei Liu, Prof.	Peking University	hwliu@pku.edu.cn
Gongke Li, Prof.	Sun Yat-sen University	cesgkl@mail.sysu.edu.cn
Yi Chen. Prof.	Chinese Academy of Sciences	chenyi@iccas.ac.cn
Bi-Feng Liu, Prof.	Huazhong University	bfliu@mail.hust.edu.cn
Shunxing Li, Prof.	Minnan Normal University	lishunxing@mnnu.edu.cn
Yu Bai, Prof.	Peking University	yu.bai@pku.edu.cn
Hai-Fang Li, Prof.	Tsinghua University	lihaifang@mail.tsinghua.edu.cn
Yanqing Tian, Prof.	South University	tianyq@sustc.edu.cn
Shaomin Shuang, Prof.	Shanxi University	smshuang@sxu.edu.cn
Jifeng Liu, Prof.	Tianjin University	jfliu@tust.edu.cn
Hai-Long Wu, Prof.	Hunan University	hlwu@hnu.cn
Xiaoping Wu, Prof.	Fuzhou University	wapple@fzu.edu.cn
Jianzhong Lu, Prof.	Fudan University	jzlu@shmu.edu.cn
Qingxiang Wang, Prof.	Fujian Normal University	axiang236@126.com
Qiong Jia, Prof.	Jilin University	jiaqiong@jlu.edu.cn
Zhuo Deng, Ms.	Xiamen University	joydeng2011@163.com
Mingcong Rong, Mr.	Xiamen University	haiyangzhixinrmc@qq.com
Ting-Ting Zhao, Ms.	Xiamen Huaxia University	ztt@hxxy.edu.cn
Ming-Li Chen, Prof.	Northeastern University	chenml@mail.neu.edu.cn
Xu-Wei Chen, Prof.	Northeastern University	chenxuwei@mail.neu.edu.cn
Ting Yang, Prof.	Northeastern University	yangting@mail.neu.edu.cn
Fengming Chen, Dr.	Tsinghua University	chenfengmingok@mail.tsinghua.edu.cn
Zhaochai Qiu, MS.	Xiamen University	308466917@qq.com
Feng Luo, Prof.	Fujian Research Institute	luofeng6789@163.com
Kailai Xu, Dr.	Sichuan University	xukailai@scu.edu.cn
Guo-Jun Zhang, Dr.	Hubei University	gjzhangtj@hotmail.com
Shin-Ichi Kawano, Dr.	Shimadzu China	kawashin@shimadzu.co.jp
Hong-Kai Wang, Mr.	Shimadzu China	bswhk@shimadzu.com.cn
Dongtao Lu, Prof.	Shanxi University	ludongtao@sxu.edu.cn

Name	Organization	E-mail
Erqun Song, Prof.	Southwest University	eqsong@swu.edu.cn
Mohamed Foda, Prof.	Huazhong Agricultural University	m.frahat@fagr.bu.edu.eg
Xiandeng Hou, Prof.	Sichuan University	houxd@scu.edu.cn
Xue Jiang, Ph.D. student	Sichuan University	jiangxue218@gmail.com
Chenghui Li, Ph.D. student	Sichuan University	lch_lucy@163.com
Lan Wu, Prof.	Sichuan University	wulan@scu.edu.cn

List of Participants from Japan

Name	Organization	E-mail
Toshiyuki Hobo, Prof.	Tokyo Metropolitan University	toshi-90@nifty.com
Kazuaki Ito, Prof.	Kinki University	itok@hiro.kindai.ac.jp
Dai Kato, Dr.	Advanced Industrial Science and Technology	dai.kato@aist.go.jp
Tsuneaki Maeda, Dr.	Advanced Industrial Science and Technology	maeda-t@aist.go.jp
Hiroshi Sato, Prof.	Nagasaki International University	satoh@niu.ac.jp
Katsumi Uchiyama, Prof.	Tokyo Metropolitan University	uchiyama-katsumi@c.metro-u.ac.jp
Masaki Watanabe, Dr.	Hitachi high-tech Science Corporation	masaki.watanabe.yk@hitachi-hightech.com
Shin-Ichi Ohira, Prof.	Kumamoto University	ohira@sci.kumamoto-u.ac.jp
Kei Toda, Prof.	Kumamoto University	todakei@sci.kumamoto-u.ac.jp
Toshihiko Imato, Prof.	Kyushu University	imato@cstf.kyushu-u.ac.jp
Takahisa Tsugoshi, Prof.	Advanced Industrial Science and Technology	tsugoshi.takahisa@aist.go.jp
Kazuichi Hayakawa, Prof.	Kanazawa University	hayakawa@p.kanazawa-u.ac.jp
Naoki Oguri, Dr.	Japan Analytical Industry Co. Ltd.	n-oguri@jai.co.jp
Daisuke Kosaki, Dr.	University Malaysia Pahang	emerald.green.2-10@hotmail.co.jp
Nobutake Nakatani, Prof.	Rakuno Gakuen University	nakatani@rakuno.ac.jp
Daniel Citterio, Prof.	Keio University	citterio@applc.keio.ac.jp
Ryozo Goto, Dr.		goto2000@yahoo.co.jp

List of Participants from Mongolia

Name	Organization	E-mail
Ganjuurjav Oyun, Dr.	Scientific food research and manufacturing SAMO Institute	ganjuuro@yahoo.com
Dondogsuren Narantuya, Ms.	Scientific food research and manufacturing SAMO Institute	narantuya0620@gmail.com
Enkhbat Anudari, Ms.	Scientific food research and manufacturing SAMO Institute	

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PLENARY LECTURES

PL.01

Study of DNA/Small Molecule Interaction by Dual Polarization Interferometry

Xiurong Yang*, State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, China. E-mail: xryang @ciac.ac.cn

PL.02

Inkjet-printed analytical devices made from paper

Daniel Citterio* and Koji Suzuki, Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, 223-8522 Yokohama, Japan. E-mail: citterio@applc.keio.ac.jp

PL.03

Determination of trans fatty acids in daily consumed foods using a silver ion cartridge solid phase extraction method coupled with GCxGC-TOFMS

Dongwon Seo[1], **Jaeho Ha**[1,2*], [1]Food Analysis Center, Korea Food Research Institute, [2]Korea University of Science and Technology. E-mail: jhkfri@gmail.com

PL.04

Generation of Droplets of Liquid for Mass Spectrometry

Jin-Ming Lin[1*], Chen Luo[1], Yangdong Zhang[1], Fengming Chen[1,2], Katsumi Uchiyama[2], [1]Department of Chemistry, Tsinghua University, Beijing 100084, China, [2]Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Minamiohsawa, Hachioji, Tokyo 192-0364, Japan. E-mail: jmlin@mail.tsinghua.edu.cn

KEYNOTE LECTURES

KL.01

Gold-containing Nanocarriers/Nanocomposites for Anti-bacterial Applications

Bo Hu, Ning Wang, Ming-Li Chen, Xu-Wei Chen, **Jian-Hua Wang***, Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China. Email: jianhuajrz@mail.neu.edu.cn

KL.02

The synthesis of fluorescent graphitic carbon nitride nanomaterials and their application in fluorescence sensing

Xi Chen[1,2]*, Mingcong Rong[1], Yiru Wang[1], [1]Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China, [2]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China. Email: xichen@xmu.edu.cn

KL.03

Simultaneous and selective determination of inorganic nitrogen species in seawater samples

Kazuaki Ito*, Department of Biotechnology and Chemistry, Faculty of Engineering, Kinki University, 1 Umenobe, Takaya, Higashi-Hiroshima, 739-2116, Japan. Email: itok@hiro.kindai.ac.jp

KL.04

Sputtered nanocarbon film electrodes for bioelectroanalysis

Dai Kato* and Osamu Niwa, National Institute of Advanced Industrial Science and Technology (AIST), Higashi, Tsukuba, Ibaraki 305-8566, Japan. Email: dai.kato@aist.go.jp

KL.05

Odor variation on the car air conditioning evaporator according to the feeding nutrients

Man-Goo Kim*, Young-Jae Ryu, Dept. of Environmental Science, College of Natural Science, Kangwon National University, Kangwon, 200-701, Korea Email: mgkim@kangwon.ac.kr

KL.06

Break diffraction-limited barrier with wavelength-modulation fluorescence-free nanoscopy

Peng Zhang[a], Seungah Lee[b], **Seong Ho Kang**[a,b,]*, [a]Department of Chemistry, Graduate School, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea, [b]Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea. Email: shkang@khu.ac.kr

KL.07

Development of on-line SFE-SFC system and its application

Yuki Hashi, Shimadzu (China) Co., Ltd., China. Email: y-hashi@shimadzu.co.jp

KL.08

Novel Solid-Phase Microextraction and Capillary Electrochromatographic Column

Techniques for Pharmaceutical Analysis

Zilin Chen*, Wenpeng Zhang, Juan Zhang, Zixin Zhang, School of Pharmaceutical Sciences, Wuhan University, China. Email: Chenzl@whu.edu.cn

KL.09

Quantitative on-line Concentration and Reaction for Capillary Electrophoresis with Inkjet Sample Introduction

Ying Rang, Fengming Chen, Hulie Zeng, Hizuru Nakajima, Shungo Kato, Jinmig Lin, **Katsumi Uchiyama***, Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Minamiohsawa, Hachioji, Tokyo 192-0397, Japan. Email: uchiyama-katsumi@tmu.ac.jp

KL.10

Discrimination technique using fragmentless ionization mass spectrometry and multivariate analysis for food analysis.

Takahisa Tsugoshi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan. E-mail: tsugoshi.takahisa@aist.go.jp

KL.11

Introduction of 2016 CJK Symposium in China

Chunhua Ma*, College of Tea and Food Science, Wuyi University, Wuyi Rd. 16, Wuyishan 354300, China. E-mail: chma@wuyiu.edu.cn

KL.12

Fast Analysis by Microextraction Coupled to Ambient Mass Spectrometry

Xin Wang, Xianjiang Li, Yu Bai, **Huwei Liu***, Institute of Analytical Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: hwliu@pku.edu.cn

KL.13

Detection of Benzo[a]pyrene-induced Breast Cancer Stem Cells Using Quantum Dot-based High-content Assay

Yumi Shim, **Joon Myong Song***, College of Pharmacy, Seoul National University, Seoul 151-742, Korea. E-mail: jmsong@snu.ac.kr

KL.14

Determination of copper content in processed food by ICP

Jae Sung Kim, Yoon Jung Yoo, Byeong Hyeon So, Kwang Sik Jung, Hyun Mi Koo, Ji Won Lee, **Jang-Hyuk Ahn***, Sang Rag Lee, Young Ryul Kim, KOTITI Testing &

Research Institute, Seongnam 462-807 Republic of Korea. E-mail: ahn5470@hanmail.net

KL.15

Micro ion extractor for transferring inorganic and organic trace anions from a single drop of whole blood

Kei Toda*, Hiroka Nishiyama, Yukihide Nakamura, Yurika Imoto, Shin-Ichi Ohira

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

KL.16

Lysine surface modified Fe_3O_4@SiO_2@TiO_2 microspheres-based preconcentration and photocatalysis for in situ selective determination of nanomolar dissolved organic and inorganic phosphorus in seawater

Shunxing Li*, Wenjie Liang, College of Chemistry and Environment & Fujian Province Key Laboratory of Modern Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou 363000, P. R. China. E-mail: lishunxing@fjzs.edu.cn

KL.17

The research of sample preparation method based on metal organic frameworks

Gongke Li*, Yuling Hu, Zelin Huang, Haixian Lian, Yichun Huang,Suling Zhang, Yifeng Fan, Zhuomin Zhang, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, P.R.China. E-mail: cesgkl@mail.sysu.edu.cn

KL.18

Electrochemical and optical monitoring of enzyme reaction on compact disc-type microchip

Toshihiko Imato*, Departament of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395 Japan. E-mail: imato@cstf.kyushu-u.ac.jp

KL.19

LC-MS/MS analysis of sphingolipid metabolites in mice during acute exercise stress

Yong-Moon Lee*, College of Pharmacy, Chungbuk National University, Cheongju 361-763, Korea. E-mail: ymleefn@chungbuk.ac.kr

KL.20

Strategy toward the ultrafast separation

Yi Chen*, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. . E-mail: chenyi@iccas.ac.cn

KL.21

Microfluidic Chips towards Cell Signaling Analysis

Pen Chen, Yao Wang, **Bi-Feng Liu***, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, E-mail: China, bfliu@mail.hust.edu.cn

KL.22

Polycyclic Aromatic Hydrocarbons, Nitropolycyclic Aromatic Hydro- carbons and Inorganic Ions in Snow Layers at Murodo, Tateyama, Japan

Kazuichi HAYAKAWA[1,2*], Genki SUZUKI[1], Fumiya MAKINO[1], Hiroshi MORISAKI[1], Ning TANG[1], Akira TORIBA[1] and Kazuma AOKI[3], [1]Institute of Medical, Pharmacutical and Health Sciences, Kanazawa University, Japan, [2]Institute of Nature and Environmental Technology, Kanazawa University, Japan, [3]Graduate School of Science, Toyama University, Japan. E-mail: hayakawa@p.kanazawa-u.ac.jp

KL.23

Determination of Important Volatile Compounds from Aqueous Matrix

Sunyoung Bae[*], Department of Chemistry, Seoul Women's University, Nowon-Gu, Hwarangro, Seoul, Korea. E-mail: sbae@swu.ac.kr

ORAL PRESENTATIONS

OL.01

Electrochemical study on electron transfer across DNA base pairs

Jifeng Liu, School of Food Engineering and Biotechnology, Tianjin University of Science and Technology, Tianjin 300457, China. E-mail: China, jfliu@tust.edu.cn

OL.02

Application of novel nanomaterials in the phosphopeptide enrichment

Liping Li, Linnan Xu, Wen Ma, Huwei Liu, **Yu Bai***, College of Chemistry and Molecular Engineering, Peking University, Beijing, China. E-mail: yu.bai@pku.edu.cn

OL.03

Antioxidant Activity of Volatile Compounds Isolated from Broccoli (Brassica oleracea L.) sprouts by GC and GC-MS

Hae Won Jang*, Food Analysis Center, Korea Food Research Institute, Korea. E-mail: hwjkfri@kfri.re.kr

OL.04

Water Quality Monitoring of Drainage River in Kuantan, Malaysia by using Ion-exclusion/Ion-exchange Chromatography

Daisuke Kozaki[1]*, Norhasmira Idayu binti Harun[1], Nobutake Nakatani[2], Masanobu Mori[3], , Kazuhiko Tanaka[3], [1]Faculty of Industrial Sciences and Technology, University Malaysia Pahang, Malaysia, [2]Department of Environmental and Symbiotic Sciences, College of Agriculture, Food and Environmental Science, Rakuno Gakuen University, Japan, [3]Graduate school of Science and Technology, Gunma University, Japan. E-mail: daisuke@ump.edu.my

OL.05

Analytical Applications of Higher-order Calibration Methods Based on Alternating Multilinear Decomposition Algorithms

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

OL.06

Preparation and Application of Microextraction Probe for Enrichment of Organics from Aqueous Matrices

Hai-Fang Li*, Guilan Huang, Jin-Ming LIN, Department of Chemistry, Beijing Key Laboratory of Micronalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, China, E-mail: lihaifang@mail.tsinghua.edu.cn

OL.07

Multifunctional fluorescent optical sensors for bioanalysis

Yanqing Tian*, Department of Materials Science and Engineering, South University of Science and Technology of China. E-mail: tianyq@sustc.edu.cn

OL.08

Development of a Hybrid Pyrolyzer for GAS CHROMATOGYAPHY

Naoki Oguri*, Toshio Tsuchiya, Kaoru Enokido, Tamami Takeda and Akira Onishi, Japan Analytical Industry Co., Ltd. E-mail: n-oguri@jai.co.jp

OL.09

Facile preparation of a novel benyl imidazolium ionic liquids hybrid monolithic column for residue analysis of nitrogen-heterocyclic pesticides by CEC

Yan Huang, Yankai Chen, Yanxia Tang, **Xiaoping Wu***, MOE Key Laboratory of Analysis and Detection Technology for Food Safety; College of Chemistry, Fuzhou University, Fuzhou, China. E-mail: wapple@fzu.edu.cn

OL.10

New strategies for the functionalization of polymer monolith and applications to separation and preconcentration of organic compounds

Haijiao Zheng, Gang Chen, **Qiong Jia***, College of Chemistry, Jilin University, Changchun, 130012, China. E-mail: jiaqiong@jlu.edu.cn

OL.11

Electrodialytic Matrix Isolation and Preconcentration for Ionic Solutes

Shin-Ichi Ohira*, Takayuki Yamasaki, Kei Toda, Department of Chemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan. E-mail: ohira@sci.kumamoto-u.ac.jp

OL.12

Determination of arsenic species in food by LC-ICP-MS

Cheong-Tae Kim, Food Safety Research Institute, NONGSHIM CO., LTD, Seoul, Korea, E-mail: kctmass@hanmail.net

OL.13

Electrothermal vaporization or atomization on tungsten coil for analytical atomic spectrometry

Xue Jiang,[a] Chenghui Li,[a] Xiaoming Jiang,[b] Zhou Long,[b] **Xiandeng Hou***[a,b], [a]Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China, [b]Analytical & Testing Centre, Sichuan University, Chengdu, Sichuan 610064, China. E-mail: houxd@scu.edu.cn.

OL.14

Functionalized Gold-Nanomaterials Fluorescence Probe for Cyanide Detection

Dongtao Lu; Guomei Zhang, Chuan Dong, **Shaomin Shuang***, Institute of Environmental Science, College of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China. E-mail: smshuang@sxu.edu.cn

OL.15

Determination of silicate, borate and carbonate ions in natural waters using ion-exclusion chromatography coupled with charged aerosol detector

Nobutake Nakatani*[1], Yu Otsuka[1], Takuya Takahashi[1], Daisuke Kozaki[2],
Masanobu Mori[3], Kazuhiko Tanaka[3], [1]College of Agriculture, Food and Environment Sciences, Rakuno Gakuen University, [2]Faculty of Industrial Sciences and Technology, University Malaysia Pahang, [3]Graduate School of Science and Technology, Gunma

University. E-mail: nakatani@rakuno.ac.jp

OL.16

Hairpin DNA Template-based Copper Nanoparticles for the Detection of NAD$^+$

Jianzhong Lu*, School of Pharmacy, Fudan University, 826 Zhangheng Road, Shanghai, China E-mail: jzlu@shmu.edu.cn

POSTERS PRESENTATIONS

PT.01

Development of Inkjet Printing Single-cell Technology to Electrospray Ionization for Mass Spectrometer

Fengming Chen*, Shiqi Wang, Ziyi He, Hai-Fang Li, Jin-Ming LIN

Department of Chemistry, Beijing Key Laboratory of Micronalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, China. E-mail: chenfengmingok@mail.tsinghua.edu.cn

PT.02

Selective removal of cadmium from water samples by bio-functionalized composite MT@C-dot@SiO_2

Yi-Kun Li, Ting Yang, **Ming-Li Chen***, Jian-Hua Wang, Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China. E-mail: chenml@mail.neu.edu.cn

PT.03

Monitoring the dynamic mass-transferring behaviors of hemoglobin between aqueous/ionic-liquid phases with liquid core optical waveguide system

Xu-Wei Chen*, Xu Yang, Wan-Ying Zeng, Jian-Hua Wang, Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China, E-mail: chenxuwei@mail.neu.edu.cn

PT.04

Self-assembly sea urchin-like ZnO nanoparticles for headspace thin-film microextraction coupled with SERS to detect sulfur dioxide in medlar

Zhuo Deng[1]*, Ziming Zhao[1], Yiru Wang[1], Xi Chen[1,2], [1]Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China, [2]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China. E-mail: joydeng2011@163.com

PT.05

Selectively enhanced molecular emission spectroscopy of benzene, toluene and xylene with nano-MnO_2 in atmospheric ambient temperature dielectric barrier discharge

Xue Jiang [1], Chenghui Li[1], Xiandeng Hou[1,2], [1]Department of Chemistry, Sichuan University, Chengdu, 610064, Chinam, [2]Analytical & Testing Center, Sichuan University, Chengdu, 610064, China. E-mail: jiangxue218@gmail.com

PT.06

Synthesis of Highly Fluorescent P-g-C_3N_4 Nanodots for Label-free Detection of Cu^{2+} and Acetylcholinesterase Activity

Mingcong Rong[1], Chunhua Ma[2], Zhaochai Qiu[1], Xi Chen, [1]Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China, [2]College of tea and food science, Wuyi University, Wuyishan 354300, China. E-mail: haiyangzhixinrmc@126.com

PT.07

Simultaneous detection of dihydroxybenzene isomers by HKUST-1 MOF modified electrode

Yizhen Yang, **Qingxiang Wang***, College of Chemistry and Environment, Minnan Normal University, Zhangzhou 363000, P. R. China. E-mail: axiang236@126.com

PT.08

In-situ growth of gold nanoparticles on mercury-binding M13 phage for Hg^{2+} sensing

Xiao-Yan Wang, Ming-Li Chen, **Ting Yang***, Jian-Hua Wang, Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China. E-mail: yangting@mail.neu.edu.cn

PT.09

Absorption of Pb^{2+} and Cd^{2+} from Water using 3D nitrogen-doped graphene

Ting-Ting ZHAO[1], Feng LUO[2], Xin-Hong SONG[3], Xi CHEN[3], [1]Planning Department,Xiamen Huaxia University, Xiamen 361024,China, [2]Fujian Research Institute of Metric Science; Fuzhou 350003, China, [2]Quanzhou Medical College, Quanzhou, 362010, [3]Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005,China. E-mail: ztt@hxxy.edu.cn

PT.10

Online multichannel ultrasonic extraction for high throughput determination of arsenic in soil by hydride generation atomic fluorescence spectrometry

Yuefen Zhang,[a] Lan Wu,[a,b] Chengbin Zheng,[a] Xiandeng Hou,[a,b] and **Kailai Xu***[a], [a]Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China, [b]Analytical & Testing Centre, Sichuan University, Chengdu, Sichuan 610064, China. E-mail: xukailai@scu.edu.cn

PT.11

Label-free detection of microRNA by Au nanoparticles decorated reduced graphene oxide field-effect transistor biosensor

Bingjie Cai, **Guo-Jun Zhang***, School of Laboratory Medicine, Hubei University of Chinese Medicine, Wuhan 430065, China. E-mail: gjzhangtj@hotmail.com

PT.12

GC/MS analysis and sensory evaluation of odor compounds in environmental tobacco smoke (ETS)

Hiroshi Sato1)*, Masahiro Oka1), Shuhei Nagahashi1), Kaori Imi1), Naoki Mizoguchi1), Hidetaka Matsubara2), Miyuki Noguchi3), Keiichi Arashidani4)
1)Department of Pharmacy, Faculty of Pharmaceutical Sciences, Nagasaki International University, 2)Chuken Laboratory for Life and Environment, 3)Faculty of Science and Technology, Seikei University, 4)School of Health Sciences, University of Occupational and Environmental Health. E-mail: satoh@niu.ac.jp

PT.13

Application of HPLC by Using Mass Spectrometry Detector

Masaki Watanabe*, Masaki Yoshie, Norimasa Minamoto, Kousaku Toyosaki
Optical Instrument Engineering Department, Hitachi high-tech Science Corporation, 1040 Ichige, Hitachinaka, Ibaraki 312-0033 Japan. E-mail: masaki.watanabe.yk@hitachi-hightech.com

PT.14

Analytical method for arsenic speciation in foods using HPLC-ICP/MS

Dongwon Seo*, Soyoung Kim, Eunjoo Park, Jisu Park, Jaeho Ha, Tae-Gyu Nam, Jooyoung Lee, Haewon Jang, Jinbong Hwang, Food Analysis Center, Korea Food Research Institute, Seongnam 463-746, Korea. E-mail: dwseo@kfri.re.kr

PT.15

Nutritional composition of bamboo shoots (*Phyllostachys Bambusoides Sieb. et Zucc.*) in Korea

Dongwon Seo[1]*, Songjin Lee[2], Jinbong Hwang[1], Kinjin Kim[1], Soyoung Kim[1], Eunjoo Park[1], Hyunjun Lee[1], Haebin Cho[1], Seunghee Kim[1], Wonjin Yoon[1], Jaeho Ha[1], [1]Food Analysis Center, Korea Food Research Institute, Seongnam 13539, Korea, [2]Bamboo Resource Research Institute, Damyang 57365, Korea. E-mail: dwseo@kfri.re.kr

PT.16

Comparison of Macro Mineral Contents following Kind of Vegetables produced in Korea

Eun-joo Park[1*] , Soyoung Kim[1], Jinbong Hwang[1], Dongwon Seo[1], Youngmin Choi[2], Se-Na Kim[2], Jin-Sik Nam[3], [1]Department of Food analysis, Korea Food Research Institute, Gyeonggi, 13539, Korea, [2]Functional Food & Nutrition Division, National Academy of Agricultural Science, RDA, Jeonju, 04535, Korea, [3]Department of Food & Nutrition, Suwon Women's University, Gyeonggi, 18333, Korea. E-mail: Hwangjbg@kfri.re.kr

PT.17

Single molecule real-time imaging of intracellular Mg^{2+} signaling and wave propagation in single cell with subdiffraction-limit resolution

Suresh Kumar Chakkarapani[a], Seungah Lee[b], and **Seong Ho Kang**[a,b,]*, [a]Department of Chemistry, Graduate School, Kyung Hee University, [b]Department of Applied Chemistry, College of Applied Science, Kyung Hee University. E-mail: shkang@khu.ac.kr

PT.18

Novel detecting method of synthetic organic dyes by dual non-aqueous capillary electrophoresis

Moonhee Park[a], Seung-Hoon Bahang[b], Seong Ho Kang[a,c,]*, [a]Department of Chemistry, Graduate School, Kyung Hee University, [b]Criminal Investigation Command of MND, Seoul 140-701, Republic of Korea, [c]Department of Applied Chemistry, College of Applied Science, Kyung Hee University, E-mail: moonhee@khu.ac.kr

PT.19

Biomolecular quantification in axial nanoscale of plasmonic particle on nanoisland

Seungah Lee[a], Sujin Ahn[b], **Seong Ho Kang**[a,b,]*
[a]Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea, [b]Department of Chemistry, Graduate School, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea. E-mail: shkang@khu.ac.kr

PT.20

Time-Series Variation of Atmospheric Radon-222 Concentrations at Gosan Site in Jeju Island of Korea during 2012-2014

Jung-Min Song[1], Jun-Oh Bu[1], Won-Hyung Kim[1], Chang-Hee Kang[1]*, S. Chambers[2], [1]Division of Chemistry and Cosmetics, Jeju National University, Jeju 690-756, Korea, [2]Australian Nuclear Science and Technology Organisation, NSW 2232, Australia. E-mail: changhee@jejunu.ac.kr

PT.21

Effect of Asian Dust Storms on Atmospheric Aerosol Compositions in Background Site of Korea during 2012-2014

Jun-Oh Bu[1], Jung-Min Song[1], Jae-Yun Lee[1], Jong-Heon Han[1], Chang-Hee Kang[1]*, [1]Division of Chemistry and Cosmetics, Jeju National University, Jeju 690-756, Korea. E-mail: changhee@jejunu.ac.kr

PT.22

Verification of Applicability of the Validated Analytical Method with a Liquid Chromatography-Tandem Mass Spectrometry for Steroids Residues Screening in Food Products

Hwa-Mi Lee*, JaeHyun Kim, WooJin Jeon, SooJin Bang, SungMin Woo, JuYeun Lee, EunJoo Koo, JyongEun Myung, HyunUk Kim, EunYoung Lee, Soo Jung Hu, Young-Mi Jang, Chul Joo Lim, Center for Food & Drug Analysis, Gyeongin Regional Food and Drug Administration, 137, Juan-Ro, Nam-Gu, Incheon-City, 402-835, Republic of Korea. E-mail: lhm9904@gmail.com

PT.23

Method development for determination of heavy metals in turmeric powder using ICP-MS

Chang-Hee Lee, Yeon Kim, Myung-Ja Lee, Bock-Kyu Lim, Ki-Hyun Kim, Yeong-Hyeon Kim,Tae-Yong Cho, **Jae-Young Shim***, Center for Food & Drug Analysis, Busan Regional Korea Food and Drug Administration, Busan, Republic of Korea E-mail: shilvi0321@gmail.com

PT.24

Effect of Different Biomass on Value-added Products in Bio-liquid of Food Waste via Hydrothermal Carbonization

Soomi Park[1], Jonathan Lee[2], Yura Hwang[1], Soyoung Lee[1], Sunyoung Bae[1]*

Department of Chemistry, Seoul Women's University Nowon-Gu, Hwarangro, Seoul, Korea, 13[1], Davidson College 405 North Main Street, Davidson, NC 28035[2]. E-mail: sbae@swu.ac.kr

PT.25

Analysis of Polycyclic Aromatic Hydrocarbons in Water by Polyaniline Coated In-needle Microextraction

Yura Hwang, Dong-Sun Lee, Sunyoung Bae* Department of Chemistry, Seoul Women's University, Nowon-Gu, Hwarangro, Seoul, Korea. E-mail: sbae@swu.ac.kr

PT.26

TNF-α-induced insulin resistance mechanism study based on cell lysis-free quantum dot multicolor cellular imaging-based

Jieun Ki and Joon Myong Song*, College of Pharmacy, Seoul National University, Seoul 151-742, South Korea. E-mail: jmsong@snu.ac.kr

PT.27

Real time high-content cellular monitoring of the cytotoxic action of cationic polymer carriers polyethylenimine and poly-L-lysine on HepG2 cells

Gee Woo Nam and Joon Myong Song*, College of Pharmacy, Seoul National University, Seoul 151-742, South Korea. E-mail: jmsong@snu.ac.kr

PT.28

Multifunctional Composite of an Antibacterial Silver and a Potent Wound Healing Polypeptide as a Bimodal Wound Treatment

Baskaran Purushothaman and Joon Myong Song*, College of Pharmacy, Seoul National University, Seoul 151-742, South Korea. E-mail: jmsong@snu.ac.kr

PT.29

Concurrent monitoring of CD31, CD34, CD45 and CD146 endothelial progenitor cell markers for acute myocardial Infarction

Hee Ju and Joon Myong Song*, College of Pharmacy, Seoul National University, Seoul 151-742, South Korea. E-mail: jmsong@snu.ac.kr

PT.30

Optimization of Chlorophenols Detection in Water Samples using Stir bar Sorptive Extraction Coupled with Thermal Desorption-GC-MS

Mina Lee, **Yun S. KIM***, Water Quality Reserch Centre, K-water Institute, K-water, Korea. E-mail: yunskim@kwater.or.kr

PT.31

Validation of Analytical Method for Propylene Glycol and Ethylene Glycol in Foods

Ho Soo Lim, Ju Young Hwang, EunA Choi, Gun young Lee and Tae Seok Kang, Food

Additives and Packaging Division, Ministry of Food and Drug Safety, Cheongju-si, chungcheongbuk-do, Korea. E-mail: hslim70@korea.kr

PT.32

Dielectric Barrier Discharge Molecular Emission Spectrometer as Gas Chromatographic Detector for Amines

Chenghui Li [a], Xue Jiang[a], Xiandeng Hou[a,b*], [a]Department of Chemistry, Sichuan University, Chengdu, 610064, China, [b]Analytical & Testing Center, Sichuan University, Chengdu, 610064, China E-mail: houxd@scu.edu.cn

PT.33

Aptamer-bound magnetic beads and antibiotics functionalized fluorescent gold nanoclusters based dual recognition strategy for detection of bacteria

Dan Cheng, Mengqun Yu, Gan Li, Zheguo Zhu, Yang Song, **Erqun Song***, Key Laboratory of Luminescence and Real-Time Analytical Chemistry, Ministry of Education, College of Pharmaceutical Sciences, Southwest University, Chongqing, 400715, People's Republic of China. Fax: +862368251225; Tel: +862368251225. E-mail: eqsong@swu.edu.cn

PT.34

Determination of the fatty acid compositions offal meat of sheep produced in Mongolia using GC and GC-MS

G.Oyun[1], D.Narantuya[1], E.Anudari[1], D. Seo[2], **J. Ha** [2,3*], [1]Scientific food research and manufacturing "SAMO" Institute, Ulaanbaatar, Mongolia, [2] Food Analysis Center, Korea Food Research Institute, [3] Korea University of Science and Technology. E-mail: jhkfri@gmail.com

PL.01

Study of DNA/Small Molecule Interaction by Dual Polarization Interferometry

Xiurong Yang

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, xryang @ciac.ac.cn

Abstract: Dual polarization interferometry (DPI) has been developed to give accurate information of layer mass, refractive index (RI) and thickness. These facilities to reveal structural information about the biomolecular interactions taking place as the packing (from the RI) and molecule dimension (from the thickness) change, and typically give a link between a molecule's structure and its function. Functional oligonucleotides have gained many interests owing to their specific recognition ability to analytes. The study of DNA/small molecule interaction is very valuable for probing the mechanism of the interaction and establishing convenient methods to effectively understanding the functions of the small molecules.

DPI technique was used in our group to probe the interaction of deferent biosystems,[1,2,3,4,5,6] for example, the interaction of coralyne with 48-mer homoadenine oligonucleotide (polyA$_{48}$), silver ions with cytosine (C)-rich ssDNA oligonucleotides, Hg^{2+} with 21-mer thymine-rich oligonucleotide (MSO) and so on. Kinetic, thermodynamic and structural information of these interaction processes were characterized in detail. Using the binding curves from changes in mass, the association rate constant (k_a), the dissociation rate constant (k_d) and the association constant (K_a) between coralyne-polyA$_{48,}$ silver ions - cytosine (C)-rich ssDNA oligonucleotides and Hg^{2+}-MSO were calculated, respectively. Simultaneously, we constructed biosensors for respective selective detection of coralyne, cytosine, Ag+ and Hg^{2+} and so on. The selectivity of the biosensor over the other corresponding substances was confirmed.

It is expected that the biosensing strategy will be extended for biosensing of other various analytes by using other different functional oligonucleotides (aptamers or DNAzymes), simultaneously investigate the interaction between them and reveal the structral characteristics of functional DNA with and without targets.

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Keywords: Dual polarization interferometry, Biomolecole interaction, Biosensor

***Reference**:*

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Biography of the author.

Xiurong Yang: PhD, Professor, Academician of CAS State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences China E-mail: xryang @ciac.ac.cn	

Xiurong Yang is currently a professor in the State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. She received her B. S. from the University of Science and Technology of China (USTC), and Ph.D. Degree from Lund University, Sweden. She had been the Post Doctoral Research Fellow at the University of New Orleans and the University of Hawaii at Manoa, USA (1992-1995). She had been the Visiting Assistant Professor at the Hong Kong University of Sciences and Technology, Hong Kong, China (1995-1997), and the Visiting Professor in the University of Perpignan, France (2007). She had been the Director of the State Key Laboratory of Electroanalytical Chemistry and its precursor (1998 - 2009). She is now the editor in chief of Chinese J. Analytical Chemistry, and the Chair Person of the Analytical Chemistry Committee, Chinese Chemical Society. Her research interests are nanoelectrochemistry, biomolecular recognision and interaction and so on.

PL.02

Inkjet-printed analytical devices made from paper

Daniel Citterio* and Koji Suzuki
Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, 223-8522 Yokohama, Japan

Abstract: Analytical devices made from paper are increasingly drawing attention, in particular in the context of clinical diagnostics, environmental monitoring and workplace condition surveillance. Since the first publication in the field by Whitesides and coworkers in 2007,[1] research activities have grown tremendously. A common feature of all paper-based analytical devices (PADs) is the perspective to have low-cost, portable and user-friendly alternatives to the common large-scale analytical systems requiring a high level of infrastructure and technically trained operators.

The primary reasons for choosing paper as the base material of PADs are its low cost, abundant availability and easiness of disposal. But at the same time, the physical-chemical properties of paper make it a versatile functional material with characteristics not so straightforwardly achieved with more presumably “high-tech” materials. The two most important properties are the autonomous pump-free sample transport due to capillary forces in the porous paper structure in the context of microfluidic paper-based analytical devices (μPADs), and the large surface-to-volume ratio allowing for the immobilization and dry storage of assay reagents.

The use of inkjet technology is no longer limited to classical office printing applications. It enables the rapid, reproducible and contactless dispensing of picoliter order liquid droplets at defined spots on a variety of surfaces. In this way, it is suitable for the deposition of a wide range of materials required for (bio)chemical assays.[2] Furthermore, by directly enabling the transfer of electronically stored information from a computer to a paper surface, inkjet printing allows the fabrication of microfluidically-patterned surfaces with great flexibility in pattern design, without the need to use masks. The total number of required process steps is reduced, and as a further advantage, all steps can be performed using an inkjet printer. As a consequence, inkjet printing has become a popular tool in the development and fabrication of paper-based analytical devices.[3]

Since 2008, our research group is focusing on the application of inkjet printing technology for the development of paper-based (bio)analytical devices.[4-9] We have been the first to demonstrate how an inkjet printing system can be used for both the microfluidic patterning of paper surfaces and the deposition of assay reagents to obtain μPADs.[4, 5] Later on, we have developed an alternative inkjet-based patterning approach for

paper substrates relying on a solvent-free UV-light curable hydrophobic monomer composition, which is not only more environmentally friendly compared to our previous method, but more importantly, which can be printed from the most simple unmodified desktop inkjet printer.[6] This technology has more recently been applied to the fabrication of a µPAD for the determination of the glycoprotein lactoferrin in human tear fluid samples, where the detection mechanism relies on the sensitization of terbium(III) fluorescence upon binding of the cation used as the indicator to the metal-ion binding site of the protein.[7, 8] The accuracy of the developed µPAD has been evaluated by comparing the analysis results of human tear samples with the conventional enzyme-linked immunosorbent assay (ELISA) method and a good correlation between the two analytical methods has been confirmed. Compared to the ELISA approach, the strengths of the µPAD assay have been demonstrated in terms of simplicity, speed and cost.

We have also demonstrated that the combination of inkjet printing and paper is also suitable for the fabrication of non-microfluidic systems. A colorimetric sensor array for the discrimination of volatile amines has been developed by combining two simple functional elements: (1) a single chromogenic sensing dye with selectivity for amines in general, encapsulated into (2) polymer nanoparticles of different polarities. Printing of 6 types of inks incorporating the two dye encapsulating nanoparticles of different polarity in different mixture ratios onto plain copy paper resulted in a colorimetric sensor array with a polarity gradient. This array indicated high discrimination ability for 7 volatile amines with good selectivity.[9]

This lecture will give a short overview of our developments targeting inkjet-printed analytical devices made from paper. Some general approaches as well as specific challenges and potential solutions for inkjet-printable “chemical sensing inks” will be shown.

***Keywords**:* microfluidic device, colorimetric analysis, (bio)chemical sensor

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Introduction to the author:

Professor Dr. Daniel Citterio
Department of Applied Chemistry, Keio University, Yokohama, Japan
Tel/Fax: +81-45-566-1568.
E-mail: citterio@applc.keio.ac.jp

Biography of the authors.

Daniel Citterio received his Doctor of Natural Sciences degree in 1998 from the Swiss Federal Institute of Technology (ETH) in Zurich. After postdoctoral research at Keio University in the group of Prof. Dr. Koji Suzuki, he became a Research Associate at ETH in 2002. Following post-graduate studies and work at Ciba Specialty Chemicals, he returned to Keio University in 2006, where he became a tenured Associate Professor in 2009 and full Professor in Analytical Chemistry in 2014. His research interests are the development of low-cost analytical devices and the development of functional molecules for (bio)chemical sensing.

Koji Suzuki received his PhD degree in 1982 from Keio University. He became a faculty member as a Research Associate in 1982, Assistant Professor in 1988, Associate Professor in 1993, and full Professor in 1998. From 1990 – 1992, he was a Guest Professor at the Swiss Federal Institute of Technology (ETH), Zurich. He served as the Vice President of JSAC for 2011 – 2013 and as President since 2015. His research focuses on chemical and biochemical sensors based on functional molecule creation.

PL.03

Determination of trans fatty acids in daily consumed foods using a silver ion cartridge solid phase extraction method coupled with GCxGC-TOFMS

Dongwon Seo [1], Jaeho Ha [1,2*]

[1] Food Analysis Center, Korea Food Research Institute
[2] Korea University of Science and Technology

Abstract: This study aimed to develop an analytical method for accurately estimating the ratio of vaccenic to elaidic acid (V/E value). To estimate an accurate V/E value, a silver ion cartridge (SIC) solid phase extraction (SPE) method was performed for removing *cis*-fatty acids. The removal efficiency of *cis*-fatty acids was greater than 97.8%. However, the analytical values of total *trans*-fatty acids (TFAs) were not significantly different between with SIC SPE method and without SIC SPE method. Comparison tests of the V/E values produced by two different methods (without SIC SPE method and with SIC SPE method) using comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GC × GC-TOFMS) were also carried out. Those two methods exhibited significant differences in the estimated V/E values because removing *cis*-fatty acids affected the V/E value but did not affect the total TFAs. The SIC SPE method coupled with GC × GC-TOFMS suggested in this research is available to estimate accurate V/E values in commonly consumed foods, such as margarines, milk products and beef tallow.

Keywords*:* Elaidic acid, Vaccenic acid, Silver ion cartridge, GC × GC-TOFMS

Reference*:*

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Introduction to the author:

Professor Dr. Jaeho HA

Food Analysis Center, Korea Food Research Institute, 463-746, Korea
Tel: +82-31-780-9217; Fax: +82-31-780-9280.
E-mail: jhkfri@gmail.com

Biography of the authors.

Dr Jaeho Ha completed his doctorate in food chemistry with the practical combination of mass spectrometry and gas chromatography at the Korea University in 1992. He joined the Food Analysis Center at Korea Food Research Institute in 1984, where he involved himself in the analysis of food components, including micotoxin, pesticides, nutrients, fatty acid and aromas. Dr. Ha served his vice-presidency of Korean Society of Analytical Science 2000 – present. He is currently the vice president of Korea Food Research Institute and a leader of food analysis division of Korea Society of Food Science and Technology. Concurrently, Dr. Ha is applying GCxGC-TOFMS technology coupled with stir bar sorptive extraction and dynamic headspace sampling techniques for the analysis of flavors and trans fatty acids in foods. His research and activity is focused on chromatographic separation, flavor chemistry, food analysis.

PL.04

Generation of Droplets of Liquid for Mass Spectrometry

Jin-Ming Lin[1], Chen Luo[1], Yangdong Zhang[1], Fengming Chen[1,2], Katsumi Uchiyama[2]

[1]Department of Chemistry, Tsinghua University, Beijing 100084, China
[2] Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Minamiohsawa, Hachioji, Tokyo 192-0364, Japan
E-mail: jmlin@mail.tsinghua.edu.cn

Abstract: In this work, a paper spray mass spectrometry combined with droplets generated by gravity and electrostatic attraction, microfluidic chip, and inkjet methods, was developed. The qualitative and quantitative analytical performances of this technique for single droplet were demonstrated. This manually controlled interface is straightforward, low-cost and simple to implement. Moreover, paper spray ionization mass spectrometry hold promises in direct analysis of real biological/chemical microreaction samples because of its tolerance with complex matrix. As a proof-of-concept example, the droplet-based acetylcholine hydrolysis was carried out to demonstrate the validation of our method for direct analysis of micro-chemical/biological reactions. A module for cell culture was integrated to investigate cell metabolism by online microfluidic chip-MS, employing lactate efflux as a model. Three aspects were focused: real-time monitoring of the cellular metabolites, differential effects of a drug on cells of different types, and the dose-response information of a drug. The potential of this platform in cell analysis was exhibited.

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***Keywords**:* Droplets, Mass spectrometry, Paper spray ionization

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Biography of the author.

Jin-Ming Lin, PhD, FRSC
Cheung Kung Scholars Professor
Department of Chemistry
Tsinghua University
China
E-mail: jmlin@mail.tsinghua.edu.cn
Website: http://www.linlab-tsinghua-edu.org

Professor Dr. Jin-Ming Lin was graduated from Fuzhou University in 1984 and received a PhD at Tokyo Metropolitan University in 1997. He had studied and worked in Showa University and Tokyo Metropolitan University during 1992-2002. He was selected as “100 Talented Researcher Program” for Chinese Academy of Sciences at 2001 and worked in Research Center for Eco-Environmental Sciences, Chinese Academy of Science during 2002-2004. He is currently a professor of Tsinghua University since 2004. He is a General-in-Secretary *of* the Committee of Mass Spectrometry, *a Fellow of Royal Society of Chemistry, a member of council of Chinese Society for Chromatography Science, and service as Contributing Editor of Trends in Analytical Chemistry, Associate Editor of Journal of Pharmaceutical Analysis, and Associate Editor of Current Analytical Chemistry,* Editorial Boards for Talanta, Toxicological and Environmental Chemistry, Luminescence, Chinese Chemical Letters, Science China Chemistry. He received more than 20 awards for his contributions in microfluidics, chemiluminescence and separation science. He is the author and co-author of 358 original research papers published in international journals, 28 reviews, 4 books and 41 patents.

His current research is focused on microfluidic device for cell analysis, ultra weak chemiluminescence, and sample pretreatment for LC-MS and GC-MS.

KL.01

Gold-containing Nanocarriers/Nanocomposites for Anti-bacterial Applications

Bo Hu, Ning Wang, Ming-Li Chen, Xu-Wei Chen, Jian-Hua Wang*

Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China

It is known that gold nanorods (Au NRs) are generally capsules with anisotropic structure. Au NRs and their composites have been demonstrated to exhibit superb anti-bacterial effects. Thus, we report herein the development of gold nanorods or gold-silver nanocomposites for anti-bacterial applications and controlled drug release.

We constructed a hybrid bactericidal material, i.e., gold nanorods covered kanamycin-loaded hollow-SiO_2 ($HSKAu_{rod}$) nanocapsules. The hybrid combines the features of chemical drug and photo-thermal physical sterilization. Hollow-SiO_2 nanocapsules are used as carrier for drug delivery. The nanocapsules load kanamycin and are covered with gold nanorods to avoid drug leakage and realize photo-thermal treatment. The sterilizing effect to bacterial strain is investigated with *E. coli* BL21 under irradiation of near-infrared light (NIR) for 20 min. A sterilizing rate of 53.47% is achieved for the $HSKAu_{rod}$ nanocapsules with respect to a net sum sterilizing rate of 34.49% for the individual components in the $HSKAu_{rod}$ nanocapsules, e.g., carrier nanocapsules, chemical sterilization of kanamycin and physical sterilization due to the gold nanorods under NIR irradiation.

A novel bactericidal material, e.g., rod-shaped core-shell-shell Au-Ag-Au nanorods, is constructed as a nanoheater in the NIR region. The outer Au shell melts under laser irradiation and results in exposure of the inner Ag shell facilitating controlled release of the antibacterial Ag shell/layer. This offers the Au-Ag-Au nanorods a favorable bactericidal ability by combining the features of physical photothermal ablation sterilization of the outer Au shell and the antibacterial effect of the inner Ag shell to the surrounding bacteria. The sterilizing ability of Au-Ag-Au nanorods is investigated with *E. coli* O157:H7. Under low-power NIR laser irradiation (785 nm, 50 mW cm^{-2}), the Au-Ag-Au nanoheater exhibits higher photothermal conversion efficiency with respect to that for the Au-Ag nanorods. Meanwhile, a much improved stability with respect to Au-Ag nanorods is observed, i.e., a 16 days successive monitoring reveals virtually no change for the UV-vis spectrum of Au-Ag-Au nanorods. At a dosage of 10 μg mL^{-1}, a killing rate of

100% is reached for the *E. coli* O157:H7 cells under a 20-min irradiation. The bimetallic core-shell-shell nanorods provide a favorable nanoheater for *in vivo* biomedical applications.

The Au-Ag-Au nanorods have been further used for bacteria capture, separation and sterilization (killing). For this purpose, positively charged magnetic reduced graphene oxide with modification by PEI (rGO-Fe_3O_4-PEI) is prepared and then loaded with core-shell-shell Au-Ag-Au nanorods to construct a nanohybrid rGO-Fe_3O_4-Au-Ag-Au. NIR laser irradiation melts the outer Au shell and exposes the inner Ag shell facilitating controlled release of the silver shell. The nanohybrids combine physical photothermal sterilization due to the outer Au shell and antibacterial effect of the inner Ag shell. In addition, the nanohybrid exhibits high heat-conductivity due to rGO and rapid magnetic separation capability attributed to Fe_3O_4. It provides a significant improvement on bactericidal efficiency with respect to bare Au-Ag-Au nanorods and facilitates the isolation of bacteria from sample matrixes. 25 μg mL^{-1} of nanohybird causes a 100% capture and separation of *E. coli* O157:H7 (1×10^8 cfu mL^{-1}) from aqueous medium in 10 min. Meanwhile it causes a 22^{o}C temperature rise for the surrounding solution under NIR irradiation (785 nm/50 mW cm^{-2}) for 10 min. With magnetic separation, 30 μg mL^{-1} of nanohybrid results in 100% killing rate for *E. coli* O157:H7 cells. The facile bacteria separation and photothermal sterilization is potentially feasible for environmental and/or clinical treatment.

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***Introduction to the author**:*

Professor Dr. Jian-Hua Wang
Research Center for Analytical Sciences, Box332, Northeastern University, Shenyang 110819, China
Tel: +86-24-83688944; Fax: +86-24-83676698.
E-mail: jianhuajrz@mail.neu.edu.cn

Professor Jian-Hua Wang was born in 1962 in Shandong, China. He obtained his B.Sc from Department of Chemistry, Nankai University, and M.Sc from Jilin University, China. He was awarded a PhD degree by Technical University of Denmark. He has been an Associate Editor for TALANTA since Dec. 2004. He was a member of International Advisory Board for Journal of Analytical Atomic Spectrometry (2006-2010).

His current research interest is focused on the exploitation of flow analysis protocols and hyphenation techniques, isolation of trace level of analytes (metals and biomacromolecules) from complex sample matrices and life science analysis.

KL.02

The synthesis of fluorescent graphitic carbon nitride nanomaterials and their application in fluorescence sensing

Xi Chen[1,2]*, Mingcong Rong[1], Yiru Wang[1]

1. Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
2. State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China
Corresponding author email: xichen@xmu.edu.cn

Abstract:

Graphitic carbon nitride (g-C_3N_4) is a typical metal-free polymeric semiconductor, which received a lot of attention due to its special structure and properties.[1]Since its discovery, it has been widely used in the fields of sensing, bioimaging, peroxidase-like catalysis and phtoelectrocatalysis.[2] In recent years, rise with the development of carbon-based nanomaterials, nanoscale g-C_3N_4 materials, such as fluorescent g-C_3N_4 nanosheets and g-C_3N_4 nanodots, have drawn much attention because of their excellent optical and physicochemical features. The bulk g-C_3N_4 is usually obtained by high-temperature pyrolysis of small organic molecules with high content nitrogen, including melamine, cyanamide, dicyandiamide, urea and so on. There are two ways to get nanoscale g-C_3N_4. One is the up-to-down method, which include liquid phase exfoliation and chemical oxidation and hydrothermal etching of bulk g-C_3N_4. Another is the down-to-up method, which contains hydrothermal pyrolysis and microwave of organic molecules with high content nitrogen to form the s-triazine or tri-s-triazine structure of g-C_3N_4. The unique property of nanoscale g-$C_3N_4$and their potential application in fluorescence sensing also aroused our interest.

With the chemically oxidized and liquid exfoliatedg-C_3N_4 nanosheets, firstly, we developed a facile and effective fluorescence “on–off” sensing approach for the label-free selective detection of Cr(VI) based on the inner filter effect and a fluorescence “on–off–on” strategy for the determination of AA via the oxidation–reduction between Cr(VI) and AA. The developed approach provided a wide linear range of 0.6 to 300 μM for Cr(VI) and 0.5 to 200 μM for AA, with a low detection limit of 0.15 and 0.13 μM for Cr(VI) and AA.[3] Secondly, using g-C_3N_4nanosheets, we investigated their application in the determination of 2,4,6-trinitrophenol (TNP). The strong inner filter effect and molecular interactions (electrostatic, π−π,and hydrogen bonding interactions) between TNP and the g-C_3N_4nanosheets led to the fluorescence quenching of the g-C_3N_4nanosheets with efficient selectivity and sensitivity. Under optimal conditions, a detection limit of 8.2 nM was obtained.[4] The relative low quantum yield (no more than 30%) and large size (commonly 70 to 160 nm) of mostly g-C_3N_4 nanosheets are always big problems that limit their applications in imaging. By chemical oxidation and hydrothermal etching of bulk P-g-C_3N_4 obtained via pyrolysis of phytic acid and melamine, we synthesis a highly fluorescent phosphorus-doped graphitic carbon nitride nanodots (P-g-C_3N_4 nanodots). The P-g-C_3N_4 nanodots emitted strong blue fluorescence and displayed highly fluorescent responses towards Cu^{2+} by photo induced electron transfer. Under optimal conditions, a rapid detection of Cu^{2+} could be completed in 5 min with a detection limit of 2 nM, and a linearity ranging from 0 to 1 μM. Meanwhile, using acetylthiocholine as the substrate, the P-g-C_3N_4 nanodots-Cu^{2+} system could sensitively detect acetylcholinesterase through the reaction between Cu^{2+} and thiocholine, the hydrolysis product of ATCh by AChE. A linearity ranging from 0.01 to 3 mU/mL could be obtained with a detection limit of 0.01 mU/mL.

Key words: graphitic carbon nitride (g-C_3N_4); fluorescence detection; 2,4,6-trinitrophenol (TNP); Cr(VI); AA; P-g-C_3N_4 nanodots; AChE

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Professor Xi Chen

Prof. Dr. Xi Chen
Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering
Xiamen University
Xiamen 361005, China
===
Tel/Fax: +86(592) 2184530
E-mail: xichen@xmu.edu.cn

Dr. Xi Chen graduated from Fuzhou University with a Bachelor’s degree of analytical chemistry, and then obtained his Master’s degree there. Later in 1991, awarded the Monbusho Scholarship from Japanese government, he entered Kyoto Institute of Technology and received his Ph.D degree four years later. Between the year of 1996 and 1998, he performed as a postdoctoral researcher at Xiamen University, sooner after which, he was promoted as an associate professor at the department of chemistry. In 2003, he was promoted to be a full professor. He got the financial support from Japanese Society for the Promotion of Science (JSPS) to collaborate with Prof. M. Oyama, Kyoto University, in 2004 and 2009. Dr. Chen has taken charge of projects as National High Technical Development Project (863 Project) Foundation in the field of ocean, National Scientific Foundation of China and Key Project of Fujian Scientific Foundations, He was honored the Outstanding Contribution Award in 2002, and received the 1st class Scientific Progress Prize of Fujian province in 2005. His research interests cover electrochemical analysis using graphene materials, chemo/biosensors and pre-extraction materials applied in GC/HPLC. He has published over 160 scientific research articles in archival scientific journals, including *Angew. Chem. Int. Ed.*, *J. Am. Chem. Soc.* and *Anal. Chem.*

KL.03

Simultaneous and selective determination of inorganic nitrogen species in seawater samples

Kazuaki Ito[1]

[1]Department of Biotechnology and Chemistry, Faculty of Engineering, Kinki University, 1 Umenobe, Takaya, Higashi-Hiroshima, 739-2116, JAPAN

Abstract: Inorganic nitrogen compounds (ammonium, nitrite, and nitrate ions) are important measurement items because the ions are related to the phenomena such as eutrophication in water environment. Thus, a number of measurement methods have been examined for the determination of the ions. However, the determination by conventional measurement system is interfered by excess of matrix ions in seawater. In this study, determination of ammonium ions in seawater samples was examined by indophenol blue reaction method and OPA method. And, the system optimized for ammonium detection was incorporated as post column reaction system on ion chromatography (IC): Nitrite and nitrate ions were separated on ODS column equilibrated with DDAB (dilauryldimethylammonium bromide) or anion exchange column and were detected by UV method. The optimization of total system was examined for the determination of inorganic nitrogen species in seawater and the method obtained was applied to real samples.

Keywords : ion chromatography; post-column reaction; nitrite, nitrate, and ammonium ions; seawater.

Introduction to the author:

Professor Dr. Kazuaki Ito
Department of Biotechnology and Chemistry, Faculty of Engineering, Kinki University, Higashi-Hiroshima 739-2116, Japan
Tel: +81-82-434-7000; Fax: +81-434-7890. E-mail: itok@hiro.kindai.ac.jp

Biography of the author.
Kazuaki Ito, Research interest, ion chromatography for trace ions/ components in various samples.

KL.04

Sputtered nanocarbon film electrodes for bioelectroanalysis

Dai Kato* and Osamu Niwa

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

Abstract:

We have been studying nanocarbon film electrodes formed by an electron cyclotron resonance (ECR) sputtering or an unbalanced magnetron (UBM) sputtering method.1) The film provides a nanocrystalline sp^2 and sp^3 mixed bond structure with an atomically flat surface (surface roughness of 0.05 – 0.1 nm) and high conductivity (20-38 S/cm) without doping. The film electrode has excellent properties including a low background current, a wide electrochemical potential window, and little surface fouling, while maintaining relatively high electrode activity for various biomolecules.2) These characteristics allow the detection of biomolecules, especially ultratrace amount of biomolecules such as all the DNA bases, gliotransmitters, and lipopolysaccharide (LPS), which are difficult to measure at the conventional carbon electrodes. For example, this film electrode can measure all DNA bases (including DNA base derivatives e.g., 5'-methylcytosine and 8'-hydroxy 2'-deoxyguanosine) more quantitatively than conventional carbon-based electrodes.3) We used this film to develop a simple DNA methylation analysis technique. Our methylation detection technique measures the differences between the oxidation currents of both 5-methylcytosine and cytosine without needs for conventional bisulfite reaction or labeling process.

Moreover, due to their good electrochemical stability and low background current, the nanocarbon film electrode is suitable for long-term analysis including as the electrode of an HPLC detector for detecting cerebral gliotransmitter (kynurenic acid) from glial cells.4) It is recognized that the glial cells plays an important role in gliotransmission (chemical signal), different from neurotransmission (electric signal). It is recently found that kynurenic acid is increasing in epilepsy patients but its concentration is quite low (nM). Our electrode enabled to quantitatively determine cerebral kynurenic acid by direct oxidation (LOD=20 pM). Our film electrodes therefore contribute for pharmacological evaluation of new candidate drug for antiepilepsy.

Recently, we developed an electrochemical lipopolysaccharides (LPS) detection system using the nanocarbon film electrode because the atomically flat surface of the nanocarbon film electrode can be expected to achieve electrochemical measurement of LPS with low concentration (pg/mL-ng/mL). We achieved superior quantitative performance for LPS determination in terms of the low detection limit (LOD=0.2 ng/mL) by using LPS affinity probe consisting zinc-complex, which was superior result to our previous reports.5)

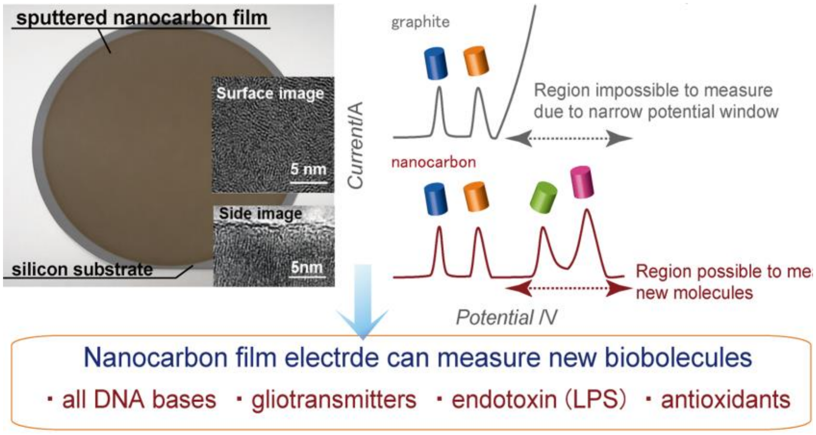

Figure 1. Sputtered nanocarbon film electrodes for bioelectroanalysis.

***Keywords**:* Nanocarbon film; lipopolysaccharide (LPS); gliotransmitter; DNA bases

***Reference**:*

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***Introduction to the author**:*

Dr. Dai Kato
Biomedical Research Institute, AIST, Japan.
Tel: +81-29-861-16158; Fax: +81-29-861-16177.
E-mail: dai.kato@aist.go.jp

Biography of the authors. Dai Kato received his PhD degree in polymer chemistry from Kumamoto University in 2003. He is a researcher in AIST. His research interests are in the borderline field between material sciences and analytical chemistry.

KL.05

Odor variation on the car air conditioning evaporator according to the feeding nutrients

Man-Goo Kim*, Young-Jae Ryu

Dept. of Environmental Science, College of Natural Science, Kangwon National University, Kangwon, 200-701, Korea,

Abstract: Odor and VOC have much attention in recent years because of their impact on car interior air quality. As to JD power, the consumer satisfaction included the odor item in the evaluation of car initial quality study. The odor source is abundant in a car interior but the air conditioner is the most important source. Automotive air conditioning (HVAC) system generates an intense odor when it turn on and/or off. One of the major mechanism of odor generation is a metabolism of microorganisms on the surface of the evaporator.

In this study, odor variation of HVAC evaporators were investigated according to feeding low concentration of nutrients as like rain and leather car seat extracted water. DI water is used as the control nutrient. Each evaporators were supplied each nutrient water three times a day. During the 12 weeks, each evaporator were tested and compared of odor intensities a day and the bench test were one time a week.

Odor intensity was measured by using human olfaction and odor caused components were analyzed GC/olfactometer.

The odor intensity of evaporator sprayed DI water was decreased but that of sprayed leather extracted water was increased, which explains that a variability of HVAC evaporator odor according to feeding nutrients.

Some of odor caused compounds detected old HVAC evaporator were reproduced in the evaporator of sprayed leather extracted water.

The odor generating mechanism in the HVAC system will be discussed

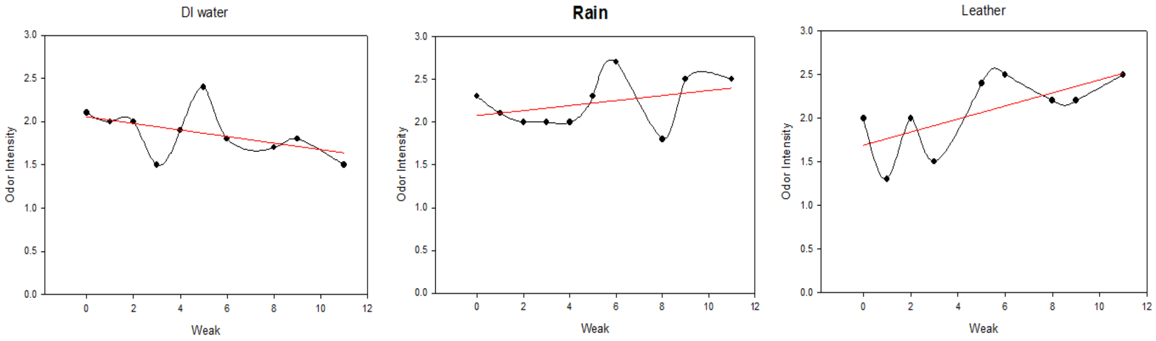

Fig. variation of odor intensity according to feeding nutrients in evaporators of automotive HVAC system during 12 weeks. (a)DI water, (b) rain and (c) Leather car seat extracted water

***Keywords**:* odor, air conditioning, car interior, nutrient,

***Reference**:*

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***Introduction to the author**:*

Professor Dr. Man-Goo Kim
Department of Environmental Science, Kangwon National University, Kangwon, Korea
Tel: +82-33-250-8576; Fax: +82-33-259-5670.
E-mail: mgkim@kangwon.ac.kr

***Biography of the authors**:*

Research interesting

Car cabin interior air quality
Emission of hazardous organics from building materials
Evaluation of Odor active compounds in products

Academic Experience

April 1986 *-Mar. 1989*	**Keio University**, Yokohama, Japan Doctor of Engineering, Dept. of Applied Chemistry, March 1989 Thesis: “Studies on analytical methods and behavior of micro organic compounds in urban suspended particulate matter”
Sept. 1991 *-Present*	**Kangwon National University**, Kangwon, Korea Assistant Professor, Associate Professor, Professor in Department of Environmental Science
April 1989 *-Sept. 1990*	**Keio University**, Yokohama, Japan Lecturer, Department of Applied chemistry

Social Experience

2008 ~ present	**Advisor**, Korean society of odor research and engineering
2004 ~ 2008	**Director**, Institute of Environmental Research, Kangwon National University
2005 ~ present	**Chairman**, Analytical division of ecolabelling of healthy building material, Korea air cleaning association
2013 ~ present	**Convenor**, ISO/TC 146/SC 6/WG 22
2015 ~ present	**Executive vice chairman**, The Korean Society of Analytical Science
2015 ~ Present	**Cochairman**, Foundation of Green Future

KL.06

Break diffraction-limited barrier with wavelength-modulation fluorescence-free nanoscopy

Peng Zhang[a], Seungah Lee[b], Seong Ho Kang[a,b,]*

[a]Department of Chemistry, Graduate School, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea
[b]Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea

Abstract: Wavelength-modulation based fluorescence-free nanoscopy was built to break the diffraction-limited barrier of optical resolution. This achievement was based on the fact that the diffraction-limited plasmonic nanoparticles could be selective detected by wavelength-modulation and the centers could be measured with precisions much better than the width of their intensity distributions. Diffraction-limited and color blended enhanced dark-field (EDF) images of neighboring gold nanoparticles (GNPs), gold nanorods (GNRs), and silver nanoparticles (SNPs) were modulated at their specific localized surface plasmon resonance (LSPR) wavelengths. The point spread functions of NPs were approximated as symmetric two-dimensional (2D) Gaussian functions and fitted with least-square algorithm to resolve the central coordinates (x, y). Due to the remarkable signal-to-noise ratio of EDF illustration system, the Cramér-Rao lower bound (CRLB) based localization precisions of GNPs, GNRs, and SNPs were measured as 2.5 nm, 5.0 nm, and 2.9 nm, respectively, which were much better than the width of their intensity distributions. Even considered the plasmonic coupling effect of particles, these localization precisions were high enough to achieve super-resolution images. Based on the corresponding localization precisions, the resolved coordinates were rendered with circularly symmetric Gaussian blobs and visualized in a reconstructed image. In addition, the rotation states of GNRs were resolved with polarizer to provide more precise information of particles. Finally, this novel method was applied in a live single cell and provided remarkable sub-diffraction limited images of NPs.

Keywords: super-resolution, fluorescence-free, wavelength-modulation

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***Introduction to the author*:**

Professor Dr. Seong Ho Kang
Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea
Tel: +82-31-201-3349; Fax: +82-31-201-2340
E-mail: shkang@khu.ac.kr

Biography of the authors.

Peng Zhang was born in Shandong, China. He received his B.E. degree from Qilu University of Technology in 2011. From 2012, he joined in Prof. Seong Ho Kang's lab, Department of Chemistry, Kyung Hee University, as a master and Ph.D. combined student. His current research focuses on single-molecule/particle detection and super-resolution microscopy.

Seungah Lee received her B.S., M.S., and Ph.D. degrees in chemistry from Chonbuk National University of Republic of Korea in 2003, 2006, and 2010, respectively. She is currently an Assistant Professor at Kyung Hee University. Her main research interests are chemical/biological analysis on biochip at single-molecule level using various detection systems.

Seong Ho Kang received his B.S. and M.S. degree in chemistry from Kyung Hee University of Republic of Korea in 1987 and 1989. He worked as a senior researcher at the research center of Hanil Pharmaceutical Co. (present, CJ Pharm. Co.) from 1989 to 1997. He received his Ph.D. degree in chemistry from the Seoul National University in 1998. He was a postdoctoral research associate scholar at Iowa State University and Ames Laboratory US Department of Energy with Dr. Edward S. Yeung from 1998 to 2000, a senior researcher at the SAIT (Samsung Advanced Institute of Science and Technology) in 2000-2002, and a professor of chemistry at Chonbuk National University in 2002-2010. He is currently a professor and department chairman at Kyung Hee University from 2010. His research interests include development of various analytical systems, methods, and techniques based on micro- and nano-separation, single-molecule/particle detection, super-resolution microscopy, micro- and nano-fluidics, and various nano-bio fusion technologies.

KL.07

Development of on-line SFE-SFC system and its application

Yuki Hashi*

Shimadzu (China) Co., Ltd.

Abstract: Sample pretreatment is always one of the key issues in a series of analytical procedures. Items such as efficiency of sample extraction, sample throughput, reproducibility, etc. are evaluated through the analytical validation. On-line sample pretreatment with an automated chromatographic system is often used for effective and reliable extraction and analysis. Previously we developed on-line pretreatment HPLC systems with the column switching techniques. The systems showed excellent performance for analysis of drugs in plasma,1) contaminants in food2) and environment.3) Supercritical fluid extraction (SFE) has been a commonly used substantial extraction technique and applied for extraction of bioactive compounds, drugs, lipids, and contaminants from natural products. SFE is also effective for metabolite analysis in dried blood spot.4) Compared with other extraction methods, SFE with supercritical carbon dioxide (SC-CO_2) has advantages such as low consumption of organic solvent and low toxicity. SC-CO_2 is also readily removed after use. Supercritical fluid chromatography (SFC) has the mutual advantages with SFE. Compared with HPLC, reduction of the viscosity of mobile phase and the improvement of the diffusion coefficient make better separation performance in SFC. For the enhancement of productivity and quality of analysis, we have developed an on-line SFE-SFC system. Devices like CO2 pump, SFE unit, BPR (back pressure regulator) were newly designed for the system. Mass spectrometers can be combined so that the system achieves the maximum performance. The system was evaluated through the applications such as residual pesticide analysis, dried blood spot analysis, and cleaning validation.

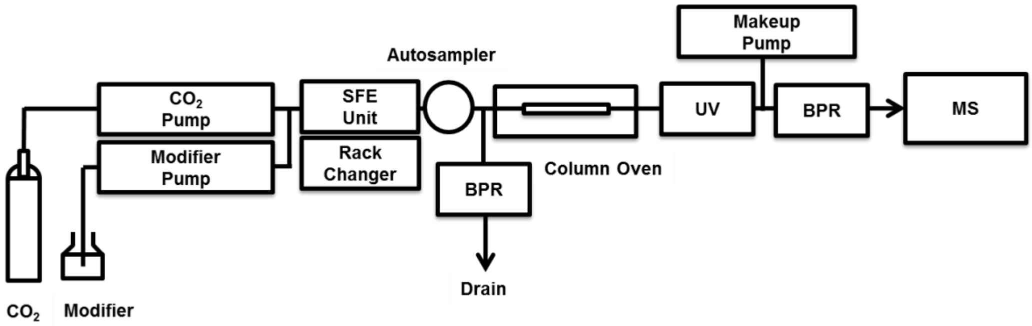

Fig. 1 On-line SFE-SFC-MS system

Keywords: supercritical fluid extraction, supercritical fluid chromatography, mass

spectrometry

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Introduction to the author:

Dr. Yuki Hashi
General Manager, Shimadzu Global COE for Applications & Technical Development, Shimadzu (China) Co., Ltd., China
Tel: +86-10-8525-2352; Fax: +86-10-8525-2330.
E-mail: y-hashi@shimadzu.co.jp

Biography of the author

Dr. Hashi graduated from Department of Chemistry, Osaka University, Osaka, Japan in 1986. At the same year, he joined Shimadzu Corporation, analytical instrument division to develop HPLC instruments especially electrochemical detector and column packing materials for protein analyses. In 1994, he moved to Shimadzu Singapore as an application manager for chromatography instruments to take care of the customers in South-East Asia as well as south Asia countries. His major area of interest is development of new application system using LC, GC, LC-MS, and GC-MS for the enhancement of analysis efficiency. Based on this research work, he has received Ph.D. degree from Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences in 2009. He is developing new analytical methods with chromatographic system extensively in the various fields such as food safety, environmental, pharmaceutical and life science (genomics and proteomics). Beside his research work, he is also actively providing the lecture of basic instrumentation in university, and contributing his papers to some technical conferences.

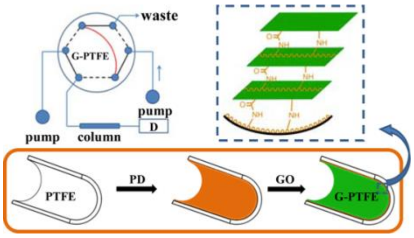
KL.08

Novel Solid-Phase Microextraction and Capillary Electrochromatographic Column Techniques for Pharmaceutical Analysis

Zilin Chen*, Wenpeng Zhang, Juan Zhang, Zixin Zhang

School of Pharmaceutical Sciences, Wuhan University

Abstract: Mussels attach to solid surfaces such as rocks in the sea. Their adhesion must be rapid, strong, and tough, or else they will be dislodged and dashed to pieces by the next incoming wave. The tight adhesion results from the adhesive protein containing polydopamine secreted by mussels. Inspired by the composition of adhesive proteins in mussels and combined with the chemical self-assembly of multilayer grapheme and mental organic frame materials on chemically resistant plastic micro-tubes such as PEEK and stainless steel tubes, we have successfully developed several novel solid phase micro-extraction [1-5] and capillary electrochromatographic columns [6-8] and applied in environmental and pharmaceutical analysis. This talk will introduce the preparation, characterization, validation and application of novel solid-phase microextraction and capillary electrochromatographic columns based on mussel-inspired polydopamine functionalization. Fig. 1 shows schematic of assemblies of multilayer graphene on chemically resistant plastic micro-tubes. Fig. 2 shows schematic procedure of preparing GO-PDA-PANI@capillary.



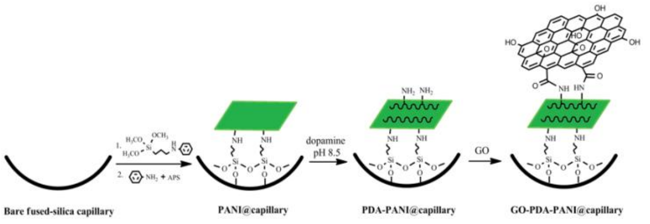


Fig. 1 (Left) Schematic of assemblies of multilayer graphene on chemically resistant plastic micro-tubes

Fig. 2 (Right) Schematic procedure of preparing GO-PDA-PANI@capillary

Keywords: Solid-phase microextraction, Capillary electrochromatographic column,

Polydopamine functionalization,

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Introduction to the author:

Professor Dr. Zilin Chen
School of Pharmaceutical Sciences, Wuhan University, Wuhan, China
Tel: +86-27-68759893; Fax: +86-27-68759850.
E-mail: Chenzl@whu.edu.cn

Dr. Zilin Chen received his Master of Science degree at Wuhan University in 1991, China and Ph. D of Engineering degree at Tokyo Metropolitan University (TMU), Japan in 2000. After receiving his Ph. D degree, he worked as postdoctoral fellow of JSPS (Japan Society for the Promotion of Science) at TMU from 2000 to 2002, as a postdoctoral researcher at NTT Microsystem Integration Labs, Japan from 2002 to 2003, and as a research assistant professor at University of Notre Dame, USA from 2004 to 2007. He joined Wuhan University as a Luojia Chair Professor in Mar. 2007. Now he works as Luojia Chair Professor, vice dean of School of Pharmaceutical Sciences and director of Institute of Pharmaceutical Analysis and Drug Screening, Wuhan University.

Dr. Chen received "New Century Prize" from Kanto Branch of Japan Society for Analytical Chemistry in 2002, and "Shourei Award" from Japan Society for Chromatographic Sciences in 2003. He was awarded "Zhu Yubi Medical Award" in 2012, and "Outstanding Contribution Award of Wuhan University" in 2010, 2013 and 2014. He has had over 100 peer-reviewed papers published in international journals including

Analytical Chemistry (ACS), Biosensors & Bioelectronics (Elsevier) and J.Chromatogr. A etc. In past several years since he came back China in 2007, he has got financial supports from National Natural Science Foundation of China (NSFC) for 2 key project and 3 normal projects, and other funds from Ministry of Education of China, Hubei Province, Wuhan Bureau of Science and Technology and Wuhan University. His research interests include pharmaceutical analysis and drug screening. He organized CJK 2010 at Wuhan.

KL.09

Quantitative on-line Concentration and Reaction for Capillary Electrophoresis with Inkjet Sample Introduction

Ying Rang, Fengming Chen, Hulie Zeng, Hizuru Nakajima, Shungo Kato, Jinmig Lin, Katsumi Uchiyama*

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Minamiohsawa, Hachioji, Tokyo 192-0397, Japan

Abstract:

A quantitative sample introduction method based upon inkjet injection was applied to capillary electrophoresis coupled with 1) stacking and sweeping on-line concentration techniques, and 2) on-line reaction system. For on-line concentration technique, methylxanthines were used as model compounds for the proof-of-concept of the method. The volume of injected sample could be easily manipulated by controlling the number of ejected droplets in the injection procedure. Under optimized conditions, a linear relationship between the ejected droplet number and peak area was obtained when the droplet number introduced into the capillary was less than 100. Under optimized quantitative on-line concentration conditions, the limit of detection for theobromine, caffeine and theophylline were 1.0, 2.0 and 1.0 μM, respectively. The inkjet injection system was evaluated by comparing it with conventional injection methods. The electropherogram of the inkjet injection mode was the same as that for hydrodynamic injection mode, and no sample discrimination was observed compared with the electrokinetic injection mode. The established method was applied to the determination of methylxanthines in bottled green tea. The recoveries of theobromine, caffeine and theophylline were 94.1, 110.6 and 86.8%, respectively. We conclude that proposed method can be used for quantitative concentration for capillary electrophoresis, thus resulting in an improved accuracy.

For on-line reaction technique, NBD-F and amino acids were alternately introduced as small plugs followed by the reaction and separation.

Keywords: quantitative; volume-control injection; capillary electrophoresis; inkjet technique; on-line concentration, on-line reaction

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Introduction to the author:

Professor Dr. Katsumi Uchiyama
Department of Applied Chemistry, Faculty of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo, Japan
Tel: +81-426 77 2835; Fax: +81-426 77 2821.
E-mail: uchiyama-katsumi@tmu.ac.jp

Biography of the authors.

Katsumi Uchiyama is Professor of Tokyo Metropolitan University. He received PhD from Hoshi University, Japan in 1982. 1995, he was an Associate Professor of Tokyo Metropolitan University; and 1997, he was a Visiting Scholar of Mt. Sinai School of Medicine (NY, USA); 2006 to now, he is a Professor of Tokyo Metropolitan University. He was awarded a “OTANI Prize” at 1983, most excellent paper in “BUNSEKI KAGAKU” at the year 2001, 2006. In 2013, he received a "CSJ award for Chemical Eductaion". From 1981to 1994, he devoted to the study on “The application of Photoacoustic spectroscopy to biological materials”. From 1995 to now, he is interested in the micro-TAS, on chip micro gas chromatography, analytical application of micro droplet and fabrication of micro chemical devices. He is member of ACS, CSJ (head of Chem-Chem-Club for young expecting scientists in 2006~2013), JSAC (vice president in 2013~2014) and JSP.

KL.10

Discrimination technique using fragmentless ionization mass spectrometry and multivariate analysis for food analysis.

Takahisa Tsugoshi*

National Institute of Advanced Industrial Science and Technology (AIST)

Abstract: Soft ionization techniques especially to be remarkable at no fragmentation during ionization have an advantage to be obtained only (quasi-)molecular ion peaks in the mass spectrum. There is less chemical reaction during the ionization, so that matrix effect for peak intensity does exist rarely. It means multivariate analysis can be applied easily, that is no need to prepare condition to calculate. According to the points aimed at, we propose to call “fragmentless ionization” for a kind of soft ionizations, e.g., ion attachment ionization and photo-ionization.

- Coffee beans -

We examined a method to discriminate Coffea Arabica (Arabica) and Coffea canephora (Robusta). In order to explore the respective biomarkers, ion attachment ionization mass spectrometer (IA-MS) equipped with a direct inlet probe (DIP) was used. It was possible to measure the solid samples directly by DIP. Furthermore, in IA ionization mass spectra, only quasi-molecular ion peaks are obtained, so that the mass spectra showed the characteristic pattern, which reflected the states in the sample. Therefore, easy screening analysis was possible. By using DIP/IA-MS, we measured nine kinds of roasted coffee beans. As a result, the peaks estimated to be Kahweol palmitate and 16-O-methylcafestol palmitate were detected from Arabica and Robusta, respectively. In addition, this method offers estimation of the mixed ratio of the Arabica and Robusta in not only roasted coffee beans milled but extract with and without heat sterilization.

- Snack Confectionery -

Samples were 10 kinds of commercial snack confectionery on the Japan’s market, so-called as chips. Each sample was crushed, and the powdered specimen was measured. The residual analysis which is one of the multivariate analysis was applied for the comparison. By the comparison between an ordinary snack and infant one that avoids any oils, peaks for palmitic acid, oleic acid, triolein, etc. were detected only from ordinary one as shown in Figure.

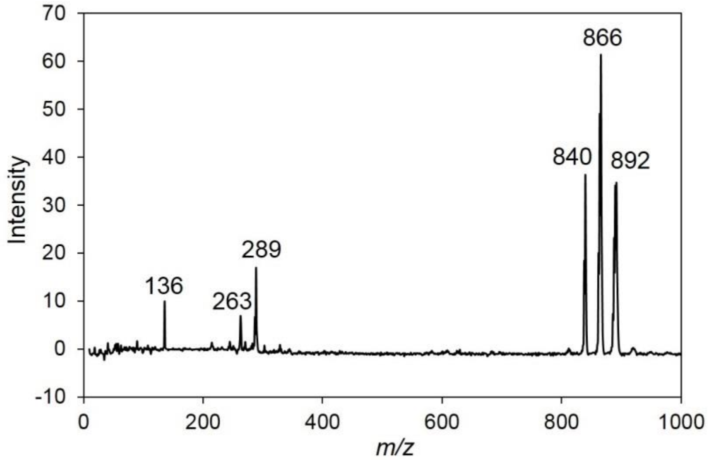

Fig. Residual analysis result between mass spectra of ordinary and infant snacks.

Keywords: coffee, snack, fragmentless ionization, ion attachment ionization, mass spectrometry, residual analysis

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Introduction to the author:

Dr. Takahisa TSUGOSHI
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.
Tel: +81-29-861-4997; Fax: +81-3-6745-1955.
E-mail: tsugoshi.takahisa@aist.go.jp

Biography of the author.

Dr. Takahisa TSUGOSHI received his BA degree in 1988 and received a PhD degree in analytical chemistry at Tokyo University of Science. He had studied and worked in Tokyo University of Science for 12 years. He was a senior research scientist of Advanced Sintering Technology Group, Advanced Manufacturing Research Institute, AIST, and is currently a senior research scientist of National Institute of Advanced Industrial Science and Technology (AIST). He is also a member of several committees and an ex-chairperson of Young Analytical Chemist Association, the Japan Society for Analytical Chemistry (JSAC). He won the Research Award 2007 of the Mass Spectrometry Society of Japan, New Century Research Award 2009 of JSAC, Advanced Analytical Technique Award (CERI Award) 2011 of JSAC, etc.

KL.11

Introduction of 2016 CJK Symposium in China

Chunhua Ma

College of Tea and Food Science, Wuyi University, Wuyi Rd. 16, Wuyishan 354300, China. E-mail:chma@wuyiu.edu.cn

Introduction for 2016 CJK symposium in China.

KL.12

Fast Analysis by Microextraction Coupled to Ambient Mass Spectrometry

Xin Wang, Xianjiang Li, Yu Bai, Huwei Liu*

Institute of Analytical Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Abstract: The determination of trace residues and contaminants in complicated matrix often requires extensive sample preparation prior to instrumental analysis. Usually, sample preparation is the bottleneck in a whole analytical procedure, and minimized preparation steps are highly desired to reduce both time and sources of error. On the other hand, most analytical methods rely on the separation by liquid chromatography (LC) or gas chromatography (GC), which make the entire method complicated and time-consuming. Ambient mass spectrometry (AMS) has been frequently used for the rapid determination or screening of analytes, even without the need of chromatography separation in some cases.

In this presentation, we report our initial efforts to combine effective microextraction with AMS for high throughput analysis of targeted compounds in complex samples, including rapid screening for synthetic antidiabetic drug adulteration in herbal dietary supplements, rapid analysis of multiple phytohormones in fruit juice, fast analysis of triazine herbicides in environmental samples and four Sudan dyes in food samples.

Keywords: Fast analysis, microextraction, ambient mass spectrometry

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Introduction to the author:

Professor Dr. Huwei Liu
Department of Chemistry, Peking University, Beijing 100871, China
Tel: +86-10-62754976; Fax: +86-10-62751708.
E-mail: hwliu@pku.edu.cn

Biography of the authors.

Dr. Huwei Liu graduated with a BA degree in 1982, and PhD in 1990 from Beijing Institute of Technology (BIT), China, then he joined Peking University. He is currently a member of Chinese Chemical Society and a vice president of Beijing Chromatography Society. He also serves as an associate editor of Journal of Separation Science and Journal of Instrumental Analysis (in Chinese), an advisory/editorial board member for Analytical Chemistry, Analytical and Bioanalytical Chemistry, Chinese Journal of Chromatography, and other nine Chinese journals. Dr. Liu's research work focuses bioanalysis and detection, including fundamentals and applications of chromatographic and electrophoretic separation techniques, as well as hyphenated methods such as LC/MS and CE/MS. The application areas cover pharmaceutical analysis, plan hormone detection, proteomics and lipidomics analysis. He is the author and co-author of more than 180 original research papers, several reviews and chapter contributions of the edited books.

Recent Publications:

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KL.13

Detection of Benzo[a]pyrene-induced Breast Cancer Stem Cells Using Quantum Dot-based High-content Assay

Yumi Shim, Joon Myong Song*

College of Pharmacy, Seoul National University, Seoul 151-742, Korea

Abstract: Cancer stem cell (CSC) hypothesis has been reported by many studies before. Due to drug and radiation resistance inherent to CSC, CSC has received great attention in the field of cancer therapy. In this study, it was found that breast CSCs were produced from MCF-7 cells by benzo[a]pyrene (BP)-induced mutation. Breast CSCs were obtained using magnetic bead-based sorting from MCF-7 cells and detected through high-content monitoring of three different markers CD44, CD24 and aldehyde dehydrogenase1(ALDH1) using a hypermulticolor cellular imaging system based on acousto-optical tunable filter (AOTF) . The BP-induced mutation was quantitatively observed via absorption spectra of BPDE-DNA adducts that were formed in MCF-7 cells by the treatment of MCF-7 cells with BP. MCF-7 cells were treated with BP at different concentration of 0.2μM, 2μM, 5μM and 10μM for 24hr. The resultant CSCs in the entire MCF-7 cells were determined to be 0.35±0.032%, 0.45±0.038%, 0.55±0.075%, 1.02±0.28% and 1.19±0.27% in control, 0.2μM, 2μM, 5μM and 10μM respectively. Until now, FACS has been used for the detection of CSCs as general tool. In this work, it is verified that the present multicolor cellular imaging is very advantageous for the detection of CSCs because spectral overlap among probes of CSC biomarkers can be eliminated and diagnostic accuracy can be greatly improved, compared with the conventional FACS.

Keywords: High-content Imaging, Cancer Stem Cell, Quantum Dot

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Introduction to the author:
Professor Dr. Joon Myong Song
Department of Pharmacy, Seoul University, Seoul 151-742, Korea
Tel: +82-2-880-7841; Fax: +82-2-880-9178.

E-mail: jmsong@snu.ac.kr

Biography of the authors.

Joon Myong Song received his PhD in 1997 at Kyushu University, in Japan. He worked as a postdoctoral research fellow from 1998 to 2004 at Iowa State University, Brookhaven National Laboratory, and Oak Ridge National Laboratory in United States. At present he is a professor and head of Department of Pharmach at College of Pharmacy School, Seoul National University in South Korea. His research area includes multifunctional nanoparticle for diagnosis and therapy and high-content cell-based drug screening and diagnosis using hyper-multicolor cellular imaging. He has published 84 peer reviewed papers in the top journals, 7 book chapters, and 10 patents.

KL.14

Determination of copper content in processed food by ICP

Jae Sung Kim, Yoon Jung Yoo, Byeong Hyeon So, Kwang Sik Jung, Hyun Mi Koo, Ji Won Lee, Jang-Hyuk Ahn*, Sang Rag Lee, Young Ryul Kim

KOTITI Testing & Research Institute, Seongnam 462-807 Republic of Korea

Introduction and Results

Quantitative analytical method for copper in processed food was established by using rapid microwave digestion and ICP(Inductively Coupled Plasma). Copper content determination was validated for the sample pre-treatment and instrumental process. Since the method could be used to conclude whether copper chlorophyll was added illegally or not although the colorant is permitted in some processed foods in Korea, establishment of copper content method in some food with complex matrix was needed. Key point of the sample pre-treatment was to prevent boil over in the microwave vessel using proper combination of pre-heat, cooling and acid concentration. Calibration curve for ICP instrumental analysis showed good linearity with 0.9999 regression coefficients and the result of recovery test showed within 90～110 %.

Keywords: Copper chlorophyll, Copper(Cu), ICP(Inductively Coupled Plasma)

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Biography

Dr. Jang-Hyuk Ahn completed his doctorate in Biological Science at the Department of Biological Science, Korea Advanced Institute of Science and Technology(KAIST) after master course for Food Science & Technology, Korea University. After 1993, he performed research in Lotte R&D Center, MFDS(Ministry of Food & Drug Safety), Namyang Dairy R&D Institute as a Food safety center leader. Currently, He is leading Water & Food Analysis Division, KOTITI Testing & Research Institute. His research is focused on analytical science and published 42 articles. He is participated in IDF - KOREA(International Dairy Federation) and KOLAS (Korea Laboratory Accredited Scheme) as a professional.

Acknowledgement

This research was supported by a grant (15162MFDS017) from Ministry of Food and Drug Safety in 2015.

KL.15

Micro ion extractor for transferring inorganic and organic trace anions from a single drop of whole blood

Kei Toda*, Hiroka Nishiyama, Yukihide Nakamura, Yurika Imoto, Shin-Ichi Ohira

Department of Chemistry, Kumamoto University, 2-39-1, Kurokami, Kumamoto 860-8555, Japan

Abstract:

Analysis of contents in biological samples, such as blood, saliva and urea etc., is important to investigate disease and health conditions. Especially blood samples contain a lot of chemicals. If the analysis can be frequently performed, tracing chemicals and metabolic dynamics will be monitored. Normally the blood analysis is performed after pretreatment to obtain serum. The pretreatment requires mL order of blood sample. In this work, we aimed to analyze trace anions from a single drop of whole blood without any other pretreatment, and micro ion extractor (MIE) device was developed.

The device for the extraction comprised of a 16-μL sample cavity, anion permeable membrane, acceptor solution layer, ion exchange membrane, isolator solution layer, and anode plate [1]. Whole blood sample was obtained by earlobe prick with a lancet. The exuded blood was aspirated (25 μL) by a micropipette and was immediately transferred to the sample well of the MIE device and covered with an anode electrode rod for electroextraction. DC voltage was applied for 1–5 min to transfer anions to the acceptor layer which was directly connected to ion chromatograph (IC) sample loop. Then the analytes of interest were determined by conductivity-based IC or IC-MS.

While iodide, thiocyanate and perchlorate were quantitatively extracted from aqueous standard solution and also from saliva but with harder condition, it was very hard to extract from blood samples. However, by optimizing the condition, 30-40% of recoveries were obtained for these anions in blood. Relative standard deviations of recovery were within 10% for the each anion and the method was successfully applied to the real blood analysis. Interestingly thiocyanate concentration was higher in blood from tobacco smokers. Also hourly sampling/analysis was repeated to obtain diurnal variations of thiocyanate and iodide. Particularly iodide concentration showed significant variations depending on the food intake.

In addition to the inorganic anions, some organic compounds were tried to analyze in the same method. For examples, medicine such as loxoprofen's pK_a is 4.2 and supposed to

be anion in the neutral medium. However transfer of such organic anions from blood was very hard and extraction efficiency was in several %. This problem was solved by investigating a new interface between the blood and acceptor. Namely a supported liquid membrane was examined to transfer the organic anions. Also indirect contact of the electrode was investigated. Finally we succeeded to detect the medicine from a single drop of whole blood.

Keywords: single drop of whole blood, micro ion extractor, thiocyanate, iodide, medicine

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Introduction to the author:

Professor Dr. Kei Toda
Department of Chemistry, Kumamoto University, 2-39-1, Kurokami, Kumamoto 860-8555, Japan
Tel: +81-96-342-3389; Fax: +81-86-342-3389.
E-mail: todakei@sci.kumamoto-u.ac.jp

Biography of the authors.

Dr. Toda graduated from Kumamoto University in 1985 receiving master degree. He joined in academics of Kumamoto University in 1994 and is professor since 2008. He has been working on thin film gas sensors, micro fluidic devices for gas analysis (micro Gas Analysis System: μGAS) and biological analysis. Environmental chemistry and atmospheric chemistry are also his interest and these developed devices are useful tools to investigate the scientific issues as well as the advanced commercial instruments.

KL.16

Lysine surface modified Fe_3O_4@SiO_2@TiO_2 microspheres-based preconcentration and photocatalysis for in situ selective determination of nanomolar dissolved organic and inorganic phosphorus in seawater

Shunxing Li*, Wenjie Liang

College of Chemistry and Environment & Fujian Province Key Laboratory of Modern Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou 363000, P. R. China

Abstract: Because of the lack of well-established methods, dissolved organic phosphorus (DOP) are rarely measured.[1] The sample pretreatment methods for dissolved inorganic phosphorus (DIP) monitoring are time-consuming, inadequate for maintaining original sample composition, show contradictory results and in some cases use preservation chemicals that can interfere with the analysis.[2] Furthermore, the processes such as precipitation, hydrolysis, and microbial uptake and release during storage, can mean that the DIP concentrations at the time of analysis may not be representative of those within the natural seawater at the time of sampling.[2] In many areas of the remote ocean, rapid biological uptake of P from sunlit euphotic zone, often driving P concentrations down to nanomolar levels.[3] The concentrations of DIP and DOP in coastal waters reveal a high level of both spatial and temporal variability.[4] Therefore, it is desirable to utilize in situ sampling methods, which avoid the majority of these issues, to accurately selective measure the concentrations of DIP and DOP in coastal water and ocean surface water for understanding eutrophication processes and P biogeochemical cycling.

A new method for in situ selective spectrophotometric determination of nanomolar dissolved DIP and DOP in seawaters is offered for the first time, which is based on solid-phase microextraction of DIP and photocatalysis induced species transformation of DOP into DIP. The procedure was shown in Figure 1.

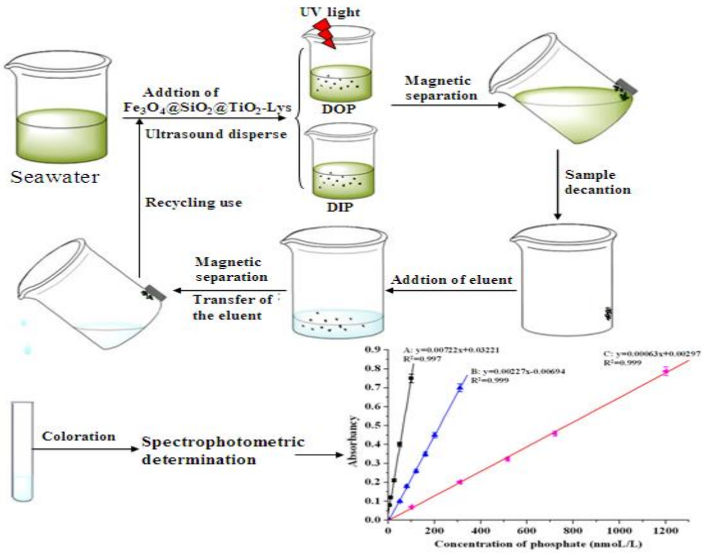

Figure 1 Procedure for in situ selective spectrophotometric determination of dissolved DIP and DOP

The zeta potential of nanosized metal oxides could be adjusted by surface modification (seen in Figure 2), which is reported by us for the first time. After surface modification with lysine, the zeta potential vs pH curve for FST could be reversed and then 98.1% of DIP anions in the seawater could be specifically adsorbed by electric attraction onto FST-Lys (1.2 mg/mL) at the pH value of natural seawater (8.1-8.3) after only stirring for 30 min. The adsorbed DIP could be eluted with hydrochloric acid solution (pH 4.0) for electric repulsion. Therefore, acid hydrolysis of DOP could be inhibited and its influence on the determination of DIP could be avoided.

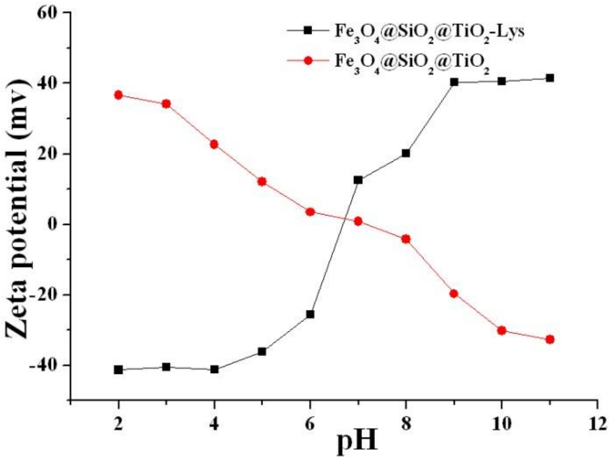

Figure 2 Zeta potential of FST-Lys and FST in different pH

This method is high sensitivity, rapid, simple, green sample pretreatment, wide linear range (3.0-1200 nmol/L), high sensitivity (detection limit of 1.42 nmol/L), and appropriate for field monitoring.

Keywords: Phosphorus speciation, preconcentration, photocatalysis, functional nanomaterials

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Introduction to the author:

Prof. Dr. Shunxing Li
College of Chemistry and Environment & Fujian Province Key Laboratory of Modern Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou 363000, P. R. China
Tel: +86-596-2591395. Fax: +86-596-2591395.
E-mail: lishunxing@fjzs.edu.cn; shunxing_li@aliyun.com

Biography of the authors.

Shunxing Li received his Ph.D. in Environmental Science from Wuhan University in 2003. He now is a professor and vice-president of the Minnna Normal University. His research interests cover metal speciation analysis, bioavailability assessment, and biogeochemical cycle, funtional nanomaterials and its application for pollutant removal.

Wenjie Liang is now a master in College of Chemistry and Environment, Minnan Normal University, majoring in funtional nanomaterials and its application for environmental analysis.

KL.17

The research of sample preparation method based on metal organic frameworks

Gongke Li*, Yuling Hu, Zelin Huang, Haixian Lian, Yichun Huang,Suling Zhang, Yifeng Fan, Zhuomin Zhang

School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, P.R.China

Abstract: Porous metal-organic frameworks (MOFs) are highly ordered crystalline materials prepared by the self-assembly of metal ions with organic linkers to yield low density network structures of diverse topology. Their unique characteristics make MOFs promising for diverse applications in analytical chemistry, for instance, as sorbents for sampling, solid-phase extraction, solid-phase microextraction, and as stationary phases for chromatography. In this paper, the sample preparation methods based on metal organic frameworks were researched.

A facile and efficient strategy about the synthesis of a novel kind of hybrid magnetic metal organic framework MOF-5 via chemical bonding assembly was reported. The as-synthesized materials combine the favorable attributes of both magnetic characteristics and high porosity, making them excellent candidates for magnetic separation and enrichment of trace analytes. Their potential applications as magnetic adsorbents were explored by preconcentrating polycyclic aromatic hydrocarbons (PAHs) and gibberellic acid (GAs) from environmental, food and plant samples prior to gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS), respectively. The results showed that the magnetic MOF-5 exhibited superior enrichment capacity for both of these nonpolar and polar analytes. In-situ solvothermal growth of metal-organic framework–5 supported on porous copper foam for noninvasive sampling of plant volatile sulfides was also studied.

A simple and mild multilayer interparticle linking strategy was proposed to fabricate a novel hybrid MOF-199 enrichment coating. Strong chemical interparticle linkages throughout the coating improved the durability and reproducibility of hybrid MOF-199 coating dramatically. This coating performed a significant extraction superiority of

ethylene over commonly-used commercial coatings, attributed to the multiple interactions including ‘molecular sieving effect’, hydrogen bonding, open metal site interaction and π-π affinity. The hybridization of multiwalled carbon nanotubes with MOF-199 further improved the enrichment capability and also acted as a hydrophobic ‘shield’ to prevent the open metal sites of MOF-199 from being occupied by water molecules. It was successfully applied for the noninvasive analysis of trace ethylene from fruit samples coupling with gas chromatography. The detection limit was 0.016 μg/L. MOF-199/graphite oxide hybrid composites coated solid-phase microextraction fiber coupled with gas chromatography for determination of organochlorine pesticides from complicated samples was also developed.

A facile method for in-situ fabrication of the Fe^{3+}-1,3,5-benzenetricarboxylic acid (BTC) metal-organic coordination polymer gel in capillary, which was efficiently applied to the online enrichment of trace polycyclic aromatic hydrocarbons (PAHs) in environmental water and amphetamines drugs in urine. Water stable metal-organic framework packed microcolumn for online sorptive extraction and direct analysis of naproxen and its metabolite from urine sample was also discussed at the same time.

Keywords: Sample preparation; metal organic frameworks, trace analysis.

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Introduction to Professor Dr. ***Gongke Li***

Institute of Analytical Chemistry, School of Chemistry & Chemical Engineering
Sun Yat-sen University, 135 Xingang Xi Road, Guangzhou 510275, P.R.China
Tel/FAX: 86-20-84110922，84115107; Email: cesgkl@mail.sysu.edu.cn

Prof. Li obtained her BSc(1986) in Chemistry, MSc(1989) and PhD(1992) degrees in Analytical Chemistry from Sun Yat-sen University. She became a professor since 2000. She worked in the Tokai University of Japan as a visiting scholar from 1994 to 1996. She was the director of the Institute of Analytical Sciences of School of Chemistry and Chemical Engineering since 2001.With expertise in chromatography analysis and spectral analysis, her major research interest is focused on the developments of modern sample preparation techniques and analytical techniques for trace analysis of complex systems, such as food, biological and environmental samples. She also studies both analytical- and preparative-scale separations methods for natural products. She has published more than

280 peer-refereed journal articles, one monograph and twenty five patents for invention. She is currently a Senior Editor of Journal of Separation Science and a member of editorial board of twelve academic journals including Journal of Chromatography A, and a member of the chemical teaching Advisory Committee for Colleges and Universities of the Ministry of Education. 2 Science and Technology Awards and 2 honor prizes have been granted to her from the national and provincial governments.

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KL.18

Electrochemical and optical monitoring of enzyme reaction on compact disc-type microchip

Toshihiko Imato

Departament of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395 Japan (E-mail address: imato@cstf.kyushu-u.ac.jp)

Abstract: A flow-based analysis on a compact disc (CD)-type microchip has been recognized as one of the promising analytical methods, where sample solutions, reagent solutions in reservoirs are delivered to a detector cell through microchannels by using a centrifugal force due to rotation of the microchip. Indeed some analytical instruments based on the CD-type microchips have been launched. The analytical method using the CD-type microchip does not need any mechanical pumping system, neither connectors and switching valves for changing flow direction, compared to a conventional flow-base analytical method using a mechanical pumping system or an electro-osmotic flow system. One of the advantages of the analytical method based on the CD-type microchip is that the flow sequence can be controlled by selecting rotation speed, because the critical rotation speed, at which a solution in a reservoir is started to flow, is dependent of the poison the reservoirs on the CD-type microchip.

In our previous work [1,2], we have attempted to use a CD-type microchip for the determination of nonionic surfactant, alkylphenol polyethoxylates (APE) by using an immunoassay method, where the magnetic microbeads immobilized with an anti-APE antibody on their surface were placed at the detection position of the CD type microchip. The chemiluminescence detection was used for this assay. A surface plasmon resonance (SPR) sensor is also a promising detector for the immunoassay on the CD-type microchip. Indeed we have attempted to fabricate an SPR sensor on a CD-type microchip and applied to the immunoassay of IgA [3]. Recently we have assembled an electrochemical detector or carbon paste electrode detector onto the CD-type microchip and applied it to the determination of glucose based on an enzyme reaction with glucose oxidase [4].

In this lecture, we will review our recent works on the flow analysis based on the CD-type microchip including the work on an optical monitoring an enzyme reaction. To monitor an enzyme reaction of horseradish peroxidase (HRP), we have assembled a fluorescent detection system on the rotation turn table for the CD-type microchip, as

shown in Fig. 1. In this case, Amplex red and hydrogen peroxide were used as the substrates for HRP and a fluorescent product, resorufin, was monitored by the present optical system. To confirm the performance of the optical system, fluorescence signals obtained by a photomultiplier through a long pass filter from the reservoirs containing resorufin solution (Fig. 2a) at different concentrations were detected. The results are shown in Figs. 3. For monitoring the enzyme reaction of HRP with Amplex red containing hydrogen peroxide, an HRP solution at different concentration and a mixed solution of Amplex red and hydrogen peroxide were placed in each reservoirs of the microchip shown in Fig. 2b. When the microchip was rotated at the speed of 1200 rpm, two solutions in the reservoirs were started to flow into the spiral channel. Resorufin, the product of the enzyme reaction, was generated in the spiral channel and was detected by the optical detector. The time-course of the fluorescence signal is shown in Fig. 4. Flow behavior of liquids on the CD-type microchip will be also presented in the lecture.

Keywords: Compact disk type microchip, flow behavior, electrochemical detection, optical detection

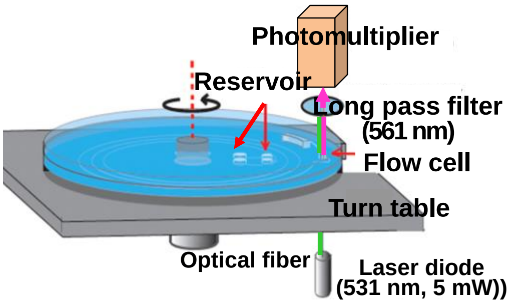

Fig. 1 A compact disk (CD)-type microchip with optical detection

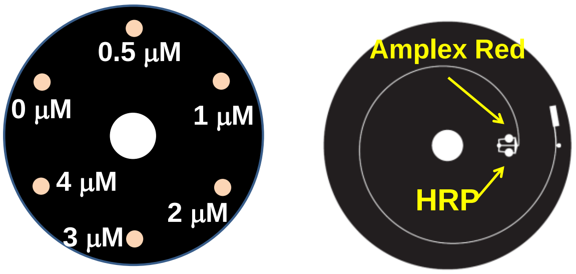

Fig. 2 CD-type microchip (a)without and (b) with a spiral channel

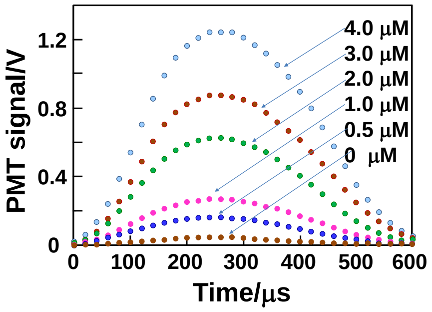

Fig. 3 PMT signal from resorufin solution of different concentration placed in reservoirs (Fig. 2a).

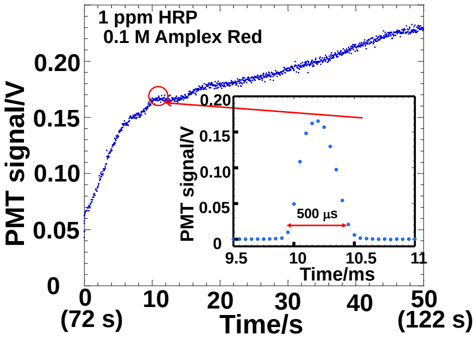

Fig. 4 PMT signal from resorufin produced from enzyme reaction of Amplex red with HRP containing H_2O_2 (Fig. 2b).

Acknowledgements

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Introduction to the author:

Professor Dr. Toshihiko Imato

B S (1976), M.C. (1978), Kyushu University, Japan
Dr. of Engineering (1988), Kyushu University under supervision by Prof. N. Ishibashi.
Research Associate (1978), Kyushu University.
Associate Professor (1988), Kyushu University.
Professor (1993), Kyushu University.
Chairperson of Japanese Association for Flow Injection Analysis (2013 -).

KL.19

LC-MS/MS analysis of sphingolipid metabolites in mice during acute exercise stress

Yong-Moon Lee

College of Pharmacy, Chungbuk National University, Cheongju 361-763, Korea

Abstract: Extracellular sphingosine 1-phosphate (S1P) binds to a family of five G-protein coupled-receptors, S1P1-5. In most vessels, S1P binds to S1P2 which mainly expressed in vascular smooth muscle cells to cause vasoconstriction. In arteries, the S1P exposure triggers Rho kinase and RhoA, the activator of Rho kinase translocation to the plasma membrane in response to stimulation with S1P. Thus the effects of S1P on blood vessel may have pathophysical relevance to S1P concentrations. Therefore, S1P signaling pathways are potential therapeutic targets for the treatment of hypertension, stroke and vasospasm. The present investigation focused on the concentration changes of S1P and its metabolites in blood, heart, lung and muscles during swimming exercise stress in mice. In high stress conditions, S1P concentration was obviously decreased (27% reduction in blood, 38% reduction in heart) while greatly increased in lung (194% increased) and muscles (375% increased). For acute exercise, S1P may be urgently required for rapid contraction of smooth muscle cells in lung and muscles. The ceramides synthesis is impaired in vascular smooth muscle cells (VSMC) from spontaneously hypertensive rats where may contribute to increased VSMC proliferation in hypertension. Indeed, in exercise condition, ceramide levels were slightly decreased 12% in blood and 20% in heart, respectively. Interestingly, ceramide levels in lung and in muscle were apparently increased. It is not still well understood why sphingolipid metabolites is increasing or decreasing by outer stress or pharmacological agents depending on the organs. Specifically, the increase of ceramide in lung may be contributed to the concomitant activation of neutral sphingomyelinase (nSMase) and acidic sphingomyelinase (aSMase). In addition, high S1P increase (almost 4- fold) in muscle is contributed by the activation of sphingosine kinase, PKC-dependent enzyme synthesizing S1P from sphingosine by phosphorylation. Taken together, it should be mentioned that S1P and ceramides concentrations in organs were found to be greatly changed in acute exercise conditions and provides additional evidence for the significance of S1P and ceramides in the cardiovascular system.

Keywords: LC-MS/MS, sphingolipid, sphingosine 1-phosphate, ceramide, blood

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Introduction to the author:

Professor Dr. Yong-Moon Lee
College of Pharmacy, Chungbuk National University, Korea
Tel: +82-43-2612825; Fax: +82-43-2682732.
E-mail: ymleefn@chungbuk.ac.kr

Biography of the authors.

Professor Lee received his Ph.D from University of Tokyo on the chemical derivatizaiton for the determination of bioactive carboxylic acids after dansyl cadaverine derivatizaiton. After he got the professor position at Chungbuk National University in 1990, he have worked on the development for the screening tool of chemopreventive natural products to cancer treatment. Since he developed analytical method with chemical derivatizaiton from 1996, he newly focused on the lipid biological mechanism in sphingolipid metabolic pathway. He developed various chemical derivatizaiton for sphingolipid analysis, including sphingolipid metabolic enzymes assay for finding specific inhbitors from natural resources. He currently worked with the analysis of harmful chemicals in drugs in supported by KFDA Research fund. He has published over 85 SCI papers and 5 reviews.

KL.20

Strategy toward the ultrafast separation

Yi Chen*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract: How to accelerate a separation is an interesting study topic becoming more and more crucial because we are facing more and more complex analytical objects and samples. Speeding up of a separation is also an urgent challenge in omic studies, and it is in theory easy but in practice tough. Herein we will take capillary electrophoresis (CE) as an example to discuss the issue. A strategic thinking to speed up the separation lies in chromatographic theory. According to Van Deemter equation, there are at least four ways available, including shortening the separation length, increasing a driving force such as electric field strength, use of better separation materials, and reduction of injection length. Use of a short separation length is easily realized but stopped by a heavy loss of resolution. Although the loss could partially or even largely be recovered by increase of the applied electric field strength, it will be limited by the self-heating effect. Exploitation and use of a highly effective separation medium like photonic crystals (PCs) were then considered and tired, and high resolution and ultra-fast separation have been achieved [1]. This is a new gate toward the acceleration of separations but has to be guaranteed by significant reduction of the sample zone length. This needs a new sample injection method. Although there were optical and hydrodynamic gating injection methods published in literature [2,3], they are hardly copied to a common laboratory. A simpler approach termed diffusion-based injection (D^2I) was hence exploited in this laboratory. It could simply be realized by touching a capillary tip on a sample surface for a while, able to inject a sample plug of less than 20 μm into the capillary tip. D^2I was shown to be suitable for the injection of not only liquid but also solid and in-between-stated samples. To the best of our knowledge, this is the first method allowing a direction injection of solid samples. It is by use of D^2I that CE can now separate some small molecules such as amino acids within seconds. For detailed discussions please join me on the conference.

Keywords: Fast separation strategy, capillary electrophoresis, solid sample injection

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Introduction to the author:

Professor Dr. Yi Chen
CAS Key Lab of Analytical Chemistry for Living Biosystems, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
Tel: +86-10-62618240; Fax: +86-10-62559373.
E-mail: chenyi@iccas.ac.cn

Biography: Dr. Yi Chen currently holds a position of professor both at Institute of Chemistry, Chinese Academy of Science (CAS), and University of CAS. He has been working on capillary electrophoresis since 1984, on surface plasmon resonance sensing and imaging since 1997, and on bio-mass spectrometry since 2006, with more than 230 publications, three books and 30 patents. Dr. Chen received twice the First-class Award of Sciences and Technology from the China Association for Instrumental Analysis, Young Scientist Award from CAS, Young Scholar Award from the Hong Kong Qiushi Science and Technology Foundation, and Young Chemist Award from the Chinese Chemical Society. He is also a Titular Member of Analytical Chemistry Division, IUPAC; the Associate Editors of *Anal. Methods, Chinese Anal. Chem., Chinese J. Chromatogr., and Anal. Instrumentations*; and members in the editing or advisory boards of *J. Chromatogr. A, J. Chromatogr. B, Sci. China B, Chinese J. Chem., Progress Chem. etc.*(15 journals in total). He has been elected the vice presidents of Chinese Society of Chromatography, Beijing Society of Chromatography, Beijing Chemical Society, and Branch of Analytical Instruments at China Instrument and Control Society.

KL.21

Microfluidic Chips towards Cell Signaling Analysis

Pen Chen, Yao Wang, Bi-Feng Liu*

College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

Abstract: Cell signaling has been recognized as a highly dynamic biological process. The involved highly dynamic signals are regulated both by complicated intracellular processes, such as cell signal transduction network, gene regulatory network, metabolic regulatory network, protein interaction network and by the fluctuations in extracellular environment, including gradients of cytokines and secreted proteins from neighboring cells, biochemical and mechanical interactions with the extracellular matrix and direct cell-cell contacts. Analysis of these dynamics, therefore, required combination of two critical technologies: high resolution imaging and high precise perturbation. As is well-known, there have been tremendous progress in high resolution imaging, however high precise perturbation has been still an immense challenge. Currently, investigation of cell signaling usually involves dynamic imaging of cells upon localized mechanical, electrical, or chemical perturbations. Chemical perturbation is a relatively gentle approach that can mimic the surrounding environmental signals to cells in vivo, which is preferred for uncovering such dynamic. Conventionally, chemical perturbations are implemented via perfusion systems, which have been useful in providing information about cell signaling. However, their limitations are impeding further development, especially the drawbacks in lack of precision for spatial and temporal control of chemical stimuli. In this presentation, we report a precision guided microfluidic chemical perfusion strategy for cell dynamic signaling with high spatial and temporal resolution. It provided a versatile platform for studying cell signaling in individual cells or among contacting cells, capable of addressing individual cells among a cell cluster without interfering with adjacent contacting cells. The high temporal resolution further allowed pulsing cells with varying durations, which can be a potentially useful tool for research in chemical biology, cell biology and pharmacology.

Keywords: microfluidics, cell signaling, chemical perfusion

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Introduction to the author:

Professor Dr. Bifeng Liu
College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan, China
Tel: +86-27-87792203; Fax: +86-27-87792170.
E-mail: bfliu@mail.hust.edu.cn

Biography of the authors.

Dr. Bifeng Liu received his Ph.D. degree of analytical chemistry in 1999 from Wuhan University (China) where he continued his postdoctoral research in the College of Life Science. From 2001, he moved to Japan as a JSPS postdoctoral fellow in Prof. S. Terabe’s group. He joined Huazhong University of Science and Technology (China) as a professor in 2003. He is now serving as Deputy Dean of the College of Life Science and Technology. His research focuses on systems biology-oriented analytical science in the areas of microfluidics (or lab-on-a-chip) for bioanalysis, mass spectrometry coupled micro-separations for functional proteomics & molecular imaging. He is the author and co-author of over 100 original research papers and invited reviews published in international journals.

KL.22

Polycyclic Aromatic Hydrocarbons, Nitropolycyclic Aromatic Hydrocarbons and Inorganic Ions in Snow Layers at Murodo, Tateyama, Japan

Kazuichi HAYAKAWA[1,2*], Genki SUZUKI[1], Fumiya MAKINO[1], Hiroshi MORISAKI[1],
Ning TANG[1], Akira TORIBA[1] and Kazuma AOKI[3]

[1]*Institute of Medical, Pharmacutical and Health Sciences, Kanazawa University, Japan*
[2]*Institute of Nature and Environmental Technology, Kanazawa University, Japan*
[3]*Graduate School of Science, Toyama University, Japan*

Introduction:

Acidic rain/snow and Asian dust storm in Japan are caused by long range transports of sulfur oxides and yellow sand, respectively. Recently, $PM_{2.5}$ has become another big environmental issue in East Asia, because $PM_{2.5}$. Polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are formed through imperfect combustion of organic matters such as fossil fuels and wood, and they are major components of $PM_{2.5}$. We found the atmospheric concentrations of PAHs and NPAHs at the Noto peninsula, Ishikawa, Japan, increased in the period from mid. October to mid. April every year, and identified that PAHs and NPAHs were mainly emitted from coal combustion processes, including coal heating, in north-east China, These results suggest that snow in Japan might be an useful environmental sample for identifying long-range transport of not only yellow sand but also $PM_{2.5}$, because snow falls on the Japan Sea coast area of Japan by the north-west wind in winter. The author reported the determination of PAHs and inorganic ions in snow collected at Murodo, Tateyama, Japan at CJK2014. In this report, we collected cake samples from different snow layers at Murodo in April 2015, and determined not only PAHs and inorganic ions but also NPAHs for the detail discussion of sources and behaviors of $PM_{2.5}$.

Experimental:

Snow cakes were collected from four different layers (L-I, L-II, L-III and L-IV, in April, 2013 and M-I, M-II and M-III, in April 2015) at Murodo (2,450 m above sea level), Tateyama, Japan. Each snow cake, more than 1 kg each, was melted at room temperature, and the solution was filtered with a GC filter (pore size 0.5 μm). After drying, the filter was weighed to calculate the amount of particulates collected. Nine inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_3^+, K^+, Ca^{2+} and Mg^{2+}) were determined by ion chromatography. Ten PAHs having four to six rings (fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BbF), benzo[*a*]pyrene (BaP), dibenz[*ah*]anthracene (DBA), benzo[*ghi*]perylene (BghiPe) and indeno[1,3,3-*cd*]pyrene (IDP)) were determined by HPLC with fluorescence detection according to our previous report.1) Three NPAHs (1- and 2-nitropyrenes (1- and 2-NPs) and 2-nitrofluoranthene (2-NFR)) were determined by HPLC with chemiluminescence detection according to our previous report.2)

Results and Discussion:

From the depth of snow, dates of four layers, L-I through VIII and M-I through III, were estimated. In L-series, L-I showed the lowest concentration of particulates and L-III showed the highest concentration of particulates. L-IV showed the highest concentration of $nssCa^{2+}$. L-IV showed the highest concentrations of PAHs and $nssSO_4^{2-}$. On the other hand, in M-series, M-I showed the highest concentration of $nssSO_4^{2-}$, PAHs and NPAHs. Back trajectory analysis suggested that air masses corresponding to L-IV mainly passed through central-east China and north-east China, respectively and that air mass corresponding M-I mainly passed through north-east China. These results suggest that $PM_{2.5}$ long-range transported from north-east China contained high concentration of PAHs, NPAHs and $nssSO_4^{2-}$. The smaller NPAH/PAH concentration ratios, such as [1-NP]/[Pyr], suggested that the major contributor was coal-burning systems but not automobiles. Monitoring of particulate weight only is not sufficient for identifying the origin of $PM_{2.5}$. Simultaneous determination of PAHs and inorganic ions are very important to differentiate the origins of $PM_{2.5}$, yellow sand and combustion of fossil fuels.

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Keywords: polycyclic aromatic hydrocarbons, nitro polycyclic aromatic hydrocarbons, inorganic ions, snow, $PM_{2.5}$, yellow sand, Tateyama

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Dr. Kazuichi Hayakawa
Professor of Faculty of Pharmaceutical Sciences, Institute of Medical, Pharmacutical and Health Sciences/Director of Institute of Nature and Environmental Technology, Kanazawa University
Kakuma-machi, Kanazawa, 920-1192 Japan
Tel: 81-76-234-4413; Fax: 81-76-234-4456; E-mail: hayakawa@p.kanazawa-u.ac.jp

KL.23

Determination of Important Volatile Compounds from Aqueous Matrix

Sunyoung Bae*

Department of Chemistry, Seoul Women's University

Abstract

Volatile fractions of samples are generally associated with low molecular weight compounds that vaporize at room temperature from various matrices. For various reasons, volatile compounds become important to be measured and characterized. Either major or minor in composition, they play important roles in many applications such as environmental, clinical, forensic, personal-care, pharmaceutical, and food-product samples. The trace compounds could be more significant than major compositions. However, due to its characteristic including the loss of compounds during sample preparation, sensitive analytical techniques are required.

Sample preparation is so difficult in trace analysis that becomes the rate-determining step of the experiment. Through preparation of the analytes, it enables minor compounds to be concentrated and detected over the limit of detection of the analytical instruments. Several sample preparation techniques would be discussed about advantages and disadvantages with experimental data in this presentation. They include solid phase microextraction fiber located in a needle (SPME), in-tube SPME, in needle capillary adsorption trap (INCAT), solid phase dynamic extraction (SPDE), single drop microextraction (SDME) and a sorbent-packed needle trap device (NTD).

Especially, sol-gel microextraction phases for sample preparation were investigated. Polydimethylsiloxane (PDMS) has been generally used for non-polar analytes while others used for polar compounds. In our lab, the different sol-gel microextraction phases were produced including PDMS/DVB (Divinylbenzene), PDMS/PEG (Polyethylene glycol), PDMS/PAA (Polyacetic acid), and PDMS/β-CD (Cyclodextrine). Needle was a platform to be coated with these phases. It is easy to handling and inexpensive to fabricate. It also shows that the selectivity and extraction efficiency of both polar and nonpolar compounds depending on coating materials in needle.

Data obtained from the real samples show that the minor compounds in trace amount would distinguish one sample from others. The quantitative information of these compounds was input for principal component analysis as multivariate statistical analysis. This approach provides the fundamental information on characterization of volatile compounds for samples and their classification for recognition.

Keyword: Volatile compounds, sol-gel microextraction, classification, preconcentration

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Introduction to the author:
Dr. Sunyoung Bae
Department of Chemistry, Seoul Women's University, Seoul, Korea
Tel: +82-2-970-5652; Fax: +82-2-970-5972
Email: sbae@swu.ac.kr

Biography of the author:
Dr. Sunyoung Bae has obtained Ph.D. from the University of Massachusetts-Lowell in 2002. She had been working at the interdisciplinary research center at the University of North Carolina-Charlotte. In 2008, she was appointed as an assistant professor in the Department of Chemistry at North Carolina A&T State University. Since 2010, she has been working at Seoul Women's University. Her research approach is to characterize physicochemical properties and interactions in micro-scale using analytical instruments that determines macro-phenomena. Dr. Bae's research topics include separation and sampling methods for GC, GC-MS, biomass conversion and its characterization. Through some projects that she has conducted, her main role is to integrate fundamental analytical chemistry into a problem-solving solution to a problem. Dr. Bae had been served as a guest editor for Journal of Hazardous Materials (Elsevier), Environmental Monitoring and Assessment (Springer), and Journal of Materials in Civil Engineering (ASCE). Currently, she has been served as an associate editor for Korean Society of Soil and Groundwater Environment and on the editorial board for the Korean Society of Analytical Sciences.

OL.01

Electrochemical study on electron transfer across DNA base pairs

Jifeng Liu*

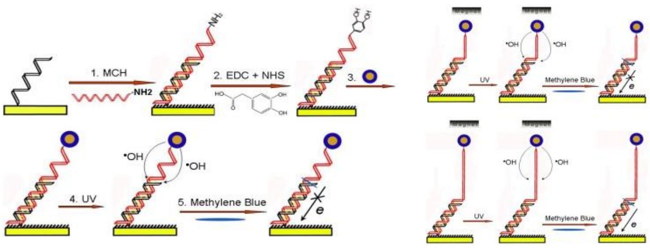
School of Food Engineering and Biotechnology, Tianjin University of Science and Technology, Tianjin 300457, China.

Abstract:

The molecular *π*-stack of base pairs within double-strand DNA (dsDNA) has been shown to mediate electron transport (ET) reactions, which has received a substantial attention because of its biological significance in DNA damage and DNA repair mechanisms as well as the DNA electronic devices. The ET process across the base pair stacking as well as the bases terminated monolayer were investigated.

1. How far can hydroxyl radicals travel?

Onto gold surface adsorbed DNA monolayer composed of double stranded part of 20 base pairs at the gold suface and extra single stranded $(AT)_n$ part at the distal of DNA monolayer. $TiO_2@\gamma\text{-}Fe_2O_3$ composite nanoparticles were attached onto the distal of single strand DNA parts. Under UV illumination, hydroxyl radicals generated at the TiO_2 shell would diffuse to the double strand parts of DNA monolayer and the single strand parts acted as ruler to measure the diffusing distance of the radicals. Thus using photocatalytic reactive nanoparticles and DNA composite modified gold electrodes, exploiting the sensitivity of DNA-mediated electron transfer to base pair stacking, we proposed an electrochemical technique to read the effective diffusing distance of hydroxyl radicals.

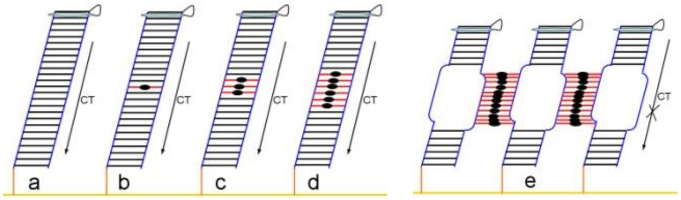


Scheme 1. (*left*) Preparation of $TiO_2@\gamma\text{-}Fe_2O_3$ core-shell particle attached dsDNA modified Au electrode ($Fe_2O_3@TiO_2/(AT)_n/dsDNA/Au$) (step 1, 2 and 3) and oxidation of DNA base pairs by photogenerated •OH radicals upon UV illumination (step 4 and 5). (*right*) The single strand part of DNA ($(AT)_n$, $n = 5, 12, 24$) acted as a spacer between base pair in the dsDNA film and the $\gamma\text{–}Fe_2O_3@TiO_2$ particle when placed a magnet above the modified surface. Top, $n < 12$; bottom, $n > 12$.

2. An electrochemical study based on thymine-Hg-thymine DNA base pairs mediated

electron transfer process

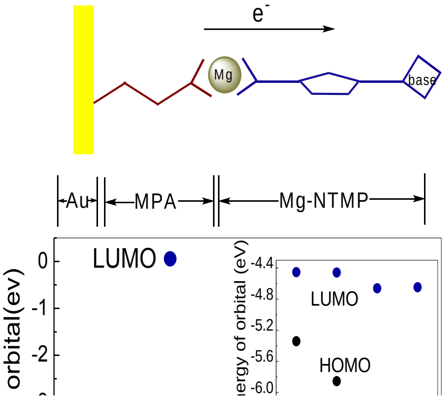
Onto Au surface adsorbed DNA monolayer composed of double stranded of 25 base pairs, and at the gold surface and distal part were matched base pairs, while at the middle of DNA monolayer were $(TT)_n$ mismatched pairs. The ET properties of the DNA monolayer was studied using Laviron's theory and it was found that when $n \leq 6$, the kinetics of CT followed the order: matched DNA base pairs < DNA duplexes with $(TT)_n$ < DNA duplexes with $(T\text{-}Hg(II)\text{-}T)_n$ and the CT kinetics increased with increasing n. However, an interesting phenomenon was found when $n \geq 12$, that is $(T\text{-}Hg(II)\text{-}T)_n$ conformation was formed between different DNA strands and the this inter-DNA $(T\text{-}Hg(II)\text{-}T)_n$ structure caused DNA monolayer deformed and CT not occur along the DNA base pairs.



Scheme 2. CT process of dsDNA with (T-Hg(II)-T) sequench. (a) matched dsDNA, (b) dsDNA with (T-Hg(II)-T)1, (c) dsDNA with (T-Hg(II)-T)3, (d) dsDNA with (T-Hg(II)-T)6, (d) dsDNA with (T-Hg(II)-T)12.

3. Study on electron transfer across nucleobases terminated surface assembly

ET process with different kinetics occurred across the nucleobases terminated multilayer assembly and the base-dependent ET properties were studied in this work. To prepare such nucleotide monophosphate (NTMP) (including guanosine, adenosine, cytidine, uridine-5´-monophosphate, and abbreviations were GMP, AMP, CMP, UMP respectively) assembly, 3-mercaptopropionic acid, Mg^{2+}, NTMP were adsorbed onto Au substrates stepwise to form nucleobases terminated surface. Cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy showed that the rate of ET kinetics decreased in the order: GMP/Mg^{2+}/MPA/Au > AMP/Mg^{2+}/MPA/Au > UMP/Mg^{2+}/MPA/Au > CMP/Mg^{2+}/MPA/Au. Nucleobases have different geometrical conformations and electrical structural properties, which determined the ET kinetics across nucleobases terminated multilayer assembly. And these differences in ET behavior were ascribed to different HOMO energies of the Mg-Nucleotide moieties (decreased in the order: GMP-Mg > AMP-Mg > UMP-Mg > CMP-Mg). This study may be valuable to the studies of DNA electronic structure, which had been utilized for DNA sequencing *via* nanopore techniques.



Scheme 3. Energy diagram for the electron transfer from the gold electrode to nucleobases across the NTMP/Mg^{2+}/MPA/Au multilayer assembly. The calculation was carried out based on B3LYP/6-31G* using Gaussian program.

Keywords: DNA base pairs, electron transfer, electrochemistry

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[2] E. Xu, Y. Lv, J. Liu, X. Gu, S. Zhang. RSC Adv. 5 (2015) 49819-23.

Introduction to the author:

Professor Dr. Jifeng Liu
School of Food Engineering and Biotechnology, Tianjin University of Science and Technology, Tianjin, China.
Tel: +86-22-60602795; Fax: +86-22-60602795.
E-mail: jfliu@tust.edu.cn

Biography of the author.

Dr. Jifeng Liu, received his PhD in Analytical Chemistry in 2004 from Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences (CAS). After postdoctoral research at École Polytechnique Fédérale de Lausanne (EPFL), he came to Liaocheng University in October 2007 and was a Taishan Schoolar professor. In January 2015, he joined the Key Laboratory of Food Nutrition and Safety, (MOE), Tianjin University of Science and Technology as a professor. His research interests are electrochemistry of bio-nanomaterial interface, electrocatalysis, and application of electrochemistry in real analysis.

OL.02

Application of novel nanomaterials in the phosphopeptide enrichment

Liping Li, Linnan Xu, Wen Ma, Huwei Liu, Yu Bai*

College of Chemistry and Molecular Engineering, Peking University, Beijing, China

Abstract: As one of the most common post-translational modifications, protein phosphorylation is of great importance in regulating various biological processes. Therefore, effective analytical methods for phosphoprotein are in urgent demand for further phosphoproteomic research. Mass spectrometry (MS) is considered as a powerful tool in the detection and identification of proteins. However, for phosphoproteomic analysis, effective enrichment approaches prior to MS analysis are often required due to serious signal suppression caused by non-phosphorylated species. Among these approaches, metal oxide affinity chromatography (MOAC) has become more and more popular in recent years [1-3]. Different surface properties of nanomaterials often lead to different enrichment performance in sensitivity, specificity or phosphoproteome coverage. Therefore, the exploration of novel nanomaterials for comprehensive phosphoproteomic analysis with enhanced sensitivity is still attracting considerable interest. In this work, binary metal oxides and other novel nanomaterials have been synthesized and characterized. All these novel nanomaterials provide attractive properties in the phosphopeotide enrichment and the target proteomic research [4-7].

Keywords: nanomaterials, MS, affinity probe, enrichment

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Introduction to the author:

Associate Professor Dr. Yu Bai
College of Chemistry and Molecular Engineering, Peking University, Beijing, China
Tel: +86-10-62758198; Fax: +86-10-62751708.
E-mail: yu.bai@pku.edu.cn

Biography of the authors.

Dr. Yu Bai is an Associate Professor of Analytical Chemistry at Peking University. She obtained her Ph. D in chemistry from the Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, in 2004. She did her post-doc in University of Toronto during 2005-2008. She got the Chinese Natural Science Foundation--Outstanding Youth Foundation in 2014. Her major research interests focus on i) Application of nanomaterials in the separation and analysis of biological samples; ii) Novel ambient ionization method and its application; iii) Disease related metabolomics and proteomics.

OL.03

Antioxidant Activity of Volatile Compounds Isolated from Broccoli (Brassica oleracea L.) sprouts by GC and GC-MS

Hae Won Jang

Food Analysis Center, Korea Food Research Institute, Korea

Abstract: Broccoli (Brassica oleracea L.) sprouts have received much attention recently because they contain various bioactive constituents, which are not present in broccoli. However, there are no reports on the biological activity of the volatile compounds from broccoli sprouts. In the present study, volatile extracts of broccoli sprouts were obtained by a steam distillation under reduced pressure, followed by a liquid–liquid continuous extraction and then examined for their antioxidant activities using aldehyde/carboxylic acid and lipid/malonaldehyde (MA) assays. All samples exhibited dose-dependent antioxidant activity. The antioxidant activity ranged from 74.5 ± 0.5% (less volatile sample) to 99.5 ± 0.5% (volatile sample) at the level of 500 μg/mL. Antioxidant activity of samples obtained from broccoli sprouts was comparable to that of known antioxidants, α-tocopherol and BHT. Subsequently, volatile extracts were analyzed by gas chromatography and gas chromatography–mass spectrometry to identify principle antioxidants. Among the 43 compounds positively identified by gas chromatography/mass spectrometry, 4-methylpentyl -isothiocyanate (2.48 μg/g) was found in the greatest concentration, followed by 4-methylthiobutylnitrile (10.63 μg/g), 5-methylthiopentylnitrile (31.64 μg/g), 3-methylthiopropylisothiocyanate (3.00 μg/g), and 4-methylthiobutylisothiocyanate (14.55 μg/g). These isothiocyanates are known to possess antioxidant properties. Possible phenolic antioxidants found are 4-(1-methylpropyl)-phenol (0.012 μg/g), 4-methylphenol (0.159 μg/g) and 2-methoxy-4-vinylphenol (0.009 μg/g). The present study demonstrates that broccoli sprouts are a good source of natural antioxidants.

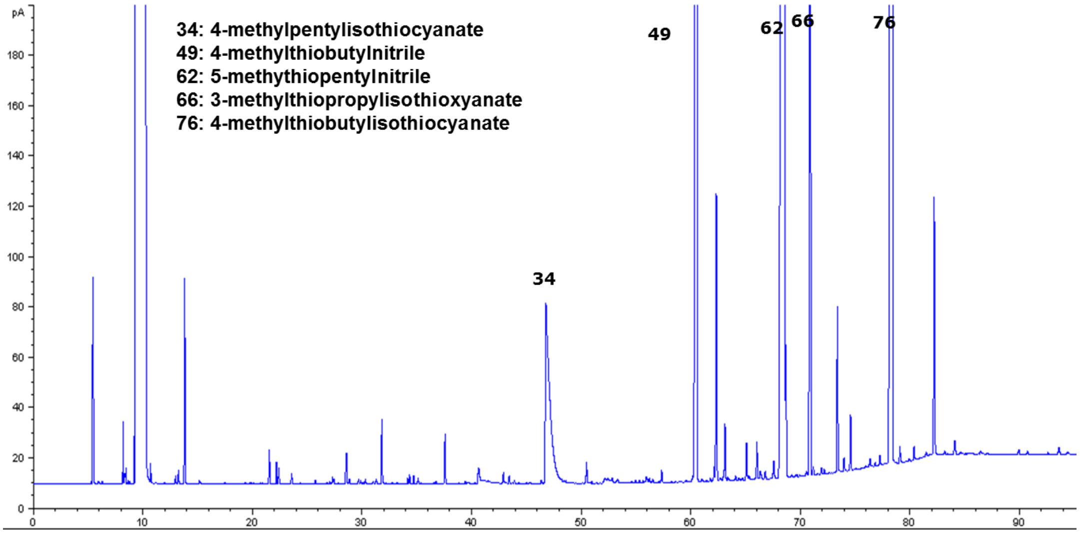

Figure 1. GC Chromatograms of cholesterol in infant formulas using GC/FID.

Keywords: broccoli sprouts, isothiocyanates, natural antioxidants, volatile compounds

Reference: Jang, H.W., Moon, J.K., Shibamoto, T., (2015), *Journal of Agriculture and Environmental chemistry,* 63, 1169-1174.

Introduction to the author:

Dr. Hae Won Jang
Food Analysis Center, Korea Food Research Institute, 463-746, Korea
Tel: +82-31-780-9377; Fax: +82-31-780-9280.
E-mail: hwjkfri@kfri.re.kr

Biography of the authors.

Dr. Hae Won Jang has obtained Ph.D. in agriculture and environmental chemistry at University of California, Davis in 2013. After the graduation, she has been working in Food Analysis Center at Korea Food Research Institute. Her research and interest areas include biological and chemical studies on extracts from natural plants and maillard reaction systems.

Determination of arsenic species in food by LC-ICP-MS

Cheong-Tae Kim

Food Safety Research Institute, NONGSHIM CO., LTD, Seoul, Korea

Abstract: Arsenic (As) is considered as one of the most important toxic elements in the environment because of its potential risk to human health and to ecosystems. Apart from drinking water, rice consumption may be the most important pathway of human As uptake. After the US-Government announced that the rice cultivated in California has high levels of inorganic As, many consumer groups are concerning about human health problems will be caused by staple food. Especially, it is especially alarming in Asian countries due to huge consumption of rice. The chronic exposure to As can lead to cancerous health hazards and other health problems. So, we conducted the development of extraction method for arsenic speciation and the determination of arsenic compounds in food stuff including rice grain purchased from markets in Korea by using LC-ICP-MS.

Around 1.0 g samples were weighed into the vessels and extracted with 10 mL of 0.28 M nitric acid at 85 ℃ for 70 min. Samples were cooled to room temperature and centrifuged at 4500 rpm for 10 min. The supernatant was filtered and kept at 4℃until analysis. Using a solution of 1% HNO3 for extracting As from food stuff was suitable. Arsenic species were quantified by IC-ICP-MS with Dionex IonPacTM AS7 RFICTM column (250 mm x 2 mm). The gradient mobile phases were 10 mM ammonium carbonate adjusted to pH 8.8 and 200 mM ammonium nitrate and ammonium phosphate adjusted to pH 9.0. The flow rate was 0.3 mL/min. Injection volume and column temperature were 25 uL and 15 ℃, respectively.

Arsenic exists in forms of various chemical species. Inorganic As species (arsenite (As^{3+}) and arsenate (As^{5+})) have been classified as carcinogenic and the methylated form, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) have been identified as cancer promoters. It is believed that arsenobetaine (AB) and arsenocholine (AC) are non-toxic. The method of As speciation by IC-ICP-MS was developed that allowed the simultaneous separation of six As species. Four species of As were mainly detected in food stuff as As^{3+}, As^{5+}, MMA and DMA. Arsenic species in samples were extracted with microwave-assisted 1 % nitric acid. The recoveries of fortified rice (50 ug/kg) were 91~112 % The LODs of As species method were 0.1~ 0.5 ug/kg.

Keywords: Arsenic, Speciation, LC/ICP/MS, Rice, Food stuff

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Introduction to the author:

Dr. Cheong-Tae Kim
Food Safety Research Institute, NONGSHIM CO., LTD, Seoul, Korea.
Tel: +82-2-820-8131; Fax: +82-2-810-9047.
E-mail: kctmass@hanmail.net

Biography of the authors:

Dr. Cheong-Tae Kim completed his doctorate in food technology with "Reduction of acrylamide in fried foods by addition of amino acids and vacuum frying." at Seoul National University in 2004. He has been worked at NONGSHIM CO. LTD since 1990. Dr. Kim has served a head of Food Safety Research Institute in his company from 2009 to present.

Dr. Kim has responsible for the food safety of raw materials and final products in his company. He has researched on the development and application of chemical analysis methods by using Mass spectrometer such as orbitrap-MS and LC/ICP/MS etc. And He has focused on studies of how to control microorganisms in products and plant facilities. Dr. Kim has been managing the all kinds of food safety compounds such as pesticides, antibiotics, GMO, allergens, food-born pathogen, irradiation foods and radioactive substances under the food safety policy of his company. His research and activity are focused on studies of chromatographic separation and identification and how to control the issues caused by biological materials.

OL.04

Water Quality Monitoring of Drainage River in Kuantan, Malaysia by using Ion-exclusion/Ion-exchange Chromatography

Daisuke Kozaki[1]*, Norhasmira Idayu binti Harun[1], Nobutake Nakatani[2], Masanobu Mori[3], , Kazuhiko Tanaka[3]

[1] Faculty of Industrial Sciences and Technology, University Malaysia Pahang, Malaysia
[2] Department of Environmental and Symbiotic Sciences, College of Agriculture, Food and Environmental Science, Rakuno Gakuen University, Japan
[3] Graduate school of Science and Technology, Gunma University, Japan

Abstract:
The water quality of drainage river (system), namely Galing River in Kuantan, Malaysia were examined effectively by using ion-exclusion/cation-exchange chromatography with water quality indices and land usage data. In Kuantan, there are 228 sewerage treatment plants, many of which were built in the early 1970's and individual septic tanks (ISTs) serve 51%, the centralized sewer system serves 47%, and individual primitive systems serve the remaining 2% of sewage/household wastewater in Kuantan. However, ISTs are not highly efficient in removing nutrients and organic compounds (COD) with removal capacities of 5–18% and 50–78%, respectively. In this study, we have focused on evaluating and grasping the effect of sewage/household wastewater discharged from housing areas in the Kuantan district on the river water quality. Based on this study, the following beneficial information were obtained effectively by using ion-exclusion/cation-exchange chromatography: (1) the pollution level (Galing River: Class I V) in the Galing River are linked with the urbanization level of the river basin area; (2) differences in the biological reactions in the different pollution level rivers are understood; (3) Galing River is among the most polluted rivers not only in Kuantan, but also in the Malay Peninsula, owing to poor water treatment of the sewage/household wastewater discharged from the river basin area.

Keywords: Ion-exclusion/cation-exchange chromatography, Urban drainage river, Malaysia

Introduction to the author:

Dr. Daisuke Kozaki
Faculty of Industrial Sciences and Technology, University Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang Kuantan, Pahang Darul Makmur, Malaysia
Tel: +60-9-549-2413; Fax: +60-9-549-2766; E-mail: daisuke@ump.edu.my

Biography of the authors:

Current research interests are the development of the water quality monitoring methods by using ion chromatography (IC) / high performance liquid chromatography (HPLC) and that application to the environmental monitoring in developed and developing countries.

OL.05

Analytical Applications of Higher-order Calibration Methods Based on Alternating Multilinear Decomposition Algorithms

Hai-Long WU* and Ru-Qin Yu

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

Abstract:
Higher-order calibration methods based on multilinear models in chemometrics are gaining more and more attention in the field of analytical science. Based on the “mathematical separation”, higher-order calibration methods enable one to achieve direct quantitative analysis of analytes of interest in complex systems even in the presence of unknown, uncalibrated interferents, which is also known as the “second-order advantage”. Additionally, higher-order calibration methods can provide some other advantages, such as higher selectivity and sensitivity. In this work, higher-order calibration methods based on alternating multilinear decomposition algorithms are firstly introduced and its general procedure, by using a simulated EEMs data array, is illustrated. Secondly, the analytical applications of these higher-order calibration methods in such sciences as environment, food, biology, medicine are provided. Finally, some case studies to further illustrate the practical analytical applications of second-order and third-order calibration methods were provided.

Keywords: Higher-order calibration; Mathematical separation; Alternating multilinear decomposition; Multilinear model; Second-order advantage; Direct quantitative analysis; Complex system; Chemometrics

Acknowledgements: The authors gratefully acknowledge the National Natural Science Foundation of China (Grant No. 21175041, 21575039) and the National Basic Research Program (No. 2012CB910602) for financial supports.

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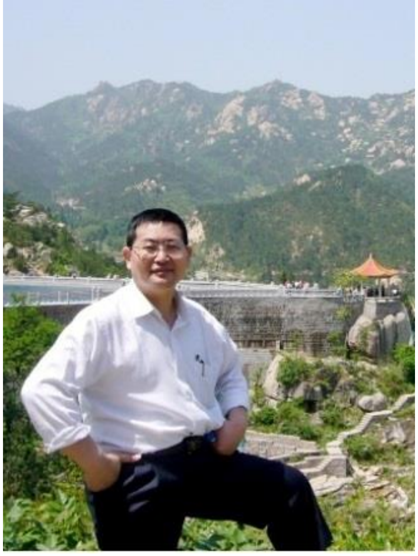

Professor Hai-Long WU

Prof. Dr. Hai-Long WU
State Key Laboratory of Chemo/Biosensing & Chemometrics
College of Chemistry and Chemical Engineering
Hunan University
Changsha 410082, China
===
Tel/Fax: +86(731) 88821818
E-mail: hlwu@hnu.edu.cn; hlwu529@gmail.com

Dr. Hai-Long Wu, born in 1961, is a Professor of Analytical Chemistry of the College of Chemistry and Chemical Engineering at Hunan University since 1999 and the Former Director of the State Key Laboratory of Chemo/Biosensing & Chemometrics (Hunan University). He received his BS in 1982, M Sc in 1985 and Dr Sc in 1992 in Analytical Chemistry from Hunan University. he worked at Hunan University during 1985-1993, then went to Japan and received his Dr Eng in Applied Chemistry from Chiba University (Japan) in 1998. Dr. Wu has published over 200 papers in chemometrics and chemical sensors in international journals. He was a winner of The Second Prize of the National Natural Sciences Award of China in 2003 and a winner of the Liang Shuquan's Award on Fundamental Research in Analytical Chemistry from The Chinese Chemical Society.

OL.06

Preparation and Application of Microextraction Probe for Enrichment of Organics from Aqueous Matrices

Hai-Fang Li, Guilan Huang, Jin-Ming LIN*

Department of Chemistry, Beijing Key Laboratory of Micronalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, China.
Corresponding author email:jmlin@mail.tsinghua.edu.cn

Abstract Fiber-based microextraction has dominant advantages for sample pretreatment by integrating sampling, extraction, and GC or LC sample introduction into one step. In recent years, fiber microextraction is generally represented by solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) [1, 2]. The former works by extraction of analytes from liquid solution onto the fiber's solid surface coating, while the latter is realized by immobilizing organic solvent inside the porous membrane of hollow fiber serving as the acceptor phase. In our work, different fiber-based microextraction methods were developed for rapid extraction of trace organic components from aqueous matrices. The poly(ethylene glycol) diacrylate (PEG-DA) coated glass fiber and multilayer-graphene bonded titanium fiber were fabricated, which presented excellent stability and extraction efficiency [3, 4]. The multilayer-graphene modified fiber could stand up for more than 200 SPME cycles. In addition to SPME methods, the polypropylene hollow fiber was directly used for LPME. Strong hydrophobic organic solvent was injected into the hollow fiber and held by the porous membrane. Dynamic hollow fiber LPME demonstrated good extraction ability with toluene as extraction phase for extraction of organic UV filters in cosmetic products [5]. To increase the extraction speed and efficiency, short hollow fiber immobilized with organic solvent was vortex microextraction of phthalate esters from aqueous matrices [6]. With the extraction solvent lost gradually from the hollow fiber during stirring, the efficient extraction was maintained by the absorption of analytes in the porous membrane. The super high enrichment factor over 1500 was obtained for phthalate esters and reduced the limit of detection as low as ng L^{-1} level with chromatographic analysis.

This work was supported by National Natural Science Foundation of China (21275088, 21227006).

Keywords: Fiber probe, solid-phase microextraction, liquid-phase microextraction

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Biography of the author

Dr. Haifang Li
Department of Chemistry, Tsinghua University, Beijing, China
Tel: +86-10-62797463
E-mail: lihaifang@mail.tsinghua.edu.cn

Dr. Hai-Fang Li got her PhD degree in the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences in 2005, then as a postdoctoral follow at the Department of Chemistry in Tsinghua University during 2005-2007. She is currently a senior engineer special for mass spectrometers. She is the author and co-author of 72 research papers published in international journals. She interests in sample pretreatment and chromatography /mass spectrometry analysis.

OL.07

Multifunctional fluorescent optical sensors for bioanalysis

Yanqing Tian

Department of Materials Science and Engineering, South University of Science and Technology of China

Abstract: Optical sensors are important tools for cellular imaging and analysis, for probing cellular metabolism, for understanding pathways and biological and physiological processes, and for diagnosing diseases and cancers. We have developed several series of fluorescent optical sensors (pH, oxygen (O_2), potassium ion (K^+), and glucose sensors) suitable for intracellular and/or extracellular imaging and analysis.

We integrated individual sensors as dual sensors using polymeric synthesis techniques for simultaneous multi-parameter measurements. Of particular value for application in the complex biological environment, some of the sensors emit two or even three colors in response to the same excitation wavelength, enabling ratiometric measurements and providing superior measurement accuracy. For example, we have prepared a dual pH/O_2 sensor with three emission colors. The tri-color sensor composed of a blue emitter as an internal build-in reference probe, a green emitter as the pH probe, and a red emitter as the oxygen sensor. The build-in reference probe is unresponsive to pH or O_2. It was demonstrated that this polymer-based tri-color sensor is capable for measuring the changes of pH and oxygen concentrations in photosynthesis cyanobacteria possessing high autofluorescence. We also integrated glucose and oxygen sensor as ratiometric dual glucose/oxygen sensors for analysis the glucose and oxygen consumption for bacterial cells and mammalian cells in real time. This dual glucose/oxygen sensor enables simultaneous measurement of glucose and oxygen, providing important information for continuous monitoring of glucose, diagnosing diabetes and hypoxia (low oxygen) related diseases and cancer, as well as the understating of biological processes of the metabolism.

Keywords: pH sensors, oxygen sensors, glucose sensors, dual sensors

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Introduction to the author:

Professor Dr. Yanqing Tian
Department of Materials Science and Engineering, South University of Science and Technology of China No 1088, Xueyuan Rd., Xili, Nanshan District, Shenzhen, Guangdong, China 518055
Tel: +86-755-88018997; Fax: +86-755-88018904.
E-mail: tianyq@sustc.edu.cn

Biography:

Yanqing Tian received his B.S. and M.S. degrees from the Department of Organic Chemistry, Jilin University (China) in 1989 and 1992. In 1995, he received his Ph.D. degree in Polymer Chemistry and Physics from Jilin University. He had been working at Jilin University as an associate professor, Sagami Chemical Research Center as a STA Fellow, Tokyo Metropolitan University as a JSPS Postdoc Fellow, University of Washington as a postdoc and then an acting instructor, and the Biodesign Institute at Arizona State University as an assistant research professor and then an associate research professor. He is now working at South University of Science and Technology of China as a professor. His research interests include synthesis and applications of functional materials like optical sensors and block copolymers for bio-sensing, bio-imaging and drug delivery; nanostructured block copolymer for improving non-linear optical materials’ co-efficiency and for enabling the application of hydrophobic two-photon absorbing materials for sensing and imaging in biological conditions; and nanostructured photo-isomerizable liquid crystals. In the analysis research field, he has led his team for developing various types of fluorescent biosensors including pH sensors, oxygen sensors, zinc ion sensors, glucose sensors, and potassium ion sensors as well as their integrated multifunctional materials for cell metabolism understanding and disease diagnosis. He has co-authored 110 refereed papers and has 3 issued patents.

OL.08

Development of a Hybrid Pyrolyzer for GAS CHROMATOGYAPHY

Naoki Oguri*, Toshio Tsuchiya, Kaoru Enokido, Tamami Takeda and Akira Onishi
Japan Analytical Industry Co., Ltd.

Abstract:

We have been developing chromatographic instruments, for instance, Curie point pyrolyzers Curie point purge and trap samplers, recycling preparative HPLC and those related attachments since 1965. On this occasion, the 50th anniversary, we have pioneered the hybrid pyrolyzer in the world.

The pyrolyzer can be pyrolyzed polymer sample by furnace or Curie point heating by selection of the heating method.

Also, it can be used for evaluated gas analysis (EGA) for the polymers with temperature rising as like as termogravimetry heating. And more, evaluated gas can be trapped into the mini-PAT (packed Tenax GR) according with interest. After trapping the mini-PAT can be desorbed and re-injected into the GC by Curie point heating in order to composition analysis of the peak.

Application for the polymer characterizations will be presented.

Keywords: Curie point pyrolyzer, furnace pyrolyzer, hybrid pyrolyzer

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大栗直毅、武田珠余、遠藤　誠、土屋俊雄、分析化学、Vol. 62, No. 7, 699(2013)

Introduction to the author:

Dr. Naoki Oguri
208 Musashi, Mizuho, Tokyo 190-1213 Japan
Tel: +81-42-557-2331; Fax: +81-42-557-1892
E-mail: n-oguri@jai.co.jp

OL.09

Facile preparation of a novel benyl imidazolium ionic liquids hybrid monolithic column for residue analysis of nitrogen-heterocyclic pesticides by CEC

Yan Huang, Yankai Chen, Yanxia Tang, Xiaoping Wu*

MOE Key Laboratory of Analysis and Detection Technology for Food Safety; College of Chemistry, Fuzhou University, Fuzhou, China

Abstract: Recently, hybrid organic-silica monolithic column have received much attention in capillary electrochromatography (CEC) and LC, due to their unique advantages of easy fabrication, pH stability, and less shrinkage [1]. C18-incorporated organic-silica monolithic column was introducd as a prevalent separation media by Malik and coworkers [2] for RP CEC separation of the majority of non-polar and weak-polar organic compounds. However, in the case of polar and charged compounds, the selectivity of C18 stationary phase is not that ideal due to the lack of more retention mechanisms.

Nitrogen-heterocyclic pesticides are a type of broad-spectrum and polar insecticides or fungicides which are widely used to control plant diseases. Since discovering its chronic mammalian toxicity such as infertility, maximum pesticide residue limits (MRLs) have been reduced. Efficient separation and determination of nitrogen-heterocyclic pesticides residue in the plants, water and soil is significant to keep foodsafety and human health.

Herein, a simple thermal-treatment “one-pot” approach for the preparation of hybrid capillary monoliths with mix-mode interaction mechanisms was developed via a sol–gel process, by using tetramethoxysilane and vinyltrimethoxysilane as precursors and 1-vinylbenzyl-3-methylimidazolium tetrafluoroborate (VBIM) as functionalized monomer respectively, in the presence of porogenic agents (PEG and urea). The effects of the ratio and content of reaction mixture, composition of porogenic solvent and initiator, on the morphology and column performances of the hybrid monoliths were investigated. The resulting monolith showed uniform monolithic network, high permeability and thermal/mechanical stability. It exhibits a typical reversed-phase chromatographic behavior with the controllable EOF over a wide pH range, owing to the incorporation of ILs, which could be used for the separation of various neutral, basic and polar analytes by CEC. A column performance varying from 84,000 to 106,600 N/m was achieved for alkylbenzenes.

Based on a mix-mode retention mechanism of hydrophobic interaction and weak interaction, especially electrostatic interaction between organic and inorganic parts, the proposed VBIM- hybrid monolithic column has been applied for the residue analysis of nitrogen-heterocyclic pesticides in vegetables by CEC. Under the optimum conditions, rapid separation of six nitrogen-heterocyclic pesticides was achieved within 10 min, with an interday RSD less than 6.5%. The linear range was 0.5 - 100 mg/L and the LODs ranged from 0.05 to 0.2 mg/L. This method was successfully applied to the determination of nitrogen-heterocyclic pesticides in vegetables with satisfying recoveries. The result in comparative experiment agrees well with that of HPLC. This research provides a novel separation medium and feasible method for the high-efficient analysis of nitrogen-heterocyclic compounds with different physical properties.

Keywords: capillary electrochromatography, ionic liquids hybrid monolithic column, nitrogen-heterocyclic pesticides

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Acknowledgements:

This work was supported by National Natural Science Foundation (Grant No. 21375019), and National Instrumentation Program (2011YQ150072) of China.

**Introduction to the author:*

Professor Dr. Xiaoping Wu
College of Chemistry, Fuzhou University, Fujian, China
Tel & Fax: +86-591-22866131.
E-mail: wapple@fzu.edu.cn

Biography of the authors.

Dr. Xiaoping Wu is a Professor of Analytical Chemistry at Fuzhou University (China). She joined Fuzhou University in 1997, and received Ph.D. degree in Physical Chemistry from Fuzhou University in 2002. Aferwards she worked as a postdoc at Fudan University, Unimicro Tech. Inc. and Vrije Universiteit Brussel, respectively. Her research interests cover capillary electrochromatography, ionic liquids-based monoliths, biomimetic electrochemical sensors, and their application in foodsafety and environmental analysis. She has published more than 60 papers in these area. She is a member of the International Society of Electrochemistry and the Chinese Chemical Society.

OL.10

New strategies for the functionalization of polymer monolith and applications to separation and preconcentration of organic compounds

Haijiao Zheng, Gang Chen, Qiong Jia*

College of Chemistry, Jilin University, Changchun, 130012, China

Abstract: Polymer monolith column is a new type of miniaturized sample pretreatment strategy based on in-tube solid phase microextraction. As an extraction medium, organic polymer monolith column has several advantages of good biocompatibility, high enrichment efficiency, simple preparation process, wide pH range, and little sample consumption, etc. It combines concentration, extraction, separation, purification, moreover, it is rapid, sensitive, simple operation, and easy to realize automation. However, it has some disadvantages, such as swelling in organic solvent and decreasing mechanical stability, which may affect its life.

Macrocyclic compounds have a variety of applications, such as molecular recognition, supramolecular self-assembly, and bionic materials. In recent years, they have been applied in the enrichment of material and has developed very rapidly. Cyclodextrin and cucurbituril are representatives of macrocyclic compounds, both of which have cavities and can easily form host guest compounds. Hydrogen bond, hydrophobic, and π-π interactions may exist between them and other compounds. In addition, they both have a variety of functional groups on the surface, which makes them easily modified. In the present study, cyclodextrin and cucurbituril were employed for the modification of organic polymer monolithic column and used as enrichment materials. The modified polymer monolithic columns were coupled with chromatography and applied to the determination of organic compounds in food, environment, and biological source.

Keywords: Polymer monolith, functionalization, preconcentration

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Introduction to the author:

Professor Dr. Qiong JIA
College of Chemistry, Jilin University, Changchun, 130012, China
E-mail: jiaqiong@jlu.edu.cn

Prof. Jia, born in 1974, obtained her PhD degree in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences in 2003. Her research interests focus on separation and preconcentration methods. She has published about 100 scientific papers in this area.

OL.11

Electrodialytic Matrix Isolation and Preconcentration for Ionic Solutes

Shin-Ichi Ohira*, Takayuki Yamasaki, Kei Toda

Department of Chemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

Abstract: Ionic solutes determination is widely applied for an evaluation of environmental and human health conditions, and industrial products. The determinations can be achieved with fully automated instruments such as ion chromatography (IC), high performance liquid chromatography (HPLC), induction coupled plasma (mass) spectrometry and so on. However most of samples cannot be directly introduced into the instruments because of hard matrices which may interfere the analysis or break the instruments. Most of cases, sample pretreatment, which removes matrices to purify the sample, was applied to every sample batchwisely. Previously, we have developed electrodialytic matrix isolation system for ionic solutes analysis [1–3]. The developed ion transfer device for matrix isolation was consisted with five solution flow channels separated with ion permeable membranes. Ionic solutes are selectively and quantitatively transferred from a sample into acceptor solutions, typically purified water. Non-ionic compounds, particulates, and proteins are not transferred. Based on the quantitative ion transfer, the enrichment of ionic solutes in sample was also achieved with a higher sample flow rate and smaller acceptor solutions. This in-line preconcentration can be applied to determine trace analyte without highly sensitive analytical instruments.

Tap water disinfection is generally achieved by addition of sodium hypochlorite. However, it is also reported that more than 600 kinds of byproducts such as trihalometanes, and chloroacetates are generated. These by-products cause cancers or liver damage. In Japan, the quality standards for tap water was set as 0.02, 0.04, and 0.2 mg L^{-1} for monochloroacetic acid (MCA), dichloroacetic acid (DCA) and trichloroacetic acid (TCA), respectively. Chloroacetates in tap water are measured with gas chromatograph–mass spectrometry (GC–MS), GC–electron captured detector (ECD), and high performance liquid chromatography–MS (HPLC–MS) for the evaluate tap water safety. Chloroacetes can also be measured with an ion chromatography (IC) with conductivity detection, and a HPLC with UV absorbance detection. However, the limits of detections of the IC or HPLC-UV for the compounds is not enough to detect the quality control levels.

In the present study, we have tried to determine chloroacetic acids in drinking water with conventional IC with UV absorbance detection. The sample, drinking water, was introduced into the electrodialytic ion transfer device without any pretreatment. Obtained acceptor solution was directly introduced ion chromatography system. Because chloroacetic acids are weak acids and relatively larger sample flow rates are required for in-line enrichment, larger applied voltage (~50 V) was required for the quantitative transfer and enrichment. The obtained limits of detection (LOD) with x10 in-line enrichment was 0.004, 0.003, and 0.02 mg L^{-1} for MCA, DCA, and TCA, respectively. These values were enough to detect Japanese quality standard for tap water. The recoveries were studied with real tap waters (*n* = 5). The obtained recoveries were 89~110%.

Keywords: Matrix isolation, electrodialysis, preconcentration, haloacetic acids

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Introduction to the author:

Dr. Shin-Ichi Ohira
Department of Chemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860–8555, Japan. Tel: +81–96–342–3384; Fax: +81–96–342–3384.
E-mail: ohira@sci.kumamoto-u.ac.jp

Biography of the authors.

Dr. Ohira received his Bachelor (2000), Master (2002), and Doctor (2005) of Science degrees from Kumamoto University. He served as Research Fellow for Young Scientists of the Japan Society for the Promotion of Science (JSPS) at Kumamoto University (2005 – 2006), Postdoctoral Fellow for Research Abroad of JSPS at Texas Tech University (2006) and The University of Texas at Arlington (UTA) (2007−2008), and Postdoctoral Research Fellow at UTA (2008−2009). He was promoted to his present position in 2009. He received Awards for Younger Researchers from the Japan Association for Flow Injection Analysis (2012), Ion Chromatography Discussion Group of the Japan Society for Analytical Chemistry (JSAC) (2012), and the JSAC (2013). His current research interests are the developments of novel analytical devices for flow-based electrodialytic ion transfer between solution phases, trace gas detection with metal organic frameworks, and detection on HPLC.

OL.12

Antioxidant Activity of Volatile Compounds Isolated from Broccoli (Brassica oleracea L.) sprouts by GC and GC-MS

Hae Won Jang

Food Analysis Center, Korea Food Research Institute, Korea

Abstract: Broccoli (Brassica oleracea L.) sprouts have received much attention recently because they contain various bioactive constituents, which are not present in broccoli. However, there are no reports on the biological activity of the volatile compounds from broccoli sprouts. In the present study, volatile extracts of broccoli sprouts were obtained by a steam distillation under reduced pressure, followed by a liquid–liquid continuous extraction and then examined for their antioxidant activities using aldehyde/carboxylic acid and lipid/malonaldehyde (MA) assays. All samples exhibited dose-dependent antioxidant activity. The antioxidant activity ranged from 74.5 ± 0.5% (less volatile sample) to 99.5 ± 0.5% (volatile sample) at the level of 500 μg/mL. Antioxidant activity of samples obtained from broccoli sprouts was comparable to that of known antioxidants, α-tocopherol and BHT. Subsequently, volatile extracts were analyzed by gas chromatography and gas chromatography–mass spectrometry to identify principle antioxidants. Among the 43 compounds positively identified by gas chromatography/mass spectrometry, 4-methylpentyl -isothiocyanate (2.48 μg/g) was found in the greatest concentration, followed by 4-methylthiobutylnitrile (10.63 μg/g), 5-methylthiopentylnitrile (31.64 μg/g), 3-methylthiopropylisothiocyanate (3.00 μg/g), and 4-methylthiobutylisothiocyanate (14.55 μg/g). These isothiocyanates are known to possess antioxidant properties. Possible phenolic antioxidants found are 4-(1-methylpropyl)-phenol (0.012 μg/g), 4-methylphenol (0.159 μg/g) and 2-methoxy-4-vinylphenol (0.009 μg/g). The present study demonstrates that broccoli sprouts are a good source of natural antioxidants.

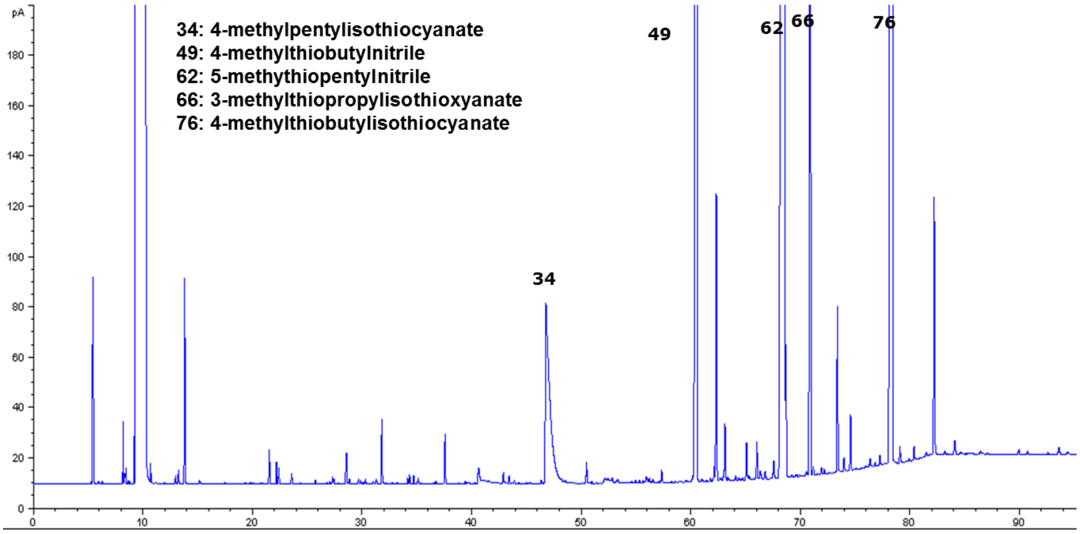

Figure 1. GC Chromatograms of cholesterol in infant formulas using GC/FID.

Keywords: broccoli sprouts, isothiocyanates, natural antioxidants, volatile compounds

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Introduction to the author:

Dr. Hae Won Jang
Food Analysis Center, Korea Food Research Institute, 463-746, Korea
Tel: +82-31-780-9377; Fax: +82-31-780-9280.
E-mail: hwjkfri@kfri.re.kr

Biography of the authors.

Dr. Hae Won Jang has obtained Ph.D. in agriculture and environmental chemistry at University of California, Davis in 2013. After the graduation, she has been working in Food Analysis Center at Korea Food Research Institute. Her research and interest areas include biological and chemical studies on extracts from natural plants and maillard reaction systems.

OL.13

Electrothermal vaporization or atomization on tungsten coil for analytical atomic spectrometry

Xue Jiang,[a] Chenghui Li,[a] Xiaoming Jiang,[b] Zhou Long,[b] Xiandeng Hou*[a,b]

[a] Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China;
[b]Analytical & Testing Centre, Sichuan University, Chengdu, Sichuan 610064, China
* Corresponding author. Tel. & Fax: (+) 86-028-8540518; E-mail: houxd@scu.edu.cn.

Tungsten coil device has been used in analytical atomic spectrometry for approximately 40 years for sample vaporization or atomization (1). These vaporizers/atomizers can be easily electrically heated up to over 3000 K at very high heating rates, with a simple power supply, and the whole device can be very compact. Here we report our recent work using tungsten coil as an electrithermal vaporizer for sample vaporization into atomizers such as new plasmas and flames, and as an atomizer or excitation source, for atomic spectrometry (2,3).

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OL.14

Functionalized Gold-Nanomaterials Fluorescence Probe for Cyanide Detection

Dongtao Lu; Guomei Zhang, Chuan Dong, Shaomin Shuang*

Institute of Environmental Science , College of Chemistry and Chemical Engineering,
Shanxi University, Taiyuan 030006, China.

Abstract: Cyanide is the most-concerning toxic anion due to its severe environmental pollutants and adverse health effects. The World Health Organization (WHO) has set the maximum permissive level of cyanide in drinking water at 1.9 μM . Fluorescent method for the detection of cyanide exhibited many advantages over other optical methods such as high sensitivity, easy operation, and multiplicity of measurable parameters.

Gold nanomaterials have been favorably adopted to design novel sensors by fluorescent methods due to their ultra small size, nontoxicity, and high fluorescence. We investigate a series of gold nanomaterials fluorescent sensor for the detection of cyanide in aqueous solution. Lysozyme stabilized gold nanoclusters (Lys-AuNCs) have been synthesized and utilized as a fluorescence probe for selective detection of cyanide (CN-). Lys-AuNCs had an average size of 4 nm and showed a red emission at 650 nm (λex=370 nm). The fluorescence intensity was linear with the CN^- concentration in the range of 5.00×10^{-6} M ~1.20×10^{-4} M with a detection limit as low as 1.9×10^{-7} M. Simultaneously, the Lys-AuNCs could be visualized with the naked eye for CN^- which might etch with Lys-AuNCs resulted in an obvious color change from light yellow to colorless under visible light (Fig.1A). N-acetyl-L-cysteine modified gold nanoparticles（NAC-AuNPs）for CN^- detection in aqueous solution have been designed, synthesized, and characterized. NAC-AuNPs showed a red emission at 690nm (λex=370 nm) and an average size was about 3 nm measured by TEM. An excellent sensitivity fluorescence probe of NAC-AuNPs for CN^- in aqueous solution was developed ranging from 1.0×10^{-7}M~1.1×10^{-6}M, with a detection limit of 6.4×10^{-8}M. In addition, the NAC-AuNPs probe possessed a good selectivity for CN^- over other common anions and was expected to be great candidate for CN^- detection in food, water and biological applications (Fig.1B). In summary, Au nanomaterial could be a novel fluorescence probe for CN^- and might be a great candidate for sensing applications in environmental analysis and fluorescence imaging.

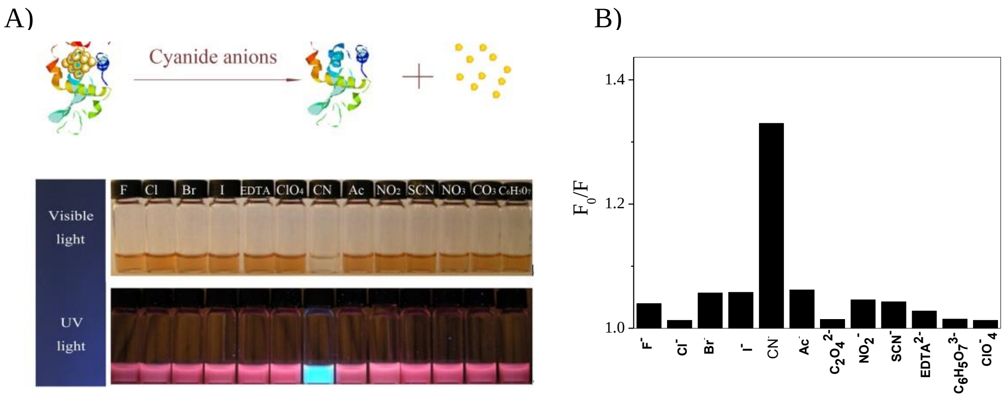

Fig.1 (A) The color (top) and the fluorescent (bottom) changes of Lys-AuNCs solution to different anions ions (concentration of all the anions ions was 3mM). (B)Selectivity of NAc-AuNPs-based sensor for CN^- (50μM) over other anions (50μM) at pH of 12.

Keywords: gold nanoparticles, cyanide detection, fluorescence probe

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Introduction to the author:

Dr. Lu Dongtao, Institute of Environmental Science, Shanxi University, Taiyuan, China
Tel: +82-351-7018525; Fax: +82-351-7011011.E-mail: ludongtao@sxu.edu.cn
Corresponding author: Prof. Shaomin Shuang, College of Chemistry and Chemical Engineering
Tel: +82-351-7018842; Fax: +82-351-7011011.E-mail: smshuang@sxu.edu.cn

Biography of the authors.

Dongtao Lu received his bachelor’s degree in biology and master’s degree in hydro-biology in 2004 and 2007 from Shanxi University, respectively. He obtained his PhD degree in environmental at Shanxi University in 2014. His research focuses on the synthesis of metal nanomaterials and development of chemical or bio-sensors.

Guomei Zhang received her BSc degree from the Shanxi University of China(Taiyuan) in 1997, her MSc degree and PhD degree in analytical and inorganic chemistry in 2003 and 2006 from Shanxi University, respectively. She joined the Chemistry Faculty of Shanxi University in 2006, and master tutor at Shanxi University since 2008 and has been a professor in 2014. Her current research interests include the DNA assembly and photoluminescence analysis of nanomaterials.

Shaomin Shuang received her BSc degree in chemistry and MSc degree in analyticalchemistry in 1986 and 1989 from Shanxi University, respectively, and PhD degree in1998 from South China University of Technology. She joined the chemistry faculty of Shanxi University in 1989, and has been a professor at Shanxi University since2002. Her current research interests include analytical chemistry and development of biosensors and chemosensors.

Chuan Dong is a professor of analytical chemistry at Shanxi University. He obtained his PhD degree at Shanxi University in 2002. Dong has published over 200 papers and 100 patents and his current research interests are biosensors, chemosensors, optical fiber sensor, fluorescence and room temperature phosphorescence, and environ-mental analysis and monitoring.

OL.15

Determination of silicate, borate and carbonate ions in natural waters using ion-exclusion chromatography coupled with charged aerosol detector

Nobutake Nakatani*[1], Yu Otsuka[1], Takuya Takahashi[1], Daisuke Kozaki[2], Masanobu Mori[3], Kazuhiko Tanaka[3]

[1]College of Agriculture, Food and Environment Sciences, Rakuno Gakuen University, [2]Faculty of Industrial Sciences and Technology, University Malaysia Pahang, [3]Graduate School of Science and Technology, Gunma University

Abstract: Weak inorganic anions of silicate, carbonate and borate ions are the important ionic species in biogeochemical cycles of silicon and carbon, and the water pollutants. In the natural waters, these anions are presents in partially dissociated or un-dissociated forms. In general, these ionic species are separately determined by the spectrophotometry or the titration method. Ion-exclusion chromatography (IEC) was developed as conventional method for separation of weak acid anions and was applied as a method for water quality monitoring [1]. Charged aerosol detector (CAD) has become useful in the analytical chemistry field and has been applied as a detector for liquid chromatography [2]. In this presentation, we introduces about the determination for weak inorganic anions of silicate, borate and carbonate ions using IEC coupled with Corona® CAD. Silicate and borate ions were separated and detected using the ultrapure water as an eluent and the addition of acetonitrile to the elution made the sensitivity for both ions higher. Carbonate ions could not detected due to the degradation into carbon dioxide during the drying process to form particles in CAD. By connecting a cation-exchange column in the K^+-form after the ion-exclusion separation, weak inorganic anions including carbonate ions could be converted to their potassium salts and detected by CAD within 15 min. The present method was successfully applied to the analysis of weak inorganic anion in natural water samples.

Keywords: charged aerosol detector, ion-exclusion chromatography, weak inorganic anions

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Introduction to the author:

Associate Professor Dr. Nobutake Nakatani
College of Agriculture, Food and Environment Sciences, Rakuno Gakuen University, 582 Bunkyodai-Midorimachi, Ebetsu, Hokkaido 069-8501, Japan
Tel & Fax: +81-11-388-4714.
E-mail: nakatani@rakuno.ac.jp

Nobutake Nakatani earned his Ph.D. from Hiroshima University in 2004. He was postdoctoral fellow in Hiroshima University under Professor Dr. Kazuhiko Tanaka and studied ion chromatography. Since 2009, he has been an associate professor of the College of Agriculture, Food and Environment Sciences at Rakuno Gakuen University.

OL.16

Hairpin DNA Template-based Copper Nanoparticles for the Detection of NAD$^+$

Jianzhong Lu
School of Pharmacy, Fudan University, 826 Zhangheng Road, Shanghai, China

Ultra-small metal nanoparticles are recognized as a promising alternative to organic fluorophores and quantum dots as they have unique physical, electrical, and optical properties. With regard to metal nanofabrication, DNA has proven an excellent template for fluorescent metal nanoparticles due to its unique nano-sized structure, excellent programmable properties, and great affinity for several metal ions. For example, DNA-templated gold, silver, palladium, platinum, and copper nanoparticles (CuNPs) are highly suitable for signal amplification due to their facile synthesis, ultrafine size, low toxicity, and photophysical properties. In the specific case of CuNPs, both double-stranded DNA (ds DNA) and single-stranded poly-thymine (ss poly T) can serve as templates. Herein, we propose a strategy utilizing hairpin-structured DNA as an efficient template for the formation of fluorescent CuNPs. A label-free analytical system based on this novel hairpin template demonstrated excellent sensitivity for the quantitative detection of NAD$^+$.

PT.01

Development of Inkjet Printing Single-cell Technology to Electrospray Ionization for Mass Spectrometer

Fengming Chen, Shiqi Wang, Ziyi He, Hai-Fang Li, Jin-Ming LIN*

Department of Chemistry, Beijing Key Laboratory of Micronalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, China.
Corresponding author email: jmlin@mail.tsinghua.edu.cn

Abstract Single cell analysis has become an important field of research in recent years, high-throughput single cell measurements of cellular responses are of great importance for a variety of applications, including drug testing, toxicology, and basic cell biology [1-2]. Fluorescence microscope allows us to observe the states of cells before and after stimulation. However, it is difficult to observe signals of a large number of cells under a microscope. Electrospray ionization mass spectrometry (ESI-MS) is a sensitive method with low sample consumption, which is especially suitable for small and even ultra-small volume analysis [3-4]. Unfortunately, many biological samples are very complicated, and the matrices, especially those containing salts, have a significant ion suppression effect, which enormously reduces the sensitivity of Nano-ESI-MS. Moreover, the salts in samples can form complicated compounds through molecular association and coordination, which makes it quite difficult to clearly identify the target compounds in the mass spectrum. It is even worse when using Nano-ESI-MS for the analysis of a single cell owing to its very small sample volume. The inkjet printing technology [5-6] can accurately and reproducibly eject picoliter volumes of droplet, with which we combined tungsten probes for selectively and controllably encapsulating one single target cell into one picoliter-volume droplet. The tungsten probes with a tip were applied for electrospray ionization of mass spectrometry (MS) detection. We report a highly accurate sample injection system to realize the single-cell mass spectrometry based on an inkjet technology.

This work was supported by National Natural Science Foundation of China (nos. 81373373, 21227006, 91213305).

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Biography of the author

Dr. Fengming Chen
Department of Chemistry, Tsinghua University, Beijing, China
Tel: +86-10-62792607
E-mail: chenfengmingok@mail.tsinghua.edu.cn

Dr. Fengming Chen got his PhD degree in Tokyo Metropolitan University in 2013, and then started to work as a postdoctoral fellow at Department of Chemistry, Tsinghua University. He is the author of four research papers published in international journals. Now he is working on drop-on-demand inkjet printing technology for CE /mass spectrometry analysis.

PT.02

Selective removal of cadmium from water samples by bio-functionalized composite MT@C-dot@SiO_2

Yi-Kun Li, Ting Yang, Ming-Li Chen*, Jian-Hua Wang

Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China

Silica gel has been widely used as adsorbent for the removal of heavy metals due to its good mechanical, chemical and thermal stability. However, the silanol groups on the surface of silica gel bind with a variety of metal species and thus result in poor selectivity. In this study, we report a bio-functionalized composite, e.g., MT@C-dot@SiO_2. The composite material provides a favorable adsorption performance toward cadmium and is used for cadmium removal from waters.

Silica gel is modified with metallothionein (MT) to improve the adsorption selectivity through the specific interactions between mercapto group and cadmium. One-step calcination is used to immobilize carbon dots (C-dots) onto the silica gel. The obtained composite shows excellent chemical stability and thus it can be used repeatedly. The MT@C-dot@SiO_2 composite has been characterized by means of FT-IR, SEM and TGA.

The adsorption capability for cadmium by MT@C-dot@SiO_2 is derived to be 304 μg g^{-1} with respect to 178 μg g^{-1} by pure silica gel. Although the improvement on the adsorption capacity for cadmium is not remarkable, while most importantly, the MT@C-dot@SiO_2 composite exhibits very high tolerance capacity to some of the commonly encountered cationic and anionic species in water bodies. When 100 μg L^{-1} cadmium solution is treated by 6 mg of the composite material, an adsorption efficiency of >90% is achieved in the presence of large amount of concomitant species, e.g., 1000 mg L^{-1} of K^+, Na^+, Mg^{2+}, Ca^{2+}, NO_3^-, HCO_3^- and 5 mg L^{-1} of Al^{3+}, Fe^{3+}, Cu^{2+}, Pb^{2+}. In general, the bio-functionalized composite MT@C-dot@SiO_2 is demonstrated to be a promising adsorbent for the selective removal of cadmium from water bodies.

Acknowledgement

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T. Yang, L. H. Liu, J. W. Liu, *J. Mater. Chem*., 22, 21909-21916 (2012)

Introduction to the author:

Professor Dr. Ming-Li Chen
Research Center for Analytical Sciences, Box332, Northeastern University, Shenyang 110819, China
Tel: +86-24-83687659; Fax: +86-24-83687659.
E-mail: chenml@mail.neu.edu.cn

Professor Ming-Li Chen was born in 1979 in Henan, China. She obtained her B. Eng. from College of Chemical Engineering, Zhengzhou University (China), and she was awarded a PhD degree by Northeastern University, China.

Her current research interest is focused on the exploitation of flow analysis protocols and hyphenation techniques, isolation of trace metal species from complex sample matrices.

PT.03

Monitoring the dynamic mass-transferring behaviors of hemoglobin between aqueous/ionic-liquid phases with liquid core optical waveguide system

Xu-Wei Chen*, Xu Yang, Wan-Ying Zeng, Jian-Hua Wang

Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China

Ionic liquids (ILs) is a group of organic salts consisting entirely of ions (anions and cations) and exist in the form of liquid at temperature <100℃. Due to the unique properties such as negligible vapor pressure, nonflammability, high chemical/thermal stability, low toxicity and favorable conductivity, ILs have been termed as green solvents and shown great promise as an attractive alternative or replacement to conventional volatile organic solvents in various fields. The potential of ILs in biological sample pretreatment are also well demonstrated by their extensive applications in the extraction/purification of protein species from complex matrixes. The ILs-based liquid-liquid extraction system not only achieve extraction without deteriorating the activities and configurations of proteins, but also eliminate the risk of protein contamination which might pose adverse effects on the subsequent biological investigations.

As a kind of novel detecting technique, liquid core waveguide could greatly enhance the detection sensitivity of conventional spectrophotometry, by extending optical path length via the formation of total internal reflection (TIR) at the interfaces. The evanescent wave induced by the TIR extend out from the surface of the higher refractive index medium and into the lower index medium, could efficiently interact with the analyte on the liquid-liquid interface, thus offering a powerful tool for real-time monitoring of the local reactions at the core-cladding interfaces, and the dynamic transferring process across the interface.

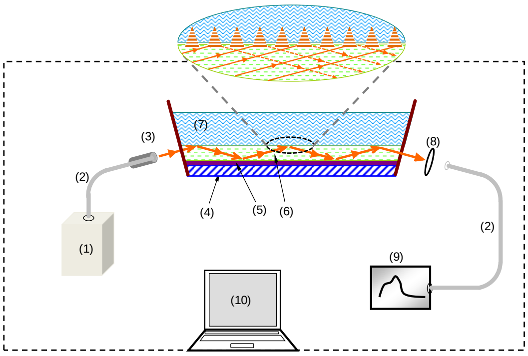

Fig. 1 Schematic diagram of ILs-based liquid core optical waveguide system. 1, Xe arc lamp; 2, optical fiber; 3, collimator; 4, support board; 5, FEP film(RI=1.338); 6, IL BmimPF$_6$ (RI=1.408); 7, protein solution; 8, convex len; 9, spectrometer ; 10, personal computer

We herein develop a solid-cladding/liquid-core/liquid-cladding sandwich optical waveguide system to monitor the dynamic transfer of hemoglobin (Hb) from aqueous phase to ILs phase. The optical waveguide system is fabricated by using a hydrophobic ILs (1-butly-3-methylimidazolium hexafluorophosphate, $BmimPF_6$) as the core, and protein solution as one of the cladding layer (Fig. 1). The monitored spectra by this optical waveguide system indicate that the transferring of Hb molecules consists of the aggregation of Hb on water/ILs interface and the dynamic extraction of Hb into ILs phase, and part of Hb would remain at the interface even after the accomplish of the extraction process. Investigations on the transfer rates of Hb under different pH and concentration suggest that the transferring of Hb from aqueous phase towards IL phase is mainly driven by the coordination interaction between the heme group of Hb and the cationic moiety of imidazolium ILs, and the hydrophobic interactions also contribute to the transferring behaviors of Hb.

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Chen XW, Sakurazawa A, Sato K, Tsunoda KI, Wang JH. Applied Spectroscopy, 66(7): 798-802(2012)

Introduction to the author:

Professor Dr. Xuwei Chen
Research Center for Analytical Sciences, Box332, Northeastern University, Shenyang 110819, China
Tel: +86-24-83687659; Fax: +86-24-83687659.
E-mail: chenxuwei@mail.neu.edu.cn

Dr. Xuwei Chen, Professor of Research Centre for Analytical Sciences at Northeastern University (China), received his PhD degree in July 2007. His current research interests focus on the isolation of trace biomacromolecules from complex biological samples.

Self-assembly sea urchin-like ZnO nanoparticles for headspace thin-film microextraction coupled with SERS to detect sulfur dioxide in medlar

Zhuo Deng[1], Ziming Zhao[1], Yiru Wang[1*], Xi Chen[1,2**]

1. Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
2. State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China
Corresponding author email: yrwang@xmu.edu.cn；xichen@xmu.edu.cn

Abstract:
Self-assembly sea urchin-like ZnO nanoparticles were used for headspace thin-film microextraction (TFME) and coupled with surface enhanced Raman spectroscopy (SERS) to perform a simple and easy operational determination of SO_2 in medlar. After head space sampling (HS), the highly volatile SO_2 was adsorbed and concentrated by the nano ZnO, and the content of SO_2 was then measured using SERS. The method showed good sensitivity and reproducibility. After condition optimization, it was satisfactory that sulfur dioxide concentration and the intensity of SERS shift at 630 cm^{-1} showed a good linearity in the range of 25−800 mg/kg. The detection limit of the method was found to be 15 mg/kg. The real samples analysis by the proposed HS-TFME-SERS method agreed very well with that by the traditional distillation and titration method, showing the method was reliable and applicable for the sulfite analysis in medlar samples. The method has shown great potentials in the fast analysis of sulfite in various sample matrixes such as acid rain, white sugar, and fresh or dried vegetables.

Keywords: Thin-film microextraction ZnO SERS sulfur dioxide

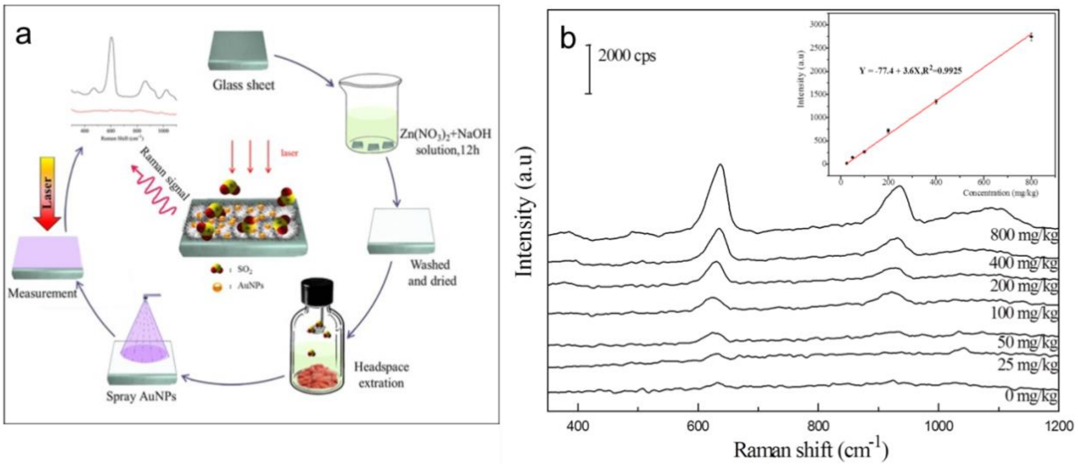

Fig. (a) Schematic illustration of the preparation of self-assembly sea urchin-like ZnO nanoparticles and HS−TFME−SERS analysis of SO_2 in medlar. (b) SERS spectra and working curve of HS-TFME-SERS method for analysis of SO_2 at different concentration. The inset figure presents the simulation curve of SERS peak intensity at 630 cm^{-1}.

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Zhuo Deng
Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University
Xiamen 361005, China
===
Tel/Fax: +86(592) 2184562 E-mail: joydeng2011@163.com

Zhuo Deng graduated from Xiamen University with a Bachelor’s degree of chemistry in 2013. She is currently a postgraduate student at the Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation at Xiamen University, Xiamen. Her research interests are in the fields of pre-extraction materials applied in surface enhanced Raman spectroscopy.

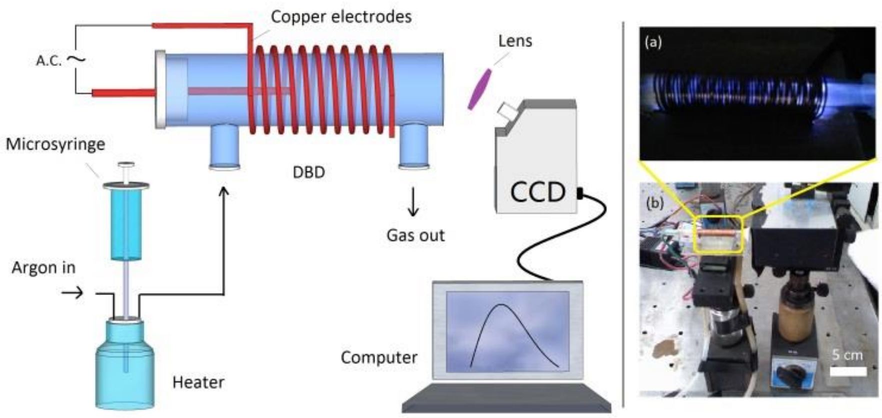
PT.05

Selectively enhanced molecular emission spectroscopy of benzene, toluene and xylene with nano-MnO_2 in atmospheric ambient temperature dielectric barrier discharge

Xue Jiang [1], Chenghui Li[1], Xiandeng Hou[1,2*]

1. Department of Chemistry, Sichuan University, Chengdu, 610064, China
2. Analytical & Testing Center, Sichuan University, Chengdu, 610064, China
Corresponding author email: houxd@scu.edu.cn

ABSTRACT: In this work, nano-MnO_2 was used to selectively enhance molecular emission spectroscopy in an atmospheric ambient temperature dielectric barrier discharge, based on which a portable spectrometer was developed for potential field analytical chemistry of trace benzene, toluene and xylene. Under the optimal conditions, the proposed method has some distinct advantages: (1) high selectivity and sensitivity for detecting BTX; (2) simple, inexpensive and compact instrumentation; (3) green analytical chemistry since no toxic reagent/solvent was used, and the exhaust is of low toxicity or at low concentration; and (4) easy operation and hyphenation to other analytical instruments, such as CE, GC and LC as a detector.



KEY WORDS: dielectric barrier discharge; nano-MnO_2; molecular emission spectroscopy; benzene, toluene and xylene

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PT.06

Synthesis of Highly Fluorescent P-g-C_3N_4 Nanodots for Label-free Detection of Cu^{2+} and Acetylcholinesterase Activity

Mingcong Rong[1], Chunhua Ma[2], Zhaochai Qiu[1], Xi Chen[1]*

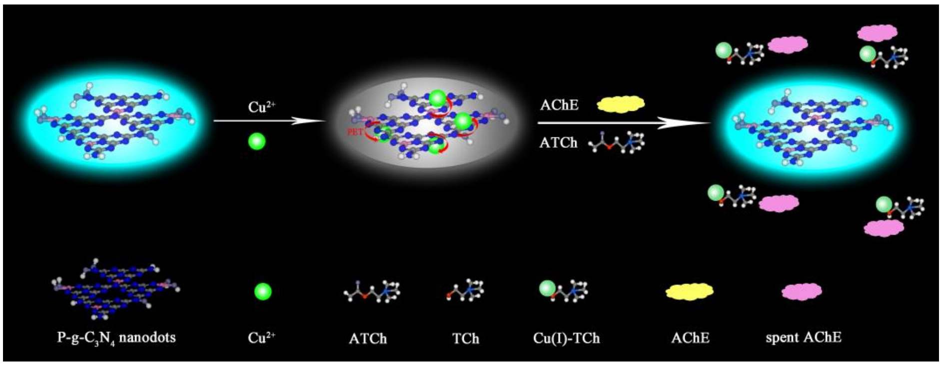
1. Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
2. College of tea and food science, Wuyi University, Wuyishan 354300, China
Corresponding author email: xichen@xmu.edu.cn

Abstract:
Graphitic carbon nitride (g-C_3N_4), a well-known graphene-like carbon-based material, received a lot of attention due to its special structure and properties.[1] In recent year, nanoscale g-C_3N_4 materials, such as fluorescent g-C_3N_4 nanosheets and g-C_3N_4 nanodots, have drawn great attention in sensing[2] and bioimaging[3] because of their excellent optical and physicochemical features. In this report, highly fluorescent phosphorus-doped graphitic carbon nitride nanodots (P-g-C_3N_4 nanodots) were synthesized by chemical oxidation and hydrothermal etching of bulk P-g-C_3N_4 obtained via pyrolysis of phytic acid and melamine. The P-g-C_3N_4 nanodots emitted strong blue fluorescence and displayed high resistance to photobleaching and high ionic strength.

Copper (Cu) is a widely used industrial metal and it is an essential trace element in various biological processes.[4] The excess accumulation of Cu^{2+} in human body causes damage to the central nervous system and induces neurodegenerative diseases such as Alzheimer's disease, Menkes syndrome, amyotrophic lateral sclerosis and Wilson's diseases.[5] Although there are some attractive fluorescence sensors using carbon nanomaterials,[6] it is still essential to develop more simple, rapid and highly sensitive detection methods for Cu^{2+}.Acetylcholinesterase (AChE) is a type of serine esterase in the central and peripheral nervous systems, it regulates the levels of neurotransmitter acetylcholine (ATCh) by catalyzing the hydrolysis reaction of ATCh to choline.[7] Many neurodegenerative diseases including Alzheimer's disease and Parkinson's disease are related to the degeneration of the cholinergic system, resulting in the amount decrease of AChE and ATCh.[8]Though great efforts have been made to detect the activity of AChE, some disadvantages still exist, such as complicated synthesis, high toxicity, expensive cost and long measurement time. Hence, novel label-free, economic, time-saving, high sensitive and selective methods are urgently needed.

Herein, a sensitive and facile fluorescence sensing approach for Cu^{2+} was developed based on theP-g-C$_3$N$_4$ nanodots by photoinduced electron transfer (PET). Under optimal conditions, a rapid detection of Cu^{2+} could be completed in 5 min with a detection limit of 2 nM, and a linearity ranging from 0 to 1 μM. Meanwhile, using acetylthiocholine (ATCh) as the substrate, the fluorescence of the P-g-C$_3$N$_4$ nanodots-Cu^{2+} system could be sensitively turned on in the presence of acetylcholinesterase (AChE) through the reaction between Cu^{2+} and thiocholine (TCh), the hydrolysis product of ATCh by AChE. A linearity ranging from 0.01 to 3 mU/mL could be obtained with a detection limit of 0.01 mU/mL.

Keywords: P-g-C$_3$N$_4$ nanodots; fluorescence; Cu^{2+}; photoinduced electron transfer (PET); acetylcholinesterase (AChE)



Scheme.Schematic illustration of the sensitive and selective fluorescence detection of Cu^{2+} and AChE activity based on the P-g-C$_3$N$_4$nanodots

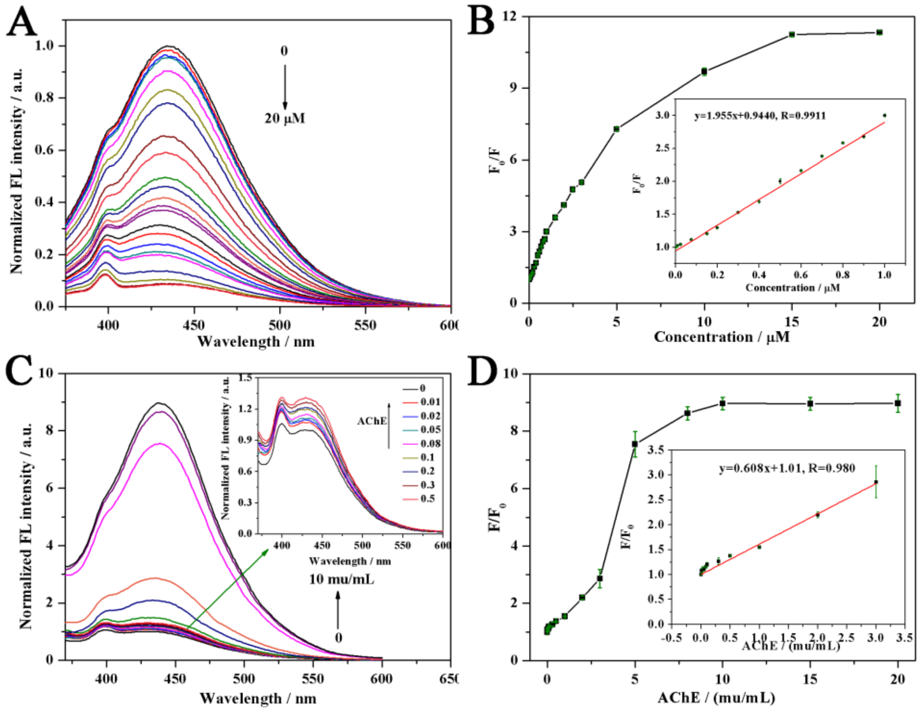


Figure.(A) Fluorescence responses of the P-g-C_3N_4 nanodots in the presence of different concentrations of Cu^{2+} in 10 mM borate buffer (pH 7.0). (B) The relationship between F_0/F and the concentration of Cu^{2+}. The inset figure presents the linear responses to Cu^{2+} ranging from 0 to 1 μM. (C) Fluorescence responses of the P-g-C_3N_4 nanodots in the presence of 15 μM Cu^{2+} and different concentrations of AChE in 10 mM borate buffer (pH 7.0). The inset figure presents the fluorescence responses of the P-g-C_3N_4 nanodots with 15 μM Cu^{2+} at low concentrations of AChE. (D) The relationship between F_0/F and the concentration of AChE. The inset figure presents the linear responses to AChE ranging from 0.01 to 3 mU/mL.

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Mingcong Rong
Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering
Xiamen University
Xiamen 361005, China
===
Tel/Fax: +86(592) 2184562
E-mail: haiyangzhixinrmc@126.com

Mingcong Rong received her M.S. degree from the Department of Chemistry and chemical engineering at the Guangxi Normal University, Guilin. She is currently a Ph.D. student at the Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation at Xiamen University, Xiamen. Her research interests are in the fields of fluorescence biosensor.

PT.07

Simultaneous detection of dihydroxybenzene isomers by HKUST-1 MOF modified electrode

Yizhen Yang, Qingxiang Wang*

College of Chemistry and Environment, Minnan Normal University, Zhangzhou 363000, P. R. China

Abstract: Catechol (CT), resorcinol (RS) and hydroquinone (HQ) are three typical dihydroxybenzene isomers (DBIs) of phenolic compounds, which usually coexist in environmental samples as pollutants.[1] Due to their high toxicity and low degradability in the ecological environment, it is necessary to develop simple and rapid analytical technology for the determination of them. The electrochemical methods attracted increasing attentions due to their advantages of fast response, low-cost, high sensitivity and excellent selectivity.[2] However, because the three isomers of CT, RS and HQ have similar chemical structure and close redox potentials on common electrode, the simultaneous determination of them are usually hardly achieved. Metal-organic frameworks (MOFs) are a type of novel three-dimensional (3D) coordination compounds with the features of controllable synthesis, structural diversity, porosity, high specific surface areas, metal active site richness, and high flexibility of the pore size/wall modification.[3] In this work, we fabricated a novel electrochemical sensing platform for the detection of DBIs through covalent immobilization of the electroactive HKUST-1 MOF on a functional matrix of chitosan (CS)-electrochemically reduced graphene oxide (ERGO) for the first time. The morphology and structure of the obtained materials and sensing interface were characterized using scanning electron microscopy (SEM), and energy-dispersive X-ray spectra (EDS). The results were displayed in Figure 1

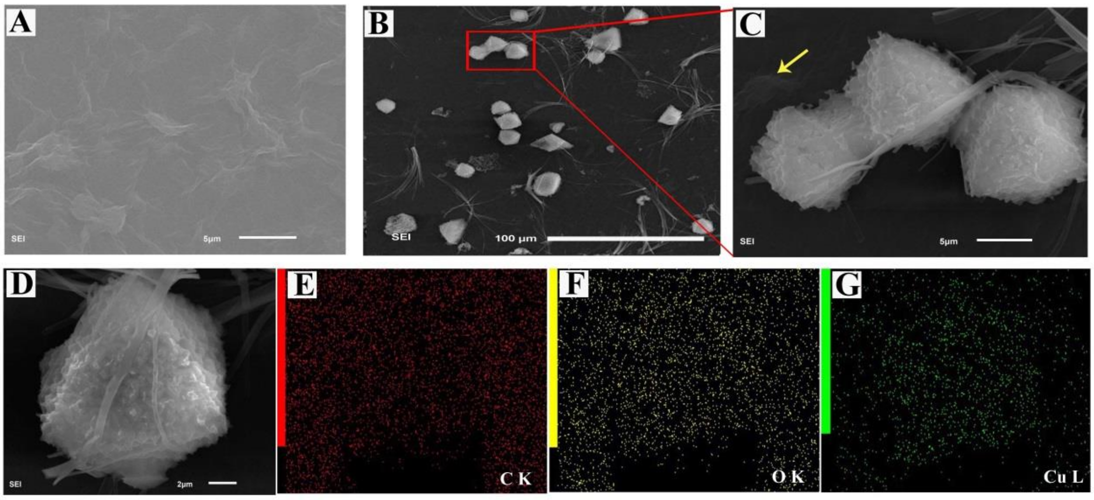

Figure 1 SEM images of CS-ERGO/GCE (A), HKUST-1/CS-ERGO/GCE with low resolution (B) and high resolution (C), SEM (D) and EDS elemental mapping analysis of a single HKUST-1 particle (E-G).

The electrochemical experiments showed that based on the unique porous nature and inherent redox-activity of the Cu(btc) MOF, the three DBIs of RS, CT, HQ can be well separated from each other with a wide peak potential difference (Figure 2A). The oxidation peak currents of HQ, CT and RS increased linearly with the concentration of their own in the ranges of 1.0 to 200 µM (Figure 2B). The regression equation was I_{pa}/µA = - 0.0321 C (µM) - 5.0185 (r = 0.9951) for HQ, I_{pa}/µA = - 0.0256 C (µM) - 8.2104 (r = 0.9900) for CT and I_{pa}/µA = - 0.0171 C (µM) - 2.2899 (r = 0.9918) for RS. The detection limits were estimated to be 0.44 µM, 0.41 µM, and 0.33 µM for HQ, CT and RS, respectively. Also the accurate determination of DBIs in the real samples could be realized by the proposed sensor, which broadens the application of the MOF materials in the analytical fields.

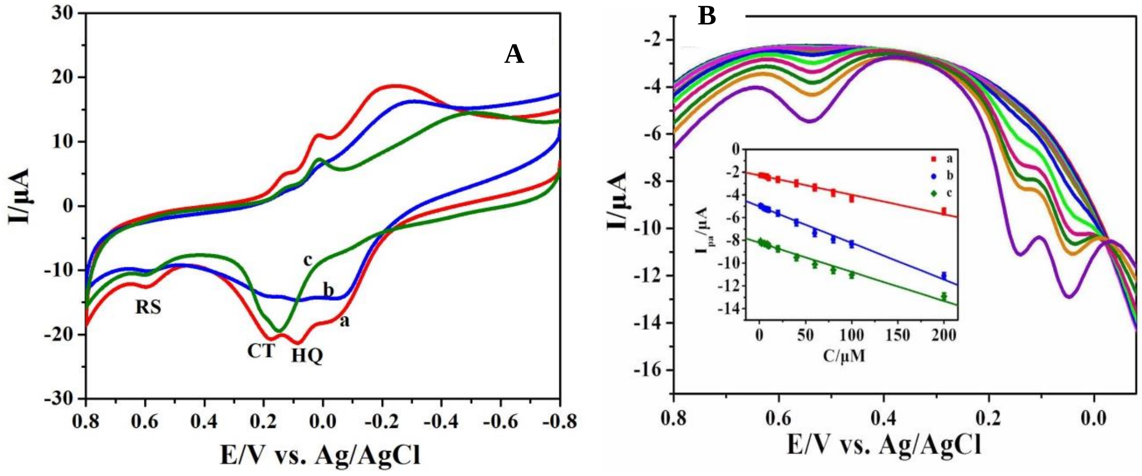

Figure 2 (A) CVs of 0.1 mM HQ, CT and RS mixture at Cu(btc)/CS-ERGO/GCE (a), Cu(btc)/CS-GO/GCE (b) and CS-ERGO/GCE (c) in 25 mM PBS (pH 7.0). (B) DPVs of

the mixtures with increasing HQ, CT and RS at Cu(btc)/CS-ERGO/GCE in 25 mM PBS (pH 7.0). Inset: the plot of I_{pa} versus the concentrations of RS (a), HQ (b) and CT (c).

Keywords: Dihydroxybenzene isomers, Graphene oxide, HKUST-1, Metal-organic frameworks

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Introduction to the author:

Professor Dr. Qingxiang Wang
College of Chemistry and Environment, Minnan Normal University, Zhangzhou 363000, P. R. China
Tel: +86-596-2591445. Fax: +86-596-2520035.
E-mail: axiang236@126.com.

Biography of the authors.

Yizhen Yang is now a master candidate in College of Chemistry and Environment, Minnan Normal University, majoring in electrochemical biosensors.

Qingxiang Wang received his Ph.D. in Applied Chemistry from Qingdao University of Science and Technology in 2007. He now is a professor of the Minnna Normal University. His research interests cover bioelectrochemistry and chemical biosensors.

PT.08

In-situ growth of gold nanoparticles on mercury-binding M13 phage for Hg^{2+} sensing

Xiao-Yan Wang, Ming-Li Chen, Ting Yang*, Jian-Hua Wang*

Research Center for Analytical Sciences, Northeastern University, Shenyang 110819, China

Routine determination of mercuric ions (Hg^{2+}) is of great importance to environmental monitoring because of its deleterious effects on human health and environment. Colorimetric detection and visual sensing of Hg^{2+} based on functionalized gold nanoparticles (Au-NPs) have been extensively reported in the last decade, taking advantage of the color change originates from the surface-plasmon resonance (SPR) properties of Au-NPs. In order to enhance the selectivity towards Hg^{2+}, the functionalization of Au-NPs by ligands or receptor molecules are always necessary, making the preparation and modification process complicated and time-consuming.

Phage displayed peptide library technology is based on the expression of recombinant random peptides on the surface of filamentous phage. It is a new approach through high-throughput selection of peptide ligands of diversity and has been used as a powerful tool in the discovery of peptides capable of exhibiting specific affinity to various metals or metal cations.

In the present study, a highly specific Hg^{2+}-binding M13 phage is obtained by means of biopanning from random heptapeptide peptide library. Positive screening against Hg(II) and negative screening against foreign metals, e.g., Fe(III), Cu(II), Zn(II) and Cd(II), are proceeded for the guarantee of selectivity. The as-selected Hg^{2+}-binding M13 phage has been used as bio-template for in-situ growth of AuNPs. Under optimized conditions, i.e., a system containing 0.03 M NaOH, 631.3 μM $HAuCl_4$ and 10^{10} pfu/mL phage, well-dispersed AuNPs with λ_{max} at 525±2 nm is prepared after reaction at room temperature for 90 min. This processgreatly reduced the preparation time and simplified the preparation procedure compared with those of previously reported approaches. In addition, the AuNPs inherits the selectivity of Hg^{2+}-binding phage towards Hg(II), which shows prominent color change in the presence of Hg^{2+}, while the addition of other metal cations, e.g., Ag^{+}, Mg^{2+}, Pb^{2+}, Cr^{3+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, and Co^{2+}, shows no obvious change.

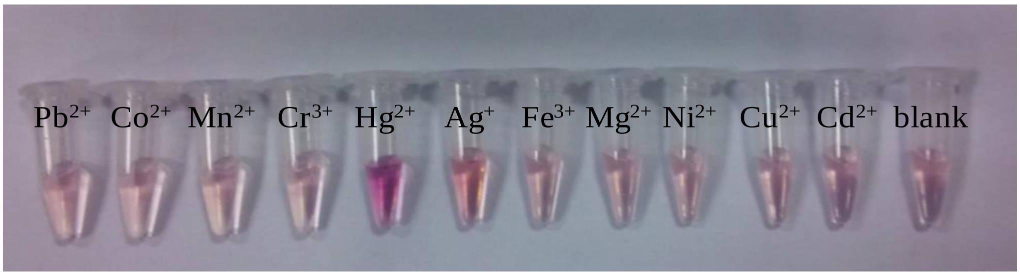

Figure 1. Color change of Au-NPs in the presence of a series of metal cations.

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Introduction to the author:

Dr. Ting Yang
Research Center for Analytical Sciences, Box332, Northeastern University, Shenyang 110819, China
Tel: +86-24-83687659; Fax: +86-24-83676698.
E-mail: yangting@mail.neu.edu.cn

Dr. Ting Yang was born in 1986. She got her B.Sc. in applied chemistry and PhD in analytical chemistry from Northeastern University, China, in 2008 and 2014, respectively, under the supervision of Prof. Jianhua Wang. In 2012-2013, she spent a year as a visiting student in the group of Dr. Dasgupta's lab at UT Arlington. She is now an assistant professor in Northeastern University. Her research interests mainly focus on genetically engineered microorganisms for the purpose of heavy metal separation and analysis.

PT.09

Absorption of Pb^{2+} and Cd^{2+} from Water using 3D nitrogen-doped graphene

Ting-Ting ZHAO[1], Feng LUO [2], Xin-Hong SONG[3], Xi CHEN*[3]

[1]Planning Department,Xiamen Huaxia University,Xiamen 361024,China
[2] Fujian Research Institute of Metric Science; Fuzhou 350003, China
[2] Quanzhou Medical College, Quanzhou, 362010
[3]Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005,China
Corresponding author email: xichen@xmu.edu.cn

Abstract:
We present an approach for the preparation of 3D nitrogen-doped grapheme (3D rGO-DA) using dopamine (DA) as both reductant and functionalization agents. Compared with reduced graphene oxide (rGO), the 3D rGO-DA prescents excellent absorption ability towards Pb^{2+} and Cd^{2+}. The adsorption capacity of Pb^{2+} and Cd^{2+} by 3D rGO-DA is found to be 75 and 65.8 mg/g, receptively. The effect factors, including adsorption time, pH and initial concentration of Pb^{2+} and Cd^{2+}, are studied. Adsorption time of 120 min and pH 5.0 are found to be the suitable condition for Pb^{2+} and Cd^{2+} adsorption. After 3 cycle absorption/desorption, the 3D rGO-DA still remained excellent absorptive capacity and can be easily removed from water after adsorption process, indicating its applicability in the water purification

Keywords: 3D graphene; Pb^{2+}; Cd^{2+};absorption

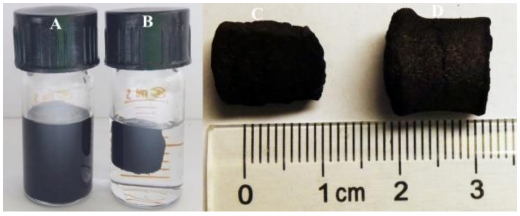

Fig. 1 Photographs of GO solution (A); 3D rGO-DA before lyophilization (B); Measurement of 3D rGO after lyophilization (C); Measurement of 3D rGO-DA after lyophilization (D)

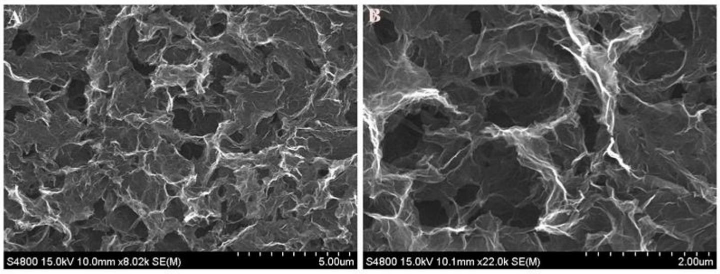

Fig. 2 SEM images of cellular structure of 3D rGO-DA shown in (A) and (B)

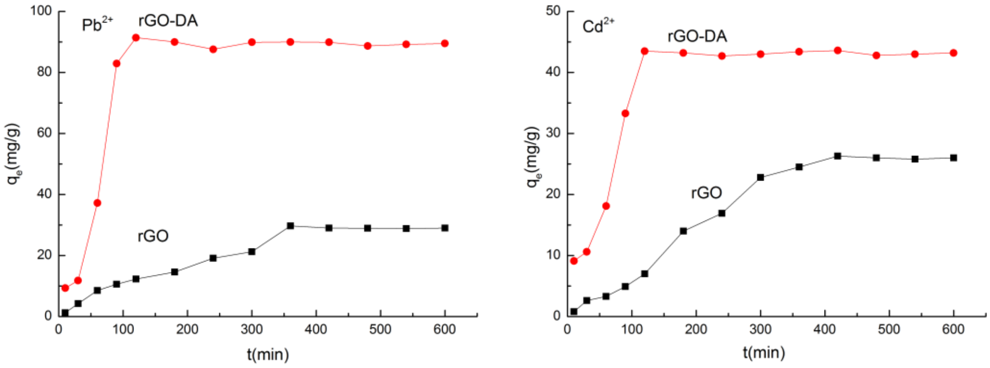

Fig. 3 Effects of adsorption time on the adsorption capacities of 3DrGO-DA on Pb^{2+} and Cd^{2+}

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Ting-Ting Zhao
Planning Department, Xiamen Huaxia University, Xiamen 361024,China

Tel/Fax: +86(592) 6276251
E-mail: ztt@hxxy.edu.cn

Ting-Ting Zhao graduated from Harbin Normal University with a Bachelor's degree of chemistry in 2010, she entered Fuzhou University and obtained her Master's degree three years later. Then she worked at Xiamen Huaxia University, she is mainly engaged in environmental water quality detection and purification materials research. She has applied for a project of Xiamen Science and Technology Program in 2014 and published 6 scientific research articles related to the project.

PT.10

Online multichannel ultrasonic extraction for high throughput determination of arsenic in soil by hydride generation atomic fluorescence spectrometry

Yuefen Zhang, [a] Lan Wu, [a,b] Chengbin Zheng,[a] Xiandeng Hou, [a,b] and Kailai Xu*[a]

[a] Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China;
[b]Analytical & Testing Centre, Sichuan University, Chengdu, Sichuan 610064, China
[*] Corresponding author. Tel. & Fax: (+) 86-028-85412290; E-mail: xukailai@scu.edu.cn.

Hydride generation (HG) is a widely used sample introduction methodology for the determination of traditional hydride forming elements and several transition and noble metals by coupling with atomic spectrometric methods. HG has advantages of high reaction yield and small matrix interference. However, when analyzing solid samples such as soil, a tedious and time-consuming procedure for digestion and/or extraction is frequently required, which usually needs hash conditions such as the use of concentrated acids, high temperatures and high pressures. To overcome the disadvantages of conventional sample pre-treatment techniques, there is an urgent need to develop new methods and strategies. Online multi-channel ultrasonic extraction coupling with hydride generation can greatly reduce the consumption of the sample and analyte loss, shorten the analysis time, and improve the detection sensitivity and accuracy.

A new analytical method was developed to determine trace arsenic in soil by coupling sequential injection multichannel ultrasonic extraction and online pre-reduction with slurry hydride generation atomic fluorescence spectrometry. Significantly enhanced sampling throughput, reduced sample and reagent consumption, and minimized potential contamination and analyte loss were achieved. Slurry samples spiked with different concentrations of As(III) and hydrochloric acid were pumped into the ultrasonic extraction chamber for 20-minute irradiation to efficiently extract As(III), which were subsequently merged with a mixture of 1% (m/v) thiourea and 0.5% (m/v) ascorbic acid to pre-reduce As(V) species to As(III), followed by the generation of AsH_3 *via* using KBH_4. Upon optimization of experimental parameters, limits of detection (LODs) ranging from 0.03 to 0.07 mg kg^{-1} were obtained, and the precisions (RSDs) of this method were better than 2.0%. The proposed method was used for the determination of trace arsenic in several Certified Reference Soil samples, with the obtained results in excellent agreement with

certified values based on a simple and fast standard addition method.

Key words: multichannel, ultrasonic extraction, soil, arsenic

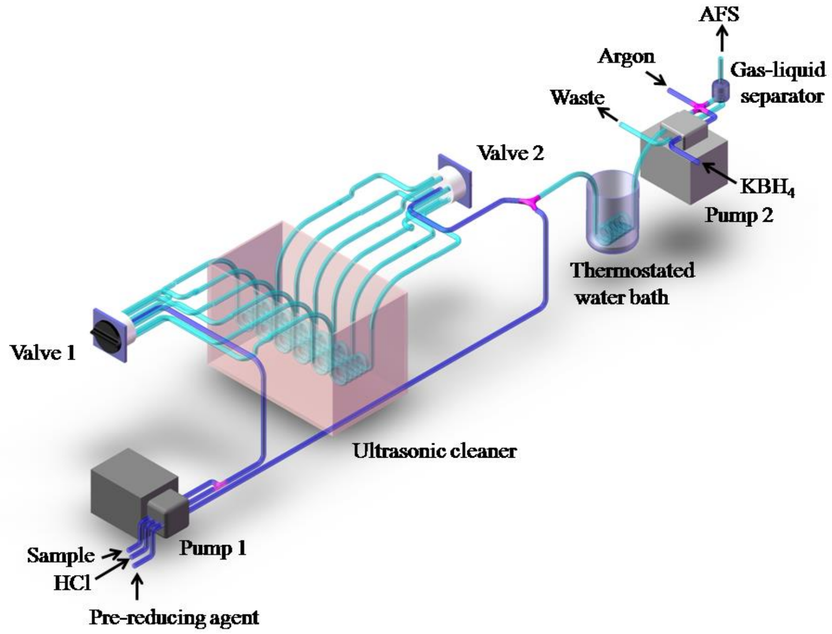

Figure 1. Schematic diagram of the experimental setup

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PT.11

Label-free detection of microRNA by Au nanoparticles decorated reduced graphene oxide field-effect transistor biosensor

Bingjie Cai, Guo-Jun Zhang *

School of Laboratory Medicine, Hubei University of Chinese Medicine, Wuhan 430065, China

Abstract: A novel method of highly sensitive and selective detection of microRNA (miRNA) is always desirable. We have ever constructed a field effect transistor (FET) biosensor based on chemically reduced graphene oxide (R-GO) for ultrasensitive, label-free and specific detection of peptide nucleic acid （PNA）-DNA hybridization. In the present presentation, we report a Au nanoparticle decorated R-GO FET biosensor for label-free detection of miRNA via PNA-miRNA hybridization. R-GO was prepared by reduction of GO with 98% hydrazine, and the FET biosensor was fabricated by drop-casting the R-GO suspension onto the sensor surface, followed by exposing the R-GO-assembled sensor surface to $HAuCl_4$ solutions to achieve Au nanoparticle decoration. After that, PNA as the capture probe was immobilized on the Au nanoparticle surface, and label-free detection of microRNA was successfully performed through PNA-miRNA hybridization by the R-GO FET biosensor. The proposed graphene-based FET biosensor is expected to be a new strategy for miRNA detection.
Scope of the symposium: Nano-bioanalytical chemistry.

Keywords: Graphene, field effect transistor biosensor, miRNA detection

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Introduction to the author:

Professor Dr. Guojun Zhang
School of Laboratory Medicine, Hubei University of Chinese Medicine, Wuhan 430065, China
Tel: +86-27-68890259; Fax: +86-27-68890259.
E-mail: gjzhangtj@hotmail.com

Biography of the authors.

Guo-Jun Zhang got a PhD degree in Medicine from the Tongji Medical School of Huazhong University of Science and Technology, P. R. China, in 1999. From 1999 to 2004, he was a Postdoctoral Fellow at Wuhan University of P. R. China, Institute for Physical High Technology Jena of Germany, Waseda University of Japan, respectively. Afterwards, he became a Visiting Lecturer in 2004, a Visiting Associate Professor in 2005 at Waseda University, Japan, and Member of Technical Staff at Institute of Microelectronics, Singapore (2006-2011), respectively. He is currently working as a professor at Hubei University of Chinese Medicine, China.

PT.12

GC/MS analysis and sensory evaluation of odor compounds in environmental tobacco smoke (ETS)

Hiroshi Sato1)*, Masahiro Oka1), Shuhei Nagahashi1), Kaori Imi1), Naoki Mizoguchi1),
Hidetaka Matsubara2), Miyuki Noguchi3), Keiichi Arashidani4)

1) Department of Pharmacy, Faculty of Pharmaceutical Sciences, Nagasaki International University
2) Chuken Laboratory for Life and Environment
3) Faculty of Science and Technology, Seikei University
4) School of Health Sciences, University of Occupational and Environmental Health

Abstract:

Background:

The details on how the various compounds of tobacco smoke contribute to tobacco odor are not yet clearly defined. Elucidation of those details may make it possible to evaluate the ETS exposure level from the point of view of tobacco odor levels. This study is focused on analyzing the elements of tobacco smoke at the detailed level with instrumental analysis and sensory evaluation and verifying the data by reproducing the tobacco odor using commercial reagents.

Methods:

1. GC/MS and quantitative analysis of tobacco smoke and tar and reproduction of tobacco odor with commercial reagents.
2. Preparation and sensory evaluation of imitation tobacco with *Hibiscus hamabo* leaves and nicotine solution.
3. Analysis of tobacco tar on wall surface and its change of properties with time
4. GC analysis and sensory evaluation of residual chemicals left on indoor surfaces by tobacco smoke (thirdhand smoke)

Result:

Compounds including nicotine, phenol and acetic acid were detected with GC/MS analysis from both tobacco smoke (Table 1) and tar. From the data obtained with sensory evaluation of imitation tobacco, nicotine was thought to be the constituent of tobacco odor; however, its behavior in the environment is fairly unstable. In the attempt to reproduce tobacco odor with commercial reagents, nicotine itself did not have any detectable smell.

Table 1 Concentration and odor intensity of secondhand smoke

Compounds	Concentration (v/vppm)	Threshold (ppm)	Odor intensity* (1~5)	Quality of odor
Ammonia	50	1.5	1.5	Irritant odor
Nicotine	0.5	0.011	1.7	Pyridine like odor
Acetaldehyde	8.9	0.0015	3.8	Irritant grassy odor
Acetic acid	0.5	0.0060	2.0	Irritant acidic odor
Phenol	0.5	0.0056	2.0	Chemical odor

*Odor intensity＝log(concentration/threshold)

Conclusion:

According to the result of this study, not the nicotine but the pyrolysis products of nicotine may be contributing to the unpleasant quality of tobacco odor. The change of the properties of nicotine and third hand smoke with time are to be further examined.

Keywords: ETS, secondhand smoke, thirdhand smoke

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Acknowledgements:

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Introduction to the author:

Dr. Hiroshi Sato
Faculty of Pharmaceutical Sciences, Department of Pharmacy, Nagasaki International University
2825-7, Huis Ten Bosch, Sasebo City, Nagasaki 859-3298 Japan
Tel: +81-956-20-5668; Fax: +81-956-20-5668
E-mail: satoh@niu.ac.jp

Dr. Hiroshi Sato received his Master degree in 1983 and received a PhD degree in Pharmaceutical Sciences (2003) at Kyushu University in Japan. He had worked in Kao Corporation during 1985-1987 and then had worked in TOTO LTD. during 1987-2006. He is currently an associate professor of Nagasaki International University. His research is focused on the environmental analysis and bioremediation.

PT.13

Application of HPLC by Using Mass Spectrometry Detector

Masaki Watanabe*, Masaki Yoshie, Norimasa Minamoto, Kousaku Toyosaki

Optical Instrument Engineering Department, Hitachi high-tech Science Corporation, 1040 Ichige, Hitachinaka, Ibaraki 312-0033 Japan

Abstract: Mass spectra data is quite informative for HPLC analysis. It can confirm compound identities, can clarify co-elutions of mixed compounds, and can detect compounds which do not have UV absorbance or fluorescence. Here we introduce a new compact mass detector equipped the atmospheric pressure ion filter technology. The atmospheric pressure ion filter is a new selective ion transfer technology, which provide selective ion detection and the robustness of routine operations. In this presentation, we introduce applications of the new mass detector combined with HPLC.

Keywords: LC/MS, mass detection

Introduction to the author:

Dr. Masaki Watanabe
Optical Instrument Department, Hitachi High-Tech Science Corporation, Hitachinaka, Ibaraki, 312-0033 Japan
Tel: +81-50-31733080; Fax: +81-29-2757099.
E-mail: masaki.watanabe.yk@hitachi-hightech.com

Biography of the authors.

Dr. Masaki Watanabe is an application scientist and an engineer of Optical Instrument Engineering Department, Hitachi high-tech Science Corporation. He received his Ph.D. of engineering from Nagoya University in 2002 and then joined Hitachi High Technologies. He is in charge of the development of application system of HPLC and LC/MS.

PT.14

Analytical method for arsenic speciation in foods using HPLC-ICP/MS

Dongwon Seo, Soyoung Kim, Eunjoo Park, Jisu Park, Jaeho Ha, Tae-Gyu Nam,*
Jooyoung Lee, Haewon Jang, Jinbong Hwang

Food Analysis Center, Korea Food Research Institute, Seongnam 463-746, Korea

Abstract: Chemical species of elements in biological and environmental samples are of importance to understand toxicity, metabolism and transport properties of elements. Therefore, speciation analysis becomes an increasing active-research field in recent years. Different atomic spectrometric methods were applied for As speciation in foods, such as high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS). In this study, the analytical method to determine five kinds of arsenic speciation; the inorganic arsenic species As(III), As(V) and the organic species arsenobetaine (AsB), dimethyl arsinate (DMA) and monomethyl arsenate (MMA) were determined in foods by HPLC-ICP/MS method. The ICP/MS operating conditions were 1500W RF power, 15 L/min plasma Ar gas flow, 0.95 L/min nebulizer gas flow, 1.2 L/min Aux. gas flow, 1.5 mL/min sample uptake rate and As ion measured were 75 *m/z*. The calibration curve showed linearity in the range between 0.9991~0.9995. Limits of detection (LOD) in As(III), As(V), AsB, DMA and MMA were measured 1.29, 0.19, 0.20, 0.15 and 0.36 ng/mL and limits of quantification (LOQ) were 4.31, 0.64, 0.66, 0.51 and 1.19 ng/mL, respectively. Intra-day for As(III), As(V), AsB, DMA and MMA were 2.74, 1.05, 1.52, 2.44 and 1.25 %, and inter-day were 6.87, 8.51, 6.10, 6.76 and 6.91 %, respectively.

Keywords: HPLC-ICP/MS, Inorganic arsenic species, Organic arsenic species, Foods

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Introduction to the author:

Dongwon Seo
Food Analysis Center, Korea Food Research Institute, 463-746, Korea

Tel: +82-31-780-9241; Fax: +82-31-780-9280.
E-mail: dwseo@kfri.re.kr

Biography of the authors:

Dongwon Seo joined the Food Analysis Center at Korea Food Research Institute in 2003, where he involved himself in the analysis of food components, including mineral nutrients and heavy metal using ICP/MS. Concurrently, he is applying GCxGC-TOFMS technology coupled with silver ion cartridge techniques for the analysis of trans fatty acids in foods. His research and activity is focused on chromatographic separation, food analysis.

PT.15

Nutritional composition of bamboo shoots (*Phyllostachys Bambusoides Sieb. et Zucc.*) in Korea

Dongwon Seo[1], Songjin Lee[2], Jinbong Hwang[1], Kinjin Kim[1], Soyoung Kim[1], Eunjoo Park[1], Hyunjun Lee[1], Haebin Cho[1], Seunghee Kim[1], Wonjin Yoon[1], Jaeho Ha[1]*

[1]Food Analysis Center, Korea Food Research Institute, Seongnam 13539, Korea
[2]Bamboo Resource Research Institute, Damyang 57365, Korea

Abstract: Bamboo shoots are of considerable nutritional value to human health since they are rich in functional nutrients like dietary fiber, protein, vitamins, bioactive compounds and low in fat and calories. Apart from the Asian countries such as China, Japan, and Korean, where it is frequently used as common food material, bamboo shoots have become very popular in many other countries where bamboo shoots are mostly imported. We assessed the quality of a bamboo shoots (*Phyllostachys Bambusoides Sieb. et Zucc.*) produced in Damyang-gun in terms of parameters that included fat, protein, carbohydrate, dietary fiber, mineral contents and fatty acids. The moisture, fat, protein, ash, carbohydrate and dietary fiber of the bamboo shoots were 92.1, 0.4, 2.4, 0.8, 4.3 and 1.8 g/100 g, respectively. Mineral contents of Ca, Fe, K, Mg, Na, P and Zn were 8.3, 0.9, 369.6, 13.1, 23.9, 53.6 and 0.8 mg/100g, respectively. Fatty acids composition (percentage results from 100g fat) of palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid were 35.3, 1.5, 8.6, 38.9 and 9.5 %, respectively.

Keywords: Bamboo shoot, Nutritional composition, mineral content, fatty acid

Reference:

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Introduction to the author:

Dongwon Seo
Food Analysis Center, Korea Food Research Institute, 463-746, Korea
Tel: +82-31-780-9241; Fax: +82-31-780-9280.
E-mail: dwseo@kfri.re.kr

Biography of the authors:

Dongwon Seo joined the Food Analysis Center at Korea Food Research Institute in 2003, where he involved himself in the analysis of food components, including mineral nutrients and heavy metal using ICP/MS. Concurrently, he is applying GCxGC-TOFMS technology coupled with silver ion cartridge techniques for the analysis of trans fatty acids in foods. His research and activity is focused on chromatographic separation, food analysis.

PT.16

Comparison of Macro Mineral Contents following Kind of Vegetables produced in Korea

Eun-joo Park[1*] , Soyoung Kim[1], Jinbong Hwang[1], Dongwon Seo[1], Youngmin Choi[2], Se-Na Kim[2], Jin-Sik Nam[3]

[1]Department of Food analysis, Korea Food Research Institute, Gyeonggi, 13539, Korea,
[2]Functional Food & Nutrition Division, National Academy of Agricultural Science, RDA, Jeonju, 04535, Korea
[3]Department of Food & Nutrition, Suwon Women's University, Gyeonggi, 18333, Korea

Abstract:

Recently, macro minerals (Na, Ca, K Mg and P) have the excellent functions associated with prevention of disease. We estimated an amount of macro minerals in the vegetables produced in Korea in order to build the food nutritional ingredient table. A SRM 1849a purchased from NIST in USA was digested by the microwave and validation of macro minerals in SRM 1849a was carried out by inductively coupled plasma optical emission spectrometer (ICP-OES). Regression analysis of correlation coefficient (R^2) was higher than 0.999 which revealed good linearity. Based on this analysis, the raw vegetables contained 0.20 to 144.98 mg/100g of sodium, 7.81 to 266.57 mg/100g of calcium, 230.57 to 812.73 mg/100g of potassium, 12.16 to 76.28 mg/100g of magnesium and phosphorus ranged from 35.32 to 123.81 mg/100g. In addition, the contents of the minerals in the blanched vegetables were 1.40 to 134.75 mg/100g of sodium, 7.80 to 177.58 mg/100g of calcium, 150.32 to 651.71 mg/100g of potassium, 11.17 to 56.63 mg/100g of magnesium and 36.20 to 136.61 mg/100g of phosphorus. Hence, it would be expected that the mineral contents could be used to draw up the food nutritional ingredient table.

Keywords: ICP-OES, Mineral, Food composition table, vegetables

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Introduction to the author:

Dr. Jinbong Hwang
Food Analysis Center, Korea Food Research Institute, 13539, Korea
Tel: +82-31-780-9128; Fax: +82-31-780-9280.
E-mail: Hwangjbg@kfri.re.kr

PT.17

Single molecule real-time imaging of intracellular Mg^{2+} signaling and wave propagation in single cell with subdiffraction-limit resolution

Suresh Kumar Chakkarapani[a], Seungah Lee[b], and Seong Ho Kang[a,b,*]

[a]Department of Chemistry, Graduate School, Kyung Hee University
[b]Department of Applied Chemistry, College of Applied Science, Kyung Hee University

Abstract:

Intercellular magnesium ion (Mg^{2+}) waves are believed to propagate through networks of human cells by the release of ATP, which functions as an extracellular messenger. However, the intracellular location of the Mg^{2+} signaling and dynamics of the wave propagation are not completely studied at the single cell level. To study the intracellular Mg^{2+} signaling with subdiffraction-limit resolution by *d*STORM, a photo-switchable intracellular magnesium fluorescent indicator dye is required. In this work, mag-fluo-4-AM an intracellular Mg^{2+} fluorescent indicator dye was photo-switched between fluorescent state and dark state by an activation and excitation laser. By localizing the centroid of the fluorophores, intracellular Mg^{2+} was located in intracellular region with subdiffraction-limit resolution. To investigate the intracellular Mg^{2+} wave propagation, Na^+ATP was added alongside mag-fluo-4-AM with the above-mentioned photo-switching condition. Intracellular magnesium wave propagation was investigated at 0.2 s temporal resolution with 21 ± 1 nm spatial resolution. This study provides the proof-of-concept for the use of *d*STORM to investigate the changes in intracellular ions with subdiffraction limit spatial resolution and a lower temporal resolution than a conventional fluorescence microscope.

Keywords: intracellular Mg^{2+}, subdiffraction-limit resolution, real-time investigation

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Introduction to the author:

Professor Dr. Seong Ho Kang

Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea
Tel: +82-31-201-3349; Fax: +82-31-201-2340.
E-mail: shkang@khu.ac.kr

Biography of the authors.

Suresh Kumar Chakkarapani received his B.Sc and M.Sc in chemistry from Madras University of India in 2009 and 2011. He worked as an assistant professor in Ramakrishna Mission Vivekananda College affiliated to Madras University from 2011 to 2014. He is currently a doctoral student at Kyung Hee University from 2014. His research interests include single molecular imaging and development of various analytical techniques for micro- and nano-separation.

Seungah Lee received her B.S., M.S., and Ph.D. from Chonbuk National University of Republic of Korea in the group of Professor Seong Ho Kang in 2003, 2006, and 2010, respectively. She is currently an Assistant Professor at Kyung Hee University. Her main research interests are chemical/biological analysis on biochip at single-molecule level using various detection systems.

Professor, Seong Ho Kang received his B.S. and M.S. degrees in chemistry from Kyung Hee University of Republic of Korea in 1987 and 1989. He worked as a senior researcher at the research center of Hanil Pharmaceutical Co. (present, CJ Pharm. Co.) from 1989 to 1997. He received his Ph.D. degree in chemistry from the Seoul National University in 1998. He was a postdoctoral research associate scholar at Iowa State University and Ames Laboratory-US Department of Energy with Dr. Edward S. Yeung from 1998 to 2000, a senior researcher at the SAIT (Samsung Advanced Institute of Science and Technology) in 2000–2002, and a professor of chemistry at Chonbuk National University in 2002–2010. He is currently a professor at Kyung Hee University from 2010. His research interests include developments of various analytical systems, methods, and techniques based on micro- and nano-separation, single-molecule detection, micro- and nano-fluidics, and various nano-bio fusion technologies.

PT.18

Novel detecting method of synthetic organic dyes by dual non-aqueous capillary electrophoresis

Moonhee Park[a], Seung-Hoon Bahang[b], Seong Ho Kang[a,c,]*

[a]Department of Chemistry, Graduate School, Kyung Hee University
[b]Criminal Investigation Command of MND, Seoul 140-701, Republic of Korea
[c]Department of Applied Chemistry, College of Applied Science, Kyung Hee University

Abstract:
Many researchers have been conducted to use a variety of devices to detect the synthetic organic dyes. A novel dual non-aqueous capillary electrophoresis (d-NACE) with laser-induced fluorescence (LIF) system was developed for simultaneous analysis of synthetic organic dyes. NACE was provided faster analysis time, lower sample consumption, and higher solubility for synthetic organic dye analysis former conventional aqueous CE techniques. In addition to NACE, two lasers and detectors were used along with a single capillary. Dual-wavelength excitation light sources were used to excite different organic dyes [i.e., 543 nm for crystal violet (CV), methyl violet B (MVB), methyl violet B base (MBB), rhodamine 6G (R6G), and rhodamine B base (RBB); 635 nm for nile blue A (NBA) and methylene blue (MB)]. The dyes were analyzed in 15 min with an excellent baseline separation (resolutions ≥ 2.6) under the electric field of 500 V/cm. The detection limits ($S/N = 3$) were 0.1 μM-40 fM, which were 10-10^5 times lower than the previous detection methods. Hence, d-NACE method was proved to be high-throughput and effectively rapid analysis technique for the highly sensitive detection of synthetic organic dyes.

Keywords: dual non-aqueous capillary electrophoresis, organic dyes, high-throughput detecting

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Introduction to the author:
Professor Dr. Seong Ho Kang
Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-

701, Republic of Korea
Tel: +82-31-201-3349; Fax: +82-31-201-2340.
E-mail: shkang@khu.ac.kr

Biography of the authors.

Moonhee Park received her B.S in chemistry from Kyonggi University of Korea in 2014. She is currently a master student at Kyung Hee University from 2014. Her research interests Capillary electrophoresis with non-aqueous solvent and development of various analytical techniques for separation.

Seung-Hoon Bahang received his B.S. and M.S. degrees in chemistry from Kyung Hee University of Republic of Korea. He is currently a section chief at Criminal Investigation Command of MND. His research interests include developments of various analytical systems, methods, and techniques based on micro- and nano-separation.

Professor, Seong Ho Kang received his B.S. and M.S. degrees in chemistry from Kyung Hee University of Republic of Korea in 1987 and 1989. He worked as a senior researcher at the research center of Hanil Pharmaceutical Co. (present, CJ Pharm. Co.) from 1989 to 1997. He received his Ph.D. degree in chemistry from the Seoul National University in 1998. He was a postdoctoral research associate scholar at Iowa State University and Ames Laboratory-US Department of Energy with Dr. Edward S. Yeung from 1998 to 2000, a senior researcher at the SAIT (Samsung Advanced Institute of Science and Technology) in 2000–2002, and a professor of chemistry at Chonbuk National University in 2002–2010. He is currently a professor at Kyung Hee University from 2010. His research interests include developments of various analytical systems, methods, and techniques based on micro- and nano-separation, single-molecule detection, micro- and nano-fluidics, and various nano-bio fusion technologies.

PT.19

Biomolecular quantification in axial nanoscale of plasmonic particle on nanoisland

Seungah Lee[a], Sujin Ahn[b], Seong Ho Kang[a,b,]*
[a]Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea
[b]Department of Chemistry, Graduate School, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea

Abstract: A spatial localization of biomolecule based on the plasmonic scatttering of sliver nanoparticle on the gold nanoisland was investigated by using polarization-sensitive total internal reflection scattering (TIRS) imaging. Immunoassay through TIRS technique based on reconstructing the three dimension (3D), indeed provides the best possible accuracy by using z-stage controller in the spatial range up to 10 nm in the z-direction. By measuring the scattering of the sliver nanoparticle through sandwich immunoreaction on gold nanoisland, we verified 3D resolution (spatial localization) of single biomolecule with high accuracy. In addition, it offers a good platform for sensitive quantitation with the limit of detection of 800 zeptomolar (zM, $\times 10^{-21}$ M) level of protein maker.

Keywords: total internal reflection scattering, zeptomolar concentration, axial nanoscale

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4. S. Lee, H. Yu, S. H. Kang, *Chem. Commun.*, 2015, 51, 945.

Introduction to the author:

Professor Dr. Seong Ho Kang
Department of Applied Chemistry, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Republic of Korea
Tel: +82-31-201-3349; Fax: +82-31-201-2340
E-mail: shkang@khu.ac.kr

Biography of the authors.

Seungah Lee received her B.S., M.S., and Ph.D. degrees in chemistry from Chonbuk National University of Republic of Korea in 2003, 2006, and 2010, respectively. She is currently an Assistant Professor at Kyung Hee University. Her main research interests are chemical/biological analysis on biochip at single-molecule level using various detection systems.

Sujin Ahn received her B.S. degree in Food Science and Biotechnology from Kyung Hee University of Republic of Korea in 2014. She is currently a researcher in department of chemistry at Kyung Hee University from 2015. Her research interest includes single molecule detection and analysis of biological species by fluorescence and fluorescence-free microscopic imaging.

Seong Ho Kang received his B.S. and M.S. degrees in chemistry from Kyung Hee University of Republic of Korea in 1987 and 1989. He worked as a senior researcher at the research center of Hanil Pharmaceutical Co. (present, CJ Pharm. Co.) from 1989 to 1997. He received his Ph.D. degree in chemistry from the Seoul National University in 1998. He was a postdoctoral research associate scholar at Iowa State University and Ames Laboratory-US Department of Energy with Dr. Edward S. Yeung from 1998 to 2000, a senior researcher at the SAIT (Samsung Advanced Institute of Science and Technology) in 2000-2002, and a professor of chemistry at Chonbuk National University in 2002-2010. He is currently a professor at Kyung Hee University from 2010. His research interests include developments of various analytical systems, methods, and techniques based on micro- and nano-separation, single-molecule detection, micro- and nano-fluidics, and various nano-bio fusion technologies.

PT.20

Time-Series Variation of Atmospheric Radon-222 Concentrations at Gosan Site in Jeju Island of Korea during 2012-2014

Jung-Min Song[1], Jun-Oh Bu[1], Won-Hyung Kim[1], Chang-Hee Kang[1]*, S. Chambers[2]

[1]Division of Chemistry and Cosmetics, Jeju National University, Jeju 690-756, Korea
[2]Australian Nuclear Science and Technology Organisation, NSW 2232, Australia

Abstract: Radon-222, a radioactive noble gas, is released into the atmosphere from soils over the continents and has a half-life of 3.8 days. Because radon fluxes from soils are typically 100 times compared to those from the ocean, radon is considered as a useful tracer for air masses which have passed over land recently. The measurement of atmospheric radon-222 concentrations at a background area is used to determine whether the air masses originate from over continents or oceans. Further, it is an excellent tracer for studying vertical mixing of greenhouse gases, boundary-layer development and dynamics, and also for validation of three-dimensional atmospheric transport models. In conjunction with other radionuclide measurements, such as ^{210}Pb, radon data provide a useful constraint for the evaluation of air transport models and the identification of global atmospheric conditions. In this study, the ambient background level of atmospheric radon at Gosan Site in Jeju Island of Korea was measured using a real-time monitoring system throughout 2012-2014, in order to evaluate the timely variation characteristics as well as background levels of atmospheric radon. The annual mean radon concentration was 2,254±1,127 mBq/m^3 during the studying period. In seasonal comparison, the order of the mean concentrations was as winter (2,734±1,124 mBq/m^3) > fall (2,686±1,026 mBq/m^3) > spring (2,063±911 mBq/m^3) > summer (1,639±1,116 mBq/m^3), showing relatively high in winter and low in summer season. The monthly mean concentrations were in the order of Nov > Jan > Oct > Dec > Sep > Feb > Mar > May > Jun > Apr > Aug > Jul, resulting the concentration on November (2,839 mBq/m^3) was more than twice as that on July (1,353 mBq/m^3). Meanwhile the hourly concentrations have increased during the nighttime (2,617 mBq/m^3 at around 7am), and decreased relatively during the daytime (1,874 mBq/m^3 at around 3pm). Compared to other foreign regions, the mean radon concentration at Gosan Site was 2.5 times lower than that at Hok Tsui of Hong Kong, but 22.1 times higher than that at Mauna Loa of Hawaii. Based on the back trajectory analysis, the frequencies of air mass moving from China continent, the Korean peninsula, the East Sea and the North Pacific Ocean were 50.4, 18.6, 18.9, 12.1%, respectively, and especially the ambient radon concentration was quite high (2,587 mBq/m^3) by the air masses moving from China continent. On the study of continental fetch analysis, the radon concentrations were high when the air masses moved from the Asia continent to Jeju Island, on the other hand, those values were low when they moved from the North Pacific Ocean.

Keywords: Radon-222, Atmospheric radon, Background level, Gosan Site

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Introduction to the author:

Dr. Chang-Hee Kang
Division of Chemistry and Cosmetics, Jeju National University, Korea
Tel: +82-64-754-3545; Fax: +82-64-756-3561
E-mail: changhee@jejunu.ac.kr

Biography of the authors.

Jung-Min Song has obtained Ph.D. degree in 2014 and is working as a Postdoctoral researcher in Division of Chemistry and Cosmetics, Jeju National University. His scientific research interests are focused on the environmental analysis for the air pollutants such as Radon-222, odorous compounds and atmospheric aerosols.

PT.21

Effect of Asian Dust Storms on Atmospheric Aerosol Compositions in Background Site of Korea during 2012-2014

Jun-Oh Bu[1], Jung-Min Song[1], Jae-Yun Lee[1], Jong-Heon Han[1], Chang-Hee Kang[1]*
[1]Division of Chemistry and Cosmetics, Jeju National University, Jeju 690-756, Korea

Abstract: The collection of atmospheric PM_{10} and $PM_{2.5}$ aerosol samples has been made at Gosan Site of Jeju Island, which is one of the background sites of Korea, during 2012-2014. Their water-soluble ionic and elemental species were analyzed in order to examine the variable characteristics of aerosol composition and pollution in relation to the Asian dust storms. The average mass concentrations of PM_{10} and $PM_{2.5}$ fine particulate matters were 128.9 ± 49.0 $\mu g/m^3$ and 41.5 ± 17.1 $\mu g/m^3$, respectively, for the Asian dust days, showing about 3-4 times higher than those of non-Asian dust days. The concentrations of PM_{10} ionic species were in the order of nss-SO_4^{2-} > NO_3^- > NH_4^+ > Cl^- > Na^+ > nss-Ca^{2+} > K^+ > Mg^{2+}, and those of $PM_{2.5}$ were nss-SO_4^{2-} > NH_4^+ > NO_3^- > Na^+ > Cl^- > K^+ > nss-Ca^{2+} > Mg^{2+} during the Asian dust days. Their concentrations were 1.4~8.4 times for PM_{10} and 1.2~4.1 times for $PM_{2.5}$, during Asian dust periods, compared to those of non-Asian dust days. Especially, the concentrations of anthropogenic and soil originated species increased highly in both PM_{10} and $PM_{2.5}$ aerosols during the periods of Asian dust storms. The composition ratio comparison resulted that the secondary pollutants (NH_4^+, nss-SO_4^{2-}, NO_3^-) were 72.8%, but those of marine species (Na^+, Cl^-, Mg^{2+}) and soil source (nss-Ca^{2+}) were 20.4% and 5.0%, respectively, for the PM_{10} ionic species during the Asian dust periods. Meanwhile, the composition ratios of the secondary pollutants, marine species, and soil source were 93.4%, 3.9%, and 0.7%, respectively, for the $PM_{2.5}$ ionic species. From the elemental analysis of atmospheric aerosols, the elemental concentrations of PM_{10} were in the order of S > Al > Na > Ca > Fe > Mg > K > Ti > Zn > Mn > Pb > Ba > Ni > V > Sr > Cu > Cr > Cd > Co > Mo, and those of $PM_{2.5}$ were S > Fe > Al > Na > K > Ca > Mg > Zn > Pb > Mn > Ti > V > Ni > Ba > Cu > Sr > Cr > Cd > Mo > Co. Therefore, the anthropogenic (S, Zn, Pb), Soil (Al, Fe, Ca) and Marine (Na, Mg) species occupied 23.4%, 44.9% and 24.0% in PM_{10} and 47.9%, 28.5%, 14.2% in $PM_{2.5}$, respectively, for the Asian dust periods. The neutralization factors by NH_3 were 0.24 in PM_{10} and 0.34 in $PM_{2.5}$ aerosols, meanwhile those by $CaCO_3$ were 0.09 and 0.01, respectively. The back trajectory analysis showed that the concentrations of anthropogenic and soil species of both PM_{10} and $PM_{2.5}$ aerosols were higher when the air mass moved from China continent to Jeju Island rather than when it came from the North Pacific Ocean.

Keywords: Asian dust, Atmospheric aerosol, Gosan Site of Jeju Island

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Introduction to the author:
Dr. Chang-Hee Kang
Division of Chemistry and Cosmetics, Jeju National University, Korea
Tel: +82-64-754-3545; Fax: +82-64-756-3561
E-mail: changhee@jejunu.ac.kr

Biography of the authors.

Jung-Oh Bu has obtained Master degree in 2013 and is studying as a doctor's course in analytical chemistry at Chemistry Department of Jeju National University. His scientific research interests are focused on the environmental analysis of air pollutants such as atmospheric aerosols, rainwater, Radon-222, etc.

PT.22

Verification of Applicability of the Validated Analytical Method with a Liquid Chromatography-Tandem Mass Spectrometry for Steroids Residues Screening in Food Products

Hwa-Mi Lee*, JaeHyun Kim, WooJin Jeon, SooJin Bang, SungMin Woo, JuYeun Lee, EunJoo Koo, JyongEun Myung, HyunUk Kim, EunYoung Lee, Soo Jung Hu, Young-Mi Jang, Chul Joo Lim.

Center for Food & Drug Analysis, Gyeongin Regional Food and Drug Administration, 137, Juan-Ro, Nam-Gu, Incheon-City, 402-835, Republic of Korea

Steroids, a group of cyclic organic compounds whose most common characteristic is an arrangement of seventeen carbon atoms in a four-ring structure, are allowed to be only used as a doctor's prescription to a patient for therapeutic purposes. But, the incidents of the illegal distribution of food products contained steroid have been reported continuously in recent years. A developed quantitative method using liquid chromatography–tandem mass spectrometry (LC–MS–MS) by the advanced analysis team in National Institute of Food and Drug Safety Evaluation was evaluated for the applicability of 30 steroids in food products including health supplements using inter-laboratory verification method. In this study, we verified by using the positive ionization mode for the analysis of steroids. The evaluation of parameters such as specificity, linearity, precision, accuracy, and adequate sensitivity like as a limit of detection led us to establish a sensitive new electrospray LC/MS method for steroid analysis. LC/MS technique, together with the combined knowledge of the LC retention behavior, the relative sensitivity, and the fragmentation pattern generated by electrospray mass spectrometry, will be extremely useful for the identification and detection of steroids.

Tel. +82-32-450-3351, Fax. +82-32-442-4622, E-mail. lhm9904@gmail.com

PT.23

Method development for determination of heavy metals in turmeric powder using ICP-MS

*Chang-Hee Lee, Yeon Kim, Myung-Ja Lee, Bock-Kyu Lim, Ki-Hyun Kim, Yeong-Hyeon Kim, Tae-Yong Cho, Jae-Young Shim**

Center for Food & Drug Analysis, Busan Regional Korea Food and Drug Administration, Busan, Republic of Korea

Turmeric, commonly known as a yellow spice, is widely consumed as curry by Korean and less frequently consumed as a beverage in itself or added in tea or dessert soup. Turmeric can also be contaminated some harmful matter, e.g. micotoxin and heavy metals. In this study, the analytical method to determine heavy metals; Arsenic (As), Cadmium (Cd), Lead (Pb) and Mercury (Hg) in turmeric powder was developed using ultra-microwave and inductively coupled plasma mass spectrometry. Limits of quantification in samples for As, Cd, Pb and Hg were measured 2.58, 0.08, 0.43, and 0.01 ug/kg, respectively. The calibration curve showed linearity in the range between 0.998~0.999. Recovery for As, Cd, Pb and Hg were 111, 91, 94, and 98%, respectively

PT.24

Effect of Different Biomass on Value-added Products in Bio-liquid of Food Waste via Hydrothermal Carbonization

Soomi Park[1], Jonathan Lee[2], Yura Hwang[1], Soyoung Lee[1], Sunyoung Bae[1]*

Department of Chemistry, Seoul Women’s University Nowon-Gu, Hwarangro, Seoul, Korea, 13[1]
Davidson College 405 North Main Street, Davidson, NC 28035[2]

Abstract: Hydrothermal carbonization (HTC) of food biomass produced bio-liquid as a by-product. During HTC reaction, various compounds were generated by hydrolysis, condensation, decarboxylation, polymerization and other reactions. From our previous experiments, a few value-added compounds from bio-liquid of food waste were characterized; butylated hydroxytoluene (BHT) and 5-(hydroxymethyl)-2-furaldehyde (HMF). BHT shows the antioxidant activity even though it also possess the toxicity and potential health hazard. HMF was treated as a renewable material to play an important role in a bio-fuel production. In this study, the quantitative information of these two compounds produced by different biomass was obtained. Liquid liquid extraction (LLE) method was applied using various solvents including dichloromethane mixed with ethyl ether and methanol, respectively. The bio-liquid sample dissolved in methanol was filtrated using a 0.2 μm syringe filter and injected into GC/FID (Hewlett Packard 5890 series Ⅱ, HP-5 capillary column, 30 m × 0.25 mm × 0.25 μm). To obtain qualitative information, one point standard addition method was chosen to correct matrix effect. The results are expected to show the effect of complexity occurred by different biomass on the amount of value-added products.

Keywords: Biomass, Hydrothermal carbonization, Bio-liquid, Value-added product, Antioxidant

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Introduction to the author:

Professor Dr. Sunyoung Bae
Department of Chemistry, Seoul Women's University, Seoul, Korea
Tel: +82-2-9705652; Fax: +82-2-9705972.
E-mail: sbae@swu.ac.kr

Biography of the authors.

Miss Soomi Park earns a Bachelor of Science degree in Chemistry at Seoul Women's University in 2015. She currently studies for a master's degree in analytical chemistry at Seoul women's university. She has presented her research at Korean Society of Soil and Groundwater Environment.

Dr. Sunyoung Bae has obtained Ph.D. from the University of Massachusetts-Lowell in 2002. She had been working at the interdisciplinary research center at the University of North Carolina-Charlotte. In 2008, she was appointed as an assistant professor in the Department of Chemistry at North Carolina A&T State University. Since 2010, she has been affiliated with Seoul Women's Universityas an assistant professor. Her research approach is to characterize physicochemical properties and interactions in micro-scale using analytical instruments that determines macro-phenomena. Currently, she has been served as an associate editor for Korean Society of Soil and Groundwater Environment and on the editorial board for the Korean Society of Analytical Sciences.

PT.25

Analysis of Polycyclic Aromatic Hydrocarbons in Water by Polyaniline Coated In-needle Microextraction

Yura Hwang, Dong-Sun Lee, Sunyoung Bae*

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

Abstract:

Polycyclic aromatic hydrocarbons (PAHs) can exist various forms with two or more fused rings. They are formed naturally or by human beings and mostly generated by the incomplete burning of coal, oil or organic substances. The concerns for PAHs are their hazardous characters being potential possibility of causing tumors and reproductive problems. PAHs are widely present in soil, surface water, ground water, drinking water and industrial products. To analyze PAHs in aqueous solution, they need to be extracted by various techniques including liquid-liquid extraction (LLE) and solid-phase microextraction (SPME). LLE method has some limits such as using a large amount of organic solvents and requiring labor-intensive work. In our study, PAHs in aqueous solution were determined based on head space in-needle microextraction (HS-INME) followed by gas chromatography-flame ionization detector (GC-FID). The INME adsorbent was polyaniline (PANI) that was electrochemically synthesized in our lab. Among various PAHs, our target compounds were naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene and fluoranthene. The parameters such as adsorbent length, adsorbent thickness, extraction temperature, extraction time and desorption time were optimized. The lengths of PANI layer were varied at 0.5 cm, 1.0 cm, 1.5 cm, and 2.0 cm. CV cycles that might control the adsorbent thickness were varied at 10 cycles, 30 cycles, and 50 cycles. Extraction temperature and time were evaluated at 25℃, 40℃, 60℃ and 10 min, 30 min, 60 min, 90 min, respectively. In addition, desorption time was evaluated by varying 15 s, 30 s, 60 s, 90 s, and 120 s. In conclusion, HS-INME with PANI as an adsorbent for PAH analysis can be efficiently performed to shorten analysis time and develop the solventless extraction method.

Keywords: Polycyclic aromatic hydrocarbons, head space in-needle microextraction, polyaniline, GC-FID

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Introduction to the author:

Dr. Sunyoung Bae
Department of Chemistry, Seoul Women's University, South Korea
Tel: +82-2-970-5652; Fax: +82-2-970-5972
E-mail: sbae@swu.ac.kr

Biography of the authors.

Miss Yura Hwang earns a Bachelor of Science degree in Chemistry at Seoul Women’s University in 2014. She currently studies for a master’s degree in analytical chemistry at Seoul women’s university. She has presented her research at various conferences including Korean Chemical Society, The Korean Society of Analytical Sciences, and Korean Society of Soil and Groundwater Environment.

Dr. Sunyoung Bae has obtained Ph.D. from the University of Massachusetts-Lowell in 2002. She had been working at the interdisciplinary research center at the University of North Carolina-Charlotte. In 2008, she was appointed as an assistant professor in the Department of Chemistry at North Carolina A&T State University. Since 2010, she has been working at Seoul Women’s University. Her research approach is to characterize physicochemical properties and interactions in micro-scale using analytical instruments that determines macro-phenomena. Currently, she has been served as an associate editor for Korean Society of Soil and Groundwater Environment and on the editorial board for the Korean Society of Analytical Sciences.

PT.26

TNF-α-induced insulin resistance mechanism study based on cell lysis-free quantum dot multicolor cellular imaging-based

Jieun Ki and Joon Myong Song*

College of Pharmacy, Seoul National University, Seoul 151-742, South Korea.

TNF-α, an inflammatory cytokine, plays an important role in insulin resistance as observed in cases of obesity and chronic inflammation. TNF-α is known to inhibit many cellular components involved in the insulin signaling cascade. Insulin receptor substrate (IRS)-1 is one of the major targets in TNF-α-induced insulin resistance and serine phosphorylation of IRS-1 enables the inhibition of insulin signaling. The mechanism of TNF-α-induced insulin resistance has been thoroughly investigated based on Western blot. Intracellular protein kinase crosstalk is commonly encountered in inflammation-associated insulin resistance. This crosstalk among the signaling molecules obscures the precise role of kinases in insulin resistance. Thus, a cell lysis-free quantum dot (QDot) multicolor cellular imaging was developed to identify the biochemical role of multiple kinases (p38, JNK, IKKβ, IRS1ser, IRS1tyr, GSK3β, and FOXO1) in inflammation-associated insulin resistance pathway with a single assay in a single run. QDot-antibody conjugates were used as nanoprobes to simultaneously monitor the activation/deactivation of the seven intracellular kinases in HepG2 cells. The effects of the test compounds on the suppression of TNF-α-induced insulin resistance were validated through kinase monitoring. Aspirin, indomethacin, cinnamic acid, and amygdalin were tested and the regulatory functions of multiple kinases were monitored simultaneously at the cellular level. The developed cellular imaging assay provides a unique platform to understand the inflammation and insulin resistance signaling pathways in type II diabetes mellitus and how they regulate each other. Amygdalin and cinnamic acid were found to inhibit serine phosphorylation of IRS-1 through targeting JNK serine kinase and enhance insulin sensitivity.

Keywords: Multicolor cellular imaging, Insulin resistance, Quantum dot, Inflammation

PT.27

Real time high-content cellular monitoring of the cytotoxic action of cationic polymer carriers polyethylenimine and poly-L-lysine on HepG2 cells

Gee Woo Nam and Joon Myong Song*

College of Pharmacy, Seoul National University, Seoul 151-742, South Korea.

Polyethylenimine (PEI) and poly-L-lysine (PLL) are cationic polymers that are commonly used as non-viral gene/drug delivery vehicles. The two polymers are highly cytotoxic, but the molecular mechanism regarding their cytotoxicity is poorly understood. Therefore, the toxicity pathway triggered by PEI and PLL were investigated through a high-content cellular imaging technique. PEI induced apoptosis via an intrinsic pathway, whereas PLL showed cytotoxicity through both intrinsic and extrinsic caspase cascades. The apoptotic activities against HepG2 cells of both PEI and PLL were dependent on the polymeric molecular weight. The structure of the PEI was also found to affect the polymer's ability to cause apoptosis. The branched PEI exhibited greater cytotoxicity than that of the linear PEI. This observation was verified through Annexin V-FITC/PI assay and real-time high-content monitoring of cytosolic calcium, mitochondrial membrane disruption, and caspase-3 activation.

PT.28

Multifunctional Composite of an Antibacterial Silver and a Potent Wound Healing Polypeptide as a Bimodal Wound Treatment

Baskaran Purushothaman and Joon Myong Song*

College of Pharmacy, Seoul National University, Seoul 151-742, South Korea.

The Hst-1-silver (II) chlorhexidine (Hst-1-[Ag(II)CHX]), a multifunctional composite containing antibacterial bi-valent silver polydiguanide and a potent wound healing polypeptide, histatin-1, for the treatment of infected wounds. The silver (II) chlorhexidine was prepared by the oxidation of Ag (I) and followed by the complexation of the oxidized metal with chlorhexidine (CHX), whereas the metal complex conjugate of the solid phase-synthesized histatin polypeptide (Hst-1), Hst-1-[Ag(II)CHX], was realized by mixing the starting materials in aqueous solution. The structural change for Hst-1 binding with silver complex was confirmed by circular dichroism spectroscopy. The cell-spreading assay was performed by using the Hst-1 and synthesized Hst-1-[Ag (II) CHX] complex on 3T3-L1 preadipocytes. The silver complex and its Hst-1 conjugates antibacterial activity was tested against several gram +ve and gram –ve bacteria, including Methicillin-resistant Staphylococcus aureus (MRSA) and Methicillin-resistant coagulase negative staphylococcus (MRCNS) by a broth micro dilution method. The experimental results revealed that the polypeptide and silver (II) polydiguanide complex retained their individual wound healing and antimicrobial activity even in their conjugate. The conjugate of higher-valent antibacterial [Ag(II)CHX] with a potent wound healing polypeptide (Hst-1) showed promise as a new multifunctional therapeutic wherein the killing and healing functions of the constituent materials are preserved together for the development of new-generation wound-care agents.

PT.29

Concurrent monitoring of CD31, CD34, CD45 and CD146 endothelial progenitor cell markers for acute myocardial Infarction

Hee Ju and Joon Myong Song*

College of Pharmacy, Seoul National University, Seoul 151-742, South Korea.

The endothelial progenitor cells (EPCs) in blood of acute myocardial infarction (AMI) patient have been observed in many previous studies. The number of circulating EPC increases in the blood of patients at the beginning of the AMI. EPC is originated from bone marrow. It executes vessel regeneration. There are many markers used for detecting EPC. Four of these markers, CD31, CD34, CD45, and CD146, were concurrently detected at the single cell level for the identification of EPC in the present preliminary study. The CD45 negative cell sorting was performed to peripheral blood mononuclear cells (PBMCs) acquired from four AMI patients with a magnetic bead sorter, since, EPCs expressed CD45 negative or dim. The resultant PBMC eluents were treated with quantum-antibody conjugates for the probing four different markers of EPCs and then applied to a high-content single cell imaging cytometer using acousto-optical tunable filter (AOTF). The use of quantum dot, with narrow emission wavelength range and AOTF enabling cellular image at a particular single wavelength, is very advantageous for accurate high-content AMI diagnosis based on simultaneous monitoring of many markers. In this work, a high-content cellular diagnostic assay using quantum dot-antibody probing material and AOTF is newly suggested to accurately identify EPCs in peripheral blood acquired from CVD patients. The number of EPC increased as compared with control in three of four AMI patients. In this approach, two EPC subtypes were found, CD31(+), CD34(+), CD45(-/dim), CD146(-) as early outgrowth EPCs and CD31(+), CD34(+), CD45(-/dim), CD146(+) as late outgrowth EPCs. Patient 1 had CD31(+), CD34(+), CD45(-/dim), CD146(+) cells whose percentage was 4.21% of cells. Patient 2 had 2.38% of CD31(+), CD34(+), CD45(-/dim), CD146(-) cells and patient 3 had 4.28% of CD31(+), CD34(+), CD45(-/dim), CD146(+) cells. This system was proved to be very appropriate for the EPC monitoring based on its potential to detect large number of molecular markers concurrently. In addition it was verified that this system provided little spectral interference and led to more accurate EPC diagnosis.

Keywords: Acute myocardial infarction, Circulating endothelial progenitor cells, Quantum dot, High content single cell cytometer, Acousto-optical tunable filter (AOTF)

PT.30

Optimization of Chlorophenols Detection in Water Samples using Stir bar Sorptive Extraction Coupled with Thermal Desorption-GC-MS

Mina Lee, Yun S. KIM *

Water Quality Reserch Centre, K-water Institute, K-water, Korea

Abstract: The rapid, accurate, and simple analytical method for the determination of trace amounts of chlorinated phenols, such as chlorophenol, 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TrCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) and pentachlorophenol (PCP), in water using stir bar sorptive extraction (SBSE)-thermal desorption unit(TDU)–gas chromatography–mass spectrometry (GC–MS) with in-situ derivatization are described. The optimization of SBSE conditions such as, extraction time, affection of salt and stirring speed are investigated. The detection limits and quantification limits of the chlorophenols in water are ranged 0.1~0.6 and 0.4~1.8 ng/mL, respectively. The average recoveries and precision of the chlorophenols in all the samples are ranged 98~109%, 2.0~6.6%, respectively. This level of detection observed based on hazard quotient a remarkable improvement over the conventional method. Moreover, the sufficient sensitivity of detection limits and quantitative limits for chlorophenols in water was estimated based on risk assessment in this work.

Keywords: Chlorophenols; Water; SBSE; Thermal desorption unit (TDU)–GC/MS

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Introduction to the author:

Researcher Ms. Mina Lee
Water Quality Reserch Centre, K-water Institute, K-water, Korea
Tel: +82-42-629-2047; Fax: +82-42-629-2099.

Principal Researcher Dr. Yun S. KIM
Water Quality Reserch Centre, K-water Institute, K-water, Korea
Tel: +82-42-629-2042; Fax: +82-42-629-2099.
E-mail: yunskim@kwater.or.kr

Biography of the authors.

Yun. S. Kim is a principal researcher in the water quality research centre of K-water institute, Daejeon, Korea. He obtained Ph.D (Bioresource Sciences; Environmental Analysis Chemistry) from Nihon University, Japan. He is interested in the development of analysis methods for emerging organic compounds in environmental samples and their risk assessments.

PT.31

Validation of Analytical Method for Propylene Glycol and Ethylene Glycol in Foods

Ho Soo Lim, Ju Young Hwang, EunA Choi, Gun young Lee and Tae Seok Kang

Food Additives and Packaging Division, Ministry of Food and Drug Safety,
Cheongju-si, chungcheongbuk-do, Korea

E-mail: hslim70@korea.kr

Abstract

A simple method was developed for the simultaneous determination of propylene glycol (PG) and ethylene glycol (EG) in foods using gas chromatography with flame ionization detector (GC-FID). PG (authorized additive used as humectant and emulsifier) and EG (unauthorized additive having a sweet taste) in foods were extracted with water:acetone (30:70), followed by the treatment of Carrez solutions and centrifugation. The resulting solution was filtered using 0.45 μm membrane syringe filter and injected into GC. The separation of PG and EG was carried out on HP-INNOWAX capillary column (30 m × 0.25 mm, 0.25 μm). The calibration curves of PG and EG were linear in the range of 1.0 to 100 μg/ml, with good correlation coefficients (r^2 >0.999). The recoveries ranged from 90% to 98% for PG, from 90% to 104% for EG at spiking levels of 10, 50, and 100 mg/kg in three samples (dumpling, coffee, candy and chocolate). The limit of detections (LOD) and limit of quantifications (LOQ) for PG and EG were 0.4 μg/ml and 1.3 μg/ml, 0.3 μg/ml and 1.0 μg/ml, respectively. For four food matrix studied, expanded uncertainties (U) expressed as percent were below 20% for PG and EG. Uncertainty associated with food matrix contributed mostly to the expanded uncertainty. This study is the first report for direct simultaneous determination of PG and EG in foods by GC-FID.

PT.32

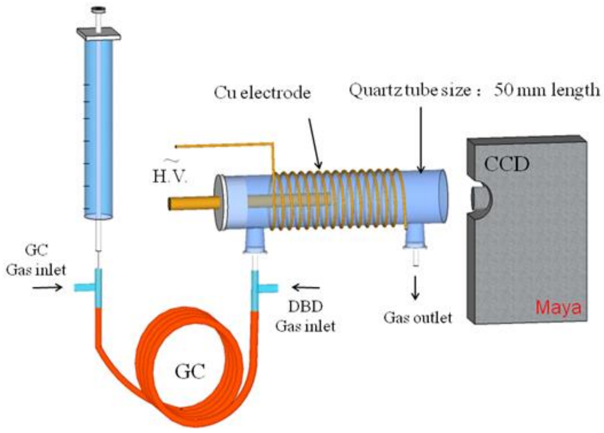
Dielectric Barrier Discharge Molecular Emission Spectrometer as Gas Chromatographic Detector for Amines

Chenghui Li [a], Xue Jiang[a], Xiandeng Hou[a,b*]

a. Department of Chemistry, Sichuan University, Chengdu, 610064, China
b. Analytical & Testing Center, Sichuan University, Chengdu, 610064, China
Corresponding author email: houxd@scu.edu.cn

ABSTRACT: Nano-SiO_2 was immobilized on the inner wall of a dielectric barrier discharge (DBD) tube, and it was coupled to a conventional gas chromatographer to investigate its performance as a molecular emission spectrometric detector for the determination of five volatile aliphatic amines. A charge coupled device (CCD) was applied to observe the nano-SiO_2-enhanced molecular emission spectra. The characteristic molecular emission bands of volatile aliphatic amines at 326.5 nm, 336.0 nm and 388.3 nm can be clearly resolved from the background emission spectra of carrier gas argon. The emission band of CN at 388.3 nm was used for quantitative detection of volatile aliphatic amines due to its high sensitivity. Nanomaterial catalysts including TiO_2, MnO_2, SiO_2 and ZnO were tested to enhance the emission signal of amines, and SiO_2 shows the best performance. The factors that influence the emission signal, such as discharge voltage, inner electrode length and carrier gas flow rate, were investigated in detail. The analytical performance of this method was evaluated by separation and detection of the mixture of five volatile aliphatic amines. Under the optimal experimental conditions, the limits of detection were found to be 4.4, 2.5, 2.2, 1.8 and 2.4 μg for dimethylamine, trimethylamine, n-butylamine, cyclohexylamine and ethylenediamine, respectively. This GC detector is not only sensitive but also fast in response to volatile aliphatic amines with good stability. Trimethylamine in a carp fish sample was monitored with storage time by the proposed method.

KEY WORDS: dielectric barrier discharge; molecular emission spectrometry; amine; GC; SiO_2



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PT.33

Aptamer-bound magnetic beads and antibiotics functionalized fluorescent gold nanoclusters based dual recognition strategy for detection of bacteria

Dan Cheng, Mengqun Yu, Gan Li, Zheguo Zhu, Yang Song, Erqun Song*

Key Laboratory of Luminescence and Real-Time Analytical Chemistry, Ministry of Education, College of Pharmaceutical Sciences, Southwest University, Chongqing, 400715, People's Republic of China. Fax: +862368251225; Tel: +862368251225. E-mail: eqsong@swu.edu.cn

Abstract: Infectious diseases and food poisoning caused by pathogenic bacteria such as *Staphylococcus aureus* (SA) have been bringing to serious public health concerns[1, 2], which makes the specific, sensitive and rapid detection of bacterial is essential and important. The common used strategies for SA including traditional microbiological method, polymerase chain reaction (PCR)-based method and antibody-based immunoassay method are limited due to the disadvantages of time-consuming, not suitable for quantification, false-positive, expensive respectively[3-5]. Thus, it is essential to develop an accurate, simple, rapid and cost-effective strategy for SA assay. Besides antibodies, nucleic acid aptamer, antibiotics are also important recognition molecules for bacteria, which have been employed for developing detection strategy of SA[6,7].

This study presents a strategy by combining the aptamer and antibiotic-based dual recognition units with magnetic enrichment and fluorescent detection together to achieve specific and sensitive assay of SA in authentic specimen (Figure 1). Aptamer-bound magnetic beads (Apt-MB) prepared based on the interaction between biotinlyated-aptamer and streptavidin-magnetic beads were employed for specific capture and enriching the target SA. And the antibiotic of vancomycin stabilized fluorescent gold nanoclusters (AuNCs@Van) synthesized facilely in one step were used for sensitive quantification of SA. Using this strategy, the determination limit of SA from complex samples containing other contaminated bacteria could achieve to the level of ppm. Compared with similar job, our work not only simplifies the preparation procedure of fluorescent detecting probes of AuNCs@Van, but also detects the added SA in milk directly with good accuracy. And moreover, aptamer and Van are cheap and widely available, making the strategy for assay of SA cost effective. Such aptamer and antibiotics based dual recognition strategy combined with magnetic enrichment and fluorescent detection of trace bacteria show

promising potential application in the bacteria-related infectious diseases and food contamination.

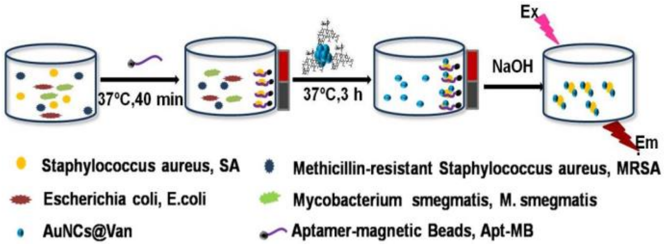

Figure 1 Illustration of Apt-MB and AuNCs@Van based dual recognition strategy for SA assay.

Keywords: aptamer, antibiotic, gold nanocluster, bacteria, dual recognition

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Introduction to the author:

Associate Professor Dr. Erqun Song
College of Pharmaceutical Sciences, Southwest University, Chongqing, China
Tel: +86-15826022758; Fax: +86-23-68251225.
E-mail: eqsong@swu.edu.cn

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Determination of the fatty acid compositions offal meat of sheep produced in Mongolia using GC and GC-MS

G.Oyun[1], D.Narantuya[1], E.Anudari[1], D. Seo[2], J. Ha [2,3*]

[1]Scientific food research and manufacturing “SAMO” Institute, Ulaanbaatar, Mongolia
[2] Food Analysis Center, Korea Food Research Institute
[3] Korea University of Science and Technology

Abstract: The fatty acid compositions of offal meat produced in Mongolian sheep (Ovis *Aries*) was analyzed using GC and GC-MS. The present study showed the result that fatty acid composition in mucous offal meat was higher than the internal organs. Among the internal organs, liver had most high value of fatty acid. Saturated and unsaturated fatty acid ratio varied differently depending on the type of animals, such as cow was 1.2: 1, and sheep 1: 1 while the horse was 1: 1.6. Thereby, fatty acid composition of offal include the palmitic acid C16 and stearic acid C18 from saturated fatty acid branch, oleic acid C18:1 of monoene, linoleic acid C18:2 of polyene from unsaturated fatty acid branch, and other acids such as C12, C14, C20, C22, C14:1, C16:1, C20:1, C18:3, C20:2, C20:3, C20:4 were found in small quantities. These results show the significant proof of similarity with the carcass meat of grazing livestock. Thus, we can consider that Mongolian grazing livestock meat has great beneficiary effect in human health regarding to the fact that the indication of eicosapentaenoic and docosahexaenoic acids were expressed in the analysis of dried offal meat, while it is not expressed in indoor farming livestock meat. Likewise, “essential fatty acids” which has positive effect in human health make out the 60-80% of total fatty acid composition in offal meat.

Keywords: saturated, unsaturated, polyenoic, monoenoic fatty acid, sheep, cow, horse, dried sample

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Introduction to the author:

Professor Dr. Jaeho HA
Food Analysis Center, Korea Food Research Institute, 463-746, Korea
Tel: +82-31-780-9217; Fax: +82-31-780-9280.
E-mail: jhkfri@gmail.com

Biography of the authors.

Dr Jaeho Ha completed his doctorate in food chemistry with the practical combination of mass spectrometry and gas chromatography at the Korea University in 1992. He joined the Food Analysis Center at Korea Food Research Institute in 1984, where he involved himself in the analysis of food components, including micotoxin, pesticides, nutrients, fatty acid and aromas. Dr. Ha served his vice-presidency of Korean Society of Analytical Science 2000 – present. He is currently the vice president of Korea Food Research Institute and a leader of food analysis division of Korea Society of Food Science and Technology. Concurrently, Dr. Ha is applying GCxGC-TOFMS technology coupled with stir bar sorptive extraction and dynamic headspace sampling techniques for the analysis of flavors and trans fatty acids in foods. His research and activity is focused on chromatographic separation, flavor chemistry, food analysis. Recently he has carried out the ODA project for the capacity building of agro-food safety system in Mongolia.