

Oral Presentation

Sample Pretreatment of Environmental Estrogens and Analytical Application Using Liquid Chromatography-Mass Spectrometry

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In recent several decades, due to excessive use and discretionary disposal of hormone pills and contraception pills, increasing content of various estrogens have enter to the environmental waters. Since these estrogens have ultra high physiology activity at very low concentration, they have become a threat to eco-environment and human health. Therefore, Estrogens have aroused the attention of the world and become a new global environmental problem.

Because of high resolution and sensitivity, liquid chromatography-mass spectrometry (LC-MS) has widely applied in environment, medical analysis, clinic detection and life science. Though LC-MS has powerful analytical ability, when it is applied for real sample analysis, complex matrices often seriously interfere the final results. In this case, to develop simple, rapid and effective pretreatment method is an important impetus to broaden the application of LC-MS technology. The aim of this work is to develop rapid and effective pretreatment method coupled with LC-MS for quantitative analysis of estrogens in various matrices. 1) Ten highly potent estrogens were identified and quantified by solid-phase extraction (SPE) followed by LC-MS. Improved two-step SPE process was employed in the work. C18 cartridge was used for both enrichment of all target estrogens and retention of some nonpolar impurities, and then a polar Florisil cartridge was subsequently used to separate the interested estrogens from the polar impurities. In the optimized condition, this method was used to verify the presence of the target analytes in Qinghe River and influent of sewage treatment plant (STP) in northwest of Beijing, China. Some estrogens were detected in the river water samples and sewage water samples at relatively high concentrations. The developed method proved to be effective for analyzing estrogen compounds in complex matrices. Moreover, the achieved results demonstrated that a lot of concern should be addressed about the potential risk of the present of estrogens in aquatic environment. 2) Triacetyl bonded silica (C₃₀) material was applied as SPE sorbent and a SPE-LC-MS method was established for the determination of 8 estrogens and their metabolites in water samples. The results showed superior performance of C₃₀ to C₁₈ by the shorter treatment time and fewer required elution solvent. Method validation using C₃₀ packed cartridge was also testified with spiked real water samples, including tap water and river water. 3) Using C₃₀ as on-line SPE material and a specially designed online analytical system which allowed large sample volume injection, a high speed and robust online SPE-HPLC-MS method was established for the analysis of five estrogens and bisphenol A (BPA) in milk samples.

Biography

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His current research is focused on sample pretreatment, chemiluminescence, capillary electrophoresis and microfluidic device. He is the author and co-author of 218 original research papers published in international journals, 21 reviews, 3 books and 31 patents.

Arsenic speciation by coupling liquid chromatography with gradient hydride generation atomic absorption spectrometry

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The accurate determination of arsenic in various sample matrices has attracted extensive attentions because of its high toxicity. The total concentration of arsenic is not sufficient to provide comprehensive information about the toxic effect, while it depends strongly on the chemical state of a specific arsenic species. Therefore, the identification of arsenic species is one of the most important issues when evaluating its toxic effects [1]. The hyphenation of liquid chromatography with hydride generation atomic spectrometry is among the most common techniques for the separation and quantification of metal species [2]. The present work focuses on the development of a suitable procedure for arsenic speciation by coupling liquid chromatography with gradient hydride generation atomic absorption spectrometry (HPLC-GHG-AAS).

Fig. 1 illustrated the HPLC-GHG-AAS system for arsenic speciation. The arsenic species were separated by the HPLC system, followed by mixing with reagents HCl and NaBH₄ to facilitate hydride generation in a reaction coil in a boiling water bath. The reaction mixture was cooled off in a cooling water bath followed by separation of hydride in a gas-liquid separator, which was afterwards quantified by a flame AAS (FAAS). The boiling water bath was used for improving the efficiency of hydride generation of arsenic species, while the cooling water bath eliminates any entrapment of water vapor into the argon stream and the quartz cell of FAAS.

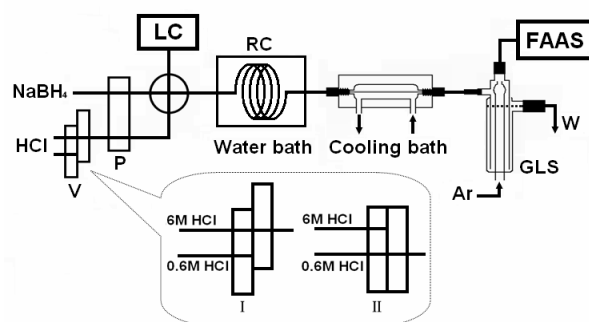


Fig.1. The HPLC-GHG-AAS system for arsenic speciation.

The separation of arsenic species was performed by using a C30 column at 25°C. The mobile phase contains 5 mM of sodium butanesulfonate, 4 mM of malonic acid, 4 mM of tetramethylammonium hydroxide and 0.1% methanol (pH=2). The mobile phase flow rate is 1.0 mL/min. The gradient hydride generation is performed such that

a 6 M of hydrochloric acid was used for the hydride generation of arsenate, arsenite and MMA, when the signal for MMA has been recorded, the controlling valve was switched to introduce a stream of 0.6 mol/L of hydrochloric acid as hydride generation medium for the other two arsenic species, i.e., DMA and TMA (Fig. 2). The detection limits for the arsenic species were summarized in Table 1.

Ultrasonic-assisted extraction was used for the pretreatment of Hijiki, i.e., 5 gram of Hijiki was taken into a 100 mL vessel to which 50 mL water was added. The mixture was sonicated for 30 min and the extract was separated by filtration for arsenic speciation by appropriate dilution. Fig. 3 showed the analytical results from a 5-fold diluted extract of Hijiki. Three arsenic species, i.e., arsenate, DMA and TMA, were identified in Hijiki samples.

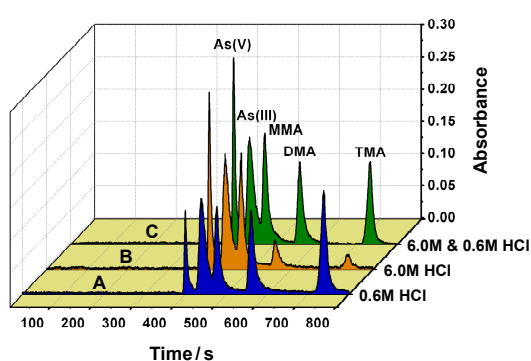


Fig. 2. Arsenic speciation in aqueous solution by the HPLC-GHG-AAS system

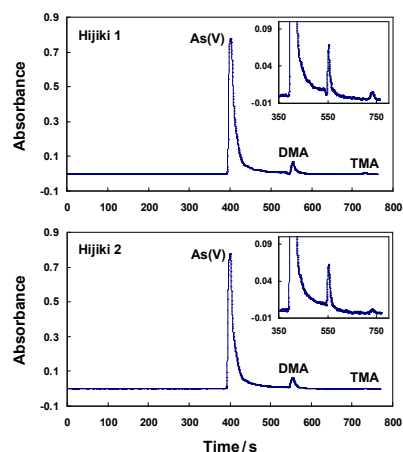


Fig. 3. Arsenic speciation in 5-fold diluted Hijiki extract

Table 1. The speciation of arsenic in Hijiki by the HPLC-HG-AAS system

Species	Found Hijiki 1 ($\mu\text{g/g}$)	Found Hijiki 2 ($\mu\text{g/g}$)	Spiked ($\mu\text{g/L}$)	Spiking Recov. Hijiki 1 (%)	Spiking Recov. Hijiki 2 (%)
As(V)	53.6 ± 9.2	60.8 ± 13.2	50	107.4	111.2
As(III)	n.d.	n.d.	50	97.9	97.1
MMA	n.d.	n.d.	50	106.9	104.9
DMA	2.7 ± 0.4	2.4 ± 0.5	50	112.5	105.7
TMA	0.34 ± 0.12	0.15 ± 0.03	50	104.6	102.2

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Polydimethylsiloxane Mini-Disk Extraction as a Novel Sampling Technique

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A novel sampling method called headspace polydimethyl-siloxane (PDMS) mini-disk extraction (HS-PDE) was developed, optimized, validated and applied for the GC/MS analysis of flavors for the first time. A prototype PDMS mini-disk (diameter: 8 mm, thickness: 0.157 mm, weight: 9.4 mg) has been designed as a sorption device. The technique uses a small PDMS mini-disk and very small volume of organic solvent. This new HS-PDE method is very simple to use, inexpensive, rapid, requires small sample amounts and solvent consumption. Because the acetonitrile for extraction is reduced to a very small volume of only 0.03 mL, there is minimal waste or exposure to toxic organic solvent and no further concentration step. Linearities of calibration curves for α -pinene, β -pinene, limonene and γ -terpinene by HS-PDE combined with GC/MS were generally good. LOD and LOQ showed very low values, and dynamic ranges were 6.00 ng~3500 ng. This method exhibited good precision and accuracy. The overall extraction efficiency of this new method was evaluated by using partition coefficients (K_{fg}) and concentration factors (CF) for several characteristic components from nutmeg and mace. Partition coefficients were in the range from 2.04×10^4 to 4.42×10^5 , while CF values were 0.88~15.03. HS-PDE was applied successfully for the analysis of flavors compositions from cumin, nutmeg and mace. The HS-PDE method is a very promising sampling technique for the characterization of volatile flavors.

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Design of Flow Injection Analysis to Realize Green Chemistry

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Summary

A sense of Green Sustainable Chemistry will be incorporated in analytical chemistry to perform advanced analytical systems. Use of conventional instruments and common reagents will be alternatives to the analytical instruments consuming large amounts of energy and natural resources. Flow injection analysis of aluminum with fluorimetric detection and sequential injection analysis of iron with chemiluminometric detection are introduced as examples.

Keywords: green sustainable chemistry, low consumption of energy and resources, conventional instruments, common reagents, alternative analytical systems

1 Introduction

Under limited energy and natural resources on earth, sciences are now directed toward environment-friendly systems: less consumption of energy and resources, reuse and recycle of materials, zero emission of pollutants and wastes. These actions are generally called as Green Sustainable Chemistry. The concept is also valid in the field of analytical chemistry, deeply related with environmental sciences. During last century, highly sensitive analyses have been established by developing high-performance analytical instruments such as ICP-AES. Analysis by ICP instruments are realized based on the consumption of a large amount of noble gases. Therefore, interests nowadays are directed toward how we can realize the sensitive analysis by convenient instruments with common reagents. Although the analytical systems thus established are based on inexpensive items, it would be highly integrated and sophisticated analytical systems.

Development of new analytical reagents has also been one of major trends in analytical chemistry. So-called “new” reagents sometimes realized high sensitivity and high selectivity. On the other hand, the “new” reagents simultaneously possess the risk of toxicity/pollution. History of useful/convenient synthesized substances tells us that they are also the one of toxicity/pollution. Analytical chemists should weigh the benefits with the possible disadvantages. The conventional instruments and common reagents will be utilized to establish the analytical systems and to meet Green Sustainable Chemistry. Flow injection analysis and sequential injection analysis systems are also helpful to reduce the chemical wastes.

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2 Determination of aluminum with 8-quinolinol by fluorophotometric flow injection analysis

Derivatizing reagent of 8-quinolinol is well known for the determination of several metal ions by fluorophotometry. Solvent extraction with organic solvents are usually utilized together to improve the fluorescence intensity and the extraction concentration. The organic solvents are volatile and they would be reduced. Micelle sensitization was utilized to improve the solubility of the complexes and to improve the sensitivity in an aqueous solution; nonionic Triton X-100 was used as a micelle-forming surfactant. By coupling with flow injection analysis, limit of detection at 3×10^{-9} M was attained for aluminum, and the analysis method was applied to river water samples. The FIA signal increased with time after the addition of 1 mM HNO₃, and the profiles suggested the decomposition of complexed aluminum species in an aqueous solution.

3 Chemiluminometric detection with luminol in sequential injection analysis

Luminol is a well-known and commonly-used reagent for the chemiluminometric detection of H₂O₂ or catalytic metal ions. Detection method of chemiluminescence is advantageous in sequential injection analysis, because the schlieren effect, when auxiliary light is used, will not occur and ghost signal is much reduced. The flat baseline realizes the high sensitive detection. Micelle sensitization on Fe³⁺/Fe²⁺ catalyzed luminol chemiluminescence was examined. Nonionic surfactant of Triton X-100 was added in the metal ion solution, luminol in weakly alkaline solution, or H₂O₂ solution. Among them, addition in the metal ion solution much improved the chemiluminescence intensity about 13 times, which will contribute to develop highly sensitive determination of the metal species.

4 Conclusion

In summary, design of analytical systems using conventional detections and common reagents will replace high-performance analytical instruments. The consumption of energy and resources will be reduced, and suspicious novel reagents will be excluded, which lead us to Green Chemistry.

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Hybrid organic-inorganic silica monolith with hydrophobic /strong cation-exchange functional groups as a novel sorbent for in-tube solid-phase microextraction

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Sample treatment has been recognized as the main bottleneck of the analytical process, especially when trace analysis in complex matrices is the purpose. As to the development of environmentally and biologically favorable analytical methods, miniaturization trends of the sample preparation with low sample requirements, and low solvent consumption has been gained much attention. In-tube solid-phase microextraction (in-tube SPME) was introduced as an excellent sample preparation technique, since it possesses several attractive features including small sample volume, simplicity and easy automation.

For in-tube SPME, the sorbent in a capillary play an important role in interference elimination and eluting the analytes more selectively. Therefore, developing sorbent with high extraction efficiency and high selectivity for in-tube SPME is always an attractive task. In this contribution, we prepared a novel hybrid organic-inorganic silica monolith with hydrophobic and strong cation-exchange functional groups in a fused silica capillary and used it as a sorbent for in-tube SPME. The hybrid silica monolith functionalized with octyl and thiol groups was conveniently synthesized by hydrolysis and polycondensation of a mixture of tetraethoxysilane (TEOS), n-octyltriethoxysilane (C8-TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) via a two-step catalytic sol-gel process. Due to the favorable chemical reactivity of mercapto pendant moieties, the obtained hybrid monolith was oxidized using hydrogen peroxide (30% w/w) to yield sulfonic acid groups, which provided strong cation-exchange sites. The obtained hybrid monolith was characterized by diffused infrared spectroscopy, elemental analysis and scanning electron microscopy. The results show that the resulting monolith contains much higher carbon (31.6%) and sulfur (4.8%) contents than traditionally bonded silica materials. The extraction performance of the hybrid monolith was evaluated using sulfonamides as model analytes by in-tube SPME on-line coupled to HPLC. The results show that the hybrid monolith with hydrophobic and strong cation-exchange functional groups exhibits high extraction efficiency towards the model analytes with satisfactory reproducibility and stability. Finally, a method for the determination of sulfonamide residues in milk was developed by the combination the hybrid monolith in-tube SPME and HPLC.

Keywords: In-tube solid-phase microextraction; Organic-inorganic hybrid materials; Silica monolith; Mixed-mode; Hydrophobic interaction/cation-exchange; Sulfonamides

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His research interests are on the development of novel separation media for liquid chromatography, capillary electrochromatography, capillary electrophoresis, and solid-phase (micro) extraction, and their applications to biomedical analysis and food analysis.

High extraction efficiency for polar aromatic compounds in nature water samples using multiwalled carbon nanotubes/Nafion solid-phase microextraction coatings

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Since solid-phase microextraction (SPME) was introduced by Arthur and Pawliszyn in 1990, it has been widely applied in many areas. Compared to traditional techniques, SPME offers many advantages such as high sensitivity, reproducibility and solventless and combines sampling, extraction, and sample introduction into a single step. This technique is based on the partitioning of analytes between the sample and the coating of SPME fiber. In order to achieve higher applicability for various compounds, various approaches including physical deposition, electrochemical procedures, direct use of uncoated fiber, epoxy-glued solid sorbents, sol-gel technology, and molecular imprinting polymers (MIPs), have been developed for the production of SPME fibers. Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer. The combination of the stable Teflon backbone with acidic sulfonic group gives Nafion excellent characteristics such as highly conductive, high operating temperature and chemical stability. In 1998, Nafion was applied as a fiber coating material for SPME. It was used to extract alcohols from hexane and gasoline samples, and exhibited better extraction efficiency than all of the commercially available coatings selected. These results indicate the great analytical potential of Nafion to be an effective solid-phase microextraction coating for polar compounds.

In this study, a novel solid-phase microextraction (SPME) fiber coated with multiwalled carbon nanotubes (MWCNTs)/Nafion was developed and applied for the extraction of polar aromatic compounds (PACs) in environmental water samples. The characteristics and the application of this fiber were investigated. Electron microscope photographs indicated that the MWCNTs/Nafion coating with average thickness of 12.5 μm was homogeneous and porous. The MWCNTs/Nafion coated fibers exhibited higher extraction efficiency towards polar aromatic compounds compared to an 85 μm commercial PA fiber. SPME experimental conditions, such as fiber coating, extraction time, stirring rate, desorption temperature and desorption time, were optimized in order to improve the extraction efficiency. The calibration curves were linear from 0.01 to 10 $\mu\text{g mL}^{-1}$ for five PACs studied except p-nitroaniline (from 0.005 to 10 $\mu\text{g mL}^{-1}$) and m-cresol (from 0.001 to 10 $\mu\text{g mL}^{-1}$), and detection limits were within the range of 0.03 to 0.57 ng mL^{-1} . Single fiber and fiber-to-fiber reproducibility were less than 7.5 (n=7) and 10.0 % (n=5), respectively. The recovery of the PACs spiked in nature water samples at 1 $\mu\text{g mL}^{-1}$ ranged from 83.3 to 106.0 %.

Biography

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Professor. Xi Chen, born in 1964, graduated from Fuzhou University with a Bachelor's degree of analytical chemistry, went on to obtain his Master's degree there. Later in 1991, awarded the Monbusho Scholarship from Japanese government, he entered Kyoto Institute of Technology to go on with his research and received the Ph.D degree four years later. During his stay in Japan, he committed himself in the research fields on the application of photosensitive materials related ruthenium in analytical chemistry.

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 that University. In 2003, he was promoted to be a full professor at the same department.

Between June to July, 2002 and 2003, he was a senior research staying at Department of Chemistry, University of Hong Kong. He got JSPS final support to collaborate with Prof. M. Oyama, Kyoto University, in 2004.

At present, he is taking charge of a National High Technical Development Project (863 Project) Foundation in the field of ocean, National Scientific Foundation of China and a Key Project of Fujian Scientific Foundation on the determination of pesticide residue. Dr. Chen is now interested in chemiluminescence, separation analysis, chemical and biosensors.

In 2001, Dr. Chen was honored the Outstanding Contribution Award for his excellent work in the 818 Subject of 863 Project and received the 1st and 3rd class Scientific Progress Prizes of Fujian province in 2002, 2005 and 2007.

Application of Flow-Based Analysis to Diabetes Care

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Summary

Vanadium has recently attracted much attention for its potential role against diabetes. Bottled drinking waters containing vanadium are now commercially available. An automated stopped-in-dual-loop flow analysis (SIDL-FA) system is proposed for the determination of trace vanadium in drinking water samples. On the other hand, measurement of albumin/creatinine ratio is useful for detection of early-stage diabetic nephropathy. In the present paper an alternative method for the successive determination of urinary albumin and creatinine by sequential injection analysis is also described. We discuss here the applicability of flow-based analyses to diabetes care.

Key word: Vanadium; Albumin; Creatinine; Flow based analysis; Spectrophotometry; Diabetes.

1 Introduction

In Japan approximately 38% of patients who started undergoing artificial dialysis in 2001 were due to their diabetic nephropathy [1]. Therefore detection of early-stage diabetic nephropathy is important.

Heyliger *et al.* reported that vanadate (vanadium in pentavalent state) appeared to have an insulin-like action in the *in vivo* experiments on diabetic rats [2]. Since then, many studies have been reported on the insulin-like effect of vanadium. Some of bottled drinking waters containing naturally occurring vanadium are now available for health benefit. However, the exact role of vanadium has yet to be established. Therefore the concentration of vanadium in such bottled waters must be strictly controlled.

Microalbuminuria is an indicator of early-stage diabetic nephropathy and can be measured using a 24 hour urine specimen. However, this method has difficulty for assessing microalbuminuria due to variations in protein concentration over time. To eliminate the uncertainty and the strain, a more convenient method to detect microalbuminuria is the albumin/creatinine ratio (ACR) measured in a random urine specimen.

2 Stopped-in-Dual-Loop Flow Analysis (SIDL-FA) of Vanadium [3,4]

The chemistry is based on the vanadium-catalyzed oxidation reaction of *p*-anisidine by bromate in the presence of Tiron as an activator to produce a dye ($\lambda_{\max} = 510 \text{ nm}$). The SIDL-FA system is shown in Fig. 1. A 100- μL coiled loop around a heated device is fitted onto each six-way injection valve. A well-mixed solution containing reagents and

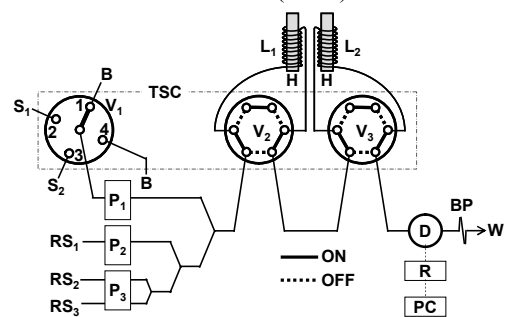


Fig. 1 Schematic flow diagram of the SIDL-FA system. B, HNO_3 ; S_1 , and S_2 , sample; RS_1 , mixture of *p*-anisidine and acetate buffer (pH 3.3); RS_2 , KBrO_3 ; RS_3 , Tiron; V_1 , selection valve; V_2 and V_3 , injection valves; P_1 , P_2 and P_3 , pumps; H, heater (105°C); L_1 , first loop; L_2 , second loop; D, spectrophotometer (510 nm); R, recorder; PC, computer; BP, back pressure restrictor.

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standard/sample is loaded into the first loop on a six-way valve, and then the same solution is loaded into the second loop on another six-way valve. The solutions are isolated by switching these two six-way valves, so that the catalytic reaction can be promoted. Then each resulting solution is dispensed to the detector with suitable time lag. The proposed SIDL-FA method allowed vanadium to be quantified in the range of 0.1 to 2 $\mu\text{g L}^{-1}$ and was applied to the determination of vanadium in drinking water samples.

3 Sequential Injection Analysis (SIA) of Albumin and Creatinine [5]

In this work, two specific reactions were used separately to determine albumin and creatinine levels. First, eosin Y was employed to form a color complex with albumin. The concentration of this complex could be monitored by absorption at 547 nm. Second, creatinine levels were determined by

Jaffe's reaction, where creatinine quantitatively produces an orange color with sodium picrate in alkaline medium. The absorbance was measured at 500 nm. These two detection reactions were introduced into a SIA system. The proposed method was applied to successively evaluate albumin and creatinine in urinary samples taken from diabetic individuals. The results obtained by the proposed method were good agreement with those obtained by official methods (Fig. 2).

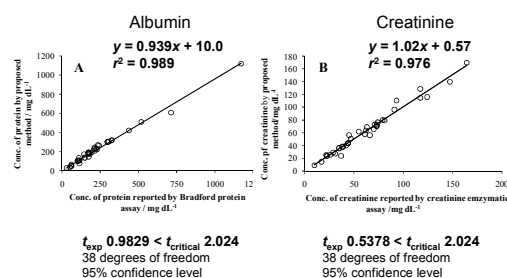


Fig. 2 Comparisons of two measurement methods, successive determination of albumin and creatinine using the proposed SIA system and Bradford protein assay (A) and creatinine enzymatic assay (B).

4 References

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New approach of simple pretreatment for GCMS analysis by using monolithic material sorption extraction for determination of 16 PAHs

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Environmental pollutions and food contaminations are biggest social concerns, nowadays. Because of the complex matrices in environmental substances and food stuffs, sample preparations for the quantitative analysis of toxic and hazardous compounds with chromatographic instruments are inevitable in order to obtain reliable results. Gas chromatography mass spectrometry (GCMS) has become the important means in the areas of qualitative and quantitative analysis of environmental monitoring and trace amount of contaminants in food stuffs. Although the performances of sensitivity and selectivity of this instrument have rapidly been improved in recent years, the sample pretreatment procedures remain the bottleneck for rapid analysis. Therefore, economical and effective pretreatment methods to eliminate matrix interferences, to achieve high throughput and to enrich the analyte for high sensitive detection are demanded.

The newly developed monolithic material sorption extraction (MMSE) has several advantages such as effective pre-concentration and cleanup of organic molecules from gaseous and liquid samples, and simple operation. Since monolithic material has wide through pore and meso pore structure, rapid permeability of organic molecules and high trap efficiency with large surface area can be realized. The thermal desorption technique together with GCMS measurement is most convenient for desorption of the analyte from the monolithic material.

MonoTrapTM (GL Science Inc, Japan) as a MMSE has been applied for the determination of 16 polycyclic aromatic hydrocarbons (PAHs) in water. After one hour extraction, MonoTrapTM device was transferred to OPTIC3 thermal desorption device (ATAS GL International BV) which was accommodated in GCMS-QP2010 Plus instrument (Shimadzu Corporation, Japan), and then GCMS analysis was carried out. All the analytical performances have been evaluated. PAH (Fluoranthene, Benzo[*b*]fluoranthene,

Benzo[*k*]fluoranthene, Benzo[*a*]pyrene) recoveries were higher than 85% for spiked water sample. There was good linear correlation between peak area and PAH concentration with a linear range of 0.1–100 ng/mL and correlation coefficients >0.995. The repeatability (RSD) at 100 ppb concentration was less than 6~15 %.

Thermal desorption GCMS combined with MMSE has been confirmed as a simple pretreatment method for determination of 16 PAHs.

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Analytical Method of Trans Fats by Comprehensive GCxGC and NMR

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Summary

The analytical condition of comprehensive GC×GC for TFA analysis has been optimized. Primary and secondary column was sp-2560(100m × 0.25mm, ID) and RTX-5(1.2m × 0.18mm, ID) respectively; primary oven temperature program of 150°C for 1min, 150-220°C at 3°C/min and 220°C for 20min, also secondary oven temperature was increase 20°C of primary oven temperature; Modulator temperature offset was 30°C; second dimension separation time was 6 sec; hot pulse time 1.20 sec and cool time between stages was 1.80 sec. The structural composition of TFAs in the triacylglycerols of the oil extracted from commercial butter and margarine has been studied using NMR spectroscopy. The intensity of the signal can also be used for quantitation. In the case of fat from butter and margarine, C₁₈ carbon allylic to a trans bond has a chemical shift of 32.6 ppm.

Key word: Trans fat, GCxGC, NMR

Introduction

In recent years there has been an increasing awareness of the influence of diet on human well-being, especially the effect of dietary fat on heart disease. It has been studied that partially hydrogenated vegetable oils contain trans unsaturation, positional isomers and conjugation not naturally occurring in vegetable oils. Although the major emphasis has been on the fatty acid composition of food fats, other characteristics have been implicated. There include triglyceride structure and configurational and positional isomers. Since the effect of trans fats on the human health may be different depending the positional isomer, the separation of individual isomer of trans fats (TFAs) has been attracted a great interest by the many separation scientists. TFAs are present in meat and dairy products as a by-product of fermentation in ruminant animals as a nature and in vegetable fats as a result of partial hydrogenation. This study was aimed to discrimination of natural(N-TFA) and hydrogenated trans fatty acid(H-TFA) by comprehensive GC×GC and NMR spectroscopy.

Materials and Methods

Lipids from butter and margarine for the TFA analysis were extracted by chloroform and methanol mixture (2:1, v/v) and evaporated to dryness. Methyl ester of TFA was obtained by the reaction in a heating block with BF₃/Methanol as a catalyst. For the NMR analysis of TFA, 50 mg of lipid was taken and solved in 500 μ L of CDCl₃.

GCxGC analysis was performed using LECO system. The column set for GCxGC analysis consisted of two columns. The primary column was SP-2560(100m x 250 μ m x 0.2 μ m, film thickness) and secondary column was RTX-5(1.5 m x 0.18mm x 0.18 μ m, film thickness).

NMR analysis was performed using Bruker Avance III 400 (Bruker, Germany). ¹H-NMR (500 MHz), ¹³C-NMR (125 MHz), 1D and DEPT, were used to predict the TFA content in butter and margarine, and estimate the position of double bond.

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Result and Discussion

The key isomers of TFA to discriminate the natural (N-TFA) and hydrogenated (H-TFA) TFAs are w9 and w11 TFAs since these two isomers are the major TFA with one double bond. To discriminate and quantify the amount of these two TFAs, the optimum analytical condition has been studied. For the separation of these two isomers, The condition of comprehensive GC×GC has been optimized: primary oven temperature program of 150 °C for 1min, 150-220 °C at 3 °C/min and 220 °C for 20min, also secondary oven temperature was increase 20 °C of primary oven temperature; Modulator temperature offset was 30 °C; second dimension separation time was 6 sec; hot pulse time 1.20 sec and cool time between stages was 1.80 sec. Since w9 and w11 TFA isomers, which are most abundant in the lipids in both natural and hydrogenated TFAs, were well separated.

High resolution ¹³C NMR spectroscopy has several applications in fat analysis and is an effective tool that can provide structural information about cis and trans isomers of fatty acid. The signal from a carbon that is allylic to a double-bond carbon provides the evidence concerning the cis and trans nature of the double bond. The intensity of the signal can also be used for quantitation. In the case of fat from butter and margarine, C₁₈ carbon allylic to a trans bond has a chemical shift of 32.6 ppm.

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Monitoring of Hazard Air Pollutants (HAPs) Inventory

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Summary

The Hazard Air Pollutants (HAPs) not only risk human health by the direct inhaling but also leads to the pollutions in different environmental medias, such as plants, water and soil through atmospheric pathways. In Korea, 53 chemicals are selected as Hazard Air Pollutants. However, there is not enough data on the source and the amount of HAPs that are being produced. This study was the research at national level on producing HAPs source inventory and the emission estimation method. Additionally, the methods on analyzing HAPs from the various sources were organized. Also, the field monitoring on HAPs emission from synthetic resin and plastic manufacture industries, one of the priority sources of HAPs. According to the result, the amount HAPs emission in this study was lower than the level reported in TRI. However, more various types of compounds were detected in this study than the compounds reported by TRI.

Key word: Hazard Air Pollutants (HAPs), Sources, Inventory, GC/MS

1. Introduction

The hazardous compounds take various pathways to enter human body. Humans inhale 15kg of air daily, which is 10 times more than the intake of water and food. The human exposure to HAPs through inhalation is crucial because the substances are directly absorbed into lung and human body. Furthermore, HAPs that are released in ambient air have high potency of harming ecosystem, as it is deposited in plants, soil and water. Since HAPs are toxic compounds that directly and indirectly pose negative influences on human health, plants and animals, different countries selected certain chemicals as HAPs. For example, United States, Germany, Japan and Korea selected 187,154,234 and 53 compounds as HAPs, respectively. In Korea, there are Toxic Release Inventory (TRI) and Stack Emission Management System (SEMS) as HAPs data. However, TRI and SEMS have certain restrictions that prevent more accurate data production. In case of TRI, the concentration levels are the values reported by the industries that produced HAPs, while SEMS only involves the level of certain compounds released from the chimney. In this study, the attempt for the creation of more accurate and realistic inventory at the national level was made. Furthermore, the source monitoring of HAPs was held based on the suggested list of different sources of HAPs, and the results were compared with the already existing data.

2. Materials and Methods

2.1 HAPs inventory

Through TRI, SEMS and other reference surveys, the main industries that are sources of HAPs production were selected and listed. The concentration estimation method was suggested using Top down approach, and the emission factor and activity research method for the main HAPs sources were suggested.

2.2 Sampling

Sample collection

The source of HAPs can be classified into two groups, point sources and non-point sources. For the point source analysis, the analytical methods suggested by Korean standard method and U.S EPA methods, depending on the chemical compound group. Non-point sources that may leak, such as flange, valve and pump have various types and appearances, and there does not exist sampling and monitoring method specific to those non-point sources. Thus, two monitoring methods for non-point sources were proposed after the numerous testing, and were applied in actual sampling and analysis.

- Vacuum Bagging method

The leakage point at the valve was covered with Teflon film and tightly sealed on the pipe, creating a bag. The air inside the bag was pumped out. As the gas leakage occurs from valve, the bag expands, and the glass filter is exerted to collect the leaked gas. However, the vacuum bagging method is only possible when the amount of leaking gas is noticeably a lot, and when there is no danger of explosion. Thus, the vacuum bagging method is inappropriate for the usage at petrochemical industry plants.

- Blow-through bagging method

The leakage point at the valve was covered with the film and tightly sealed on the pipe to create a bag. At the entrance of the sealed bag, the high purity nitrogen was injected, and the gas released from the opposite opening was collected. During the process of collecting gas samples in both vacuum bagging method and blow through bagging method, five different strategies, Tedlar bag, Absorption tube, 2,4-DNPH cartridge, Filter & Adsorbent & Impinger, Impinger, absorption tube, were applied depending on the target compound.

Instrumental Analysis

For the analysis of five different target compounds, 6 types of instrumental analysis methods were used. For the analysis of VVOC groups, Pre-concentrator and GC/MS (Entech and Agilent) were used. Thermo Desorption System and GC/MS (Gerstel TDS and Agilent) were used for the VOC groups, while Agilent GC.MSD was used for the PAHs and Aldehyde group analysis. Finally, the HCl was analyzed by UV-vis.

2.3 Monitoring

The monitoring for the HAPs sources were held in 5 plastic manufacture plants that produces HDPE, LHDPE, LLDPE, PP, PE, PVC and ABS. In possible source points in each plant, 5 samples were collected from non-point sources, 2 point sources and 2 background samples.

3. Result and Discussion

HAPs emission inventory had 77 priority sources form 12 main categories of original CAPSS. The field monitoring on HAPs emission from synthetic resin and plastic manufacture industries, one of the priority sources of HAPs. According to the result of comparison of TRI and the field monitoring of 53 HAPs compounds, the field monitoring showed more various types of HAPs compounds. The TRI reported 10 HAPs compound, while the field monitoring in this study reported 14 HAPs compounds out of 53 compounds. However, the amount of 53 HAPs emission was less than the emission amount reported by TRI. Such results were confirmed to be caused by the application of TRI default value, which led to the overestimation than the actual field monitoring emission amount.

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Professor Gon Ok was the chief researcher, and the member of Committee Board, for the development of Dioxins (PCDD/DFs and DLPCBs, 1995) and POPs(2005) Standard Method research, conducted by the environmental ministry of Korea.

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Professor Gon Ok was the chief researcher of Dioxins Exposure and Health Assessment study organized by the Korean Ministry of Environment in 2005 and 2006. From 2002 to 2008, he also led the research on Dioxins, Endocrine Disruptors, and POPs Assessment in Marine Eco-Environment, organized by Korean Ministry of Maritime Affairs & Fisheries.

In 2006, Professor Gon Ok was the Water, Land and Nature Steering Committee member of the Presidential commission on Sustainable Development in Korea.

Professor Gon Ok is currently conducting researches on the Development of National Inventory of HAPs (Hazards Air Pollutants) by Ministry of the Environment Republic of Korea.

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On-Line and On-Column Electrochemical Redox Derivatization for Enhancement of Separation Selectivity of Liquid Chromatography

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Summary

On-line and on-column electrochemical redox derivatization methods for enhancement of separation selectivity of HPLC are presented. In the former separation system, the derivatization reaction proceeds in a small flow through electrolytic cell placed between two separation columns so that an analyte compound migrates as its original form in the first column, while as its converted form in the second column. On the other hand, in the latter strategy an LC column designed for electrochemically modulated liquid chromatography (EMLC) is used for derivatization as well as separation. We can gain broad and facile control by these techniques over the distribution of redox species in the separation system and achieve highly selective separation.

Key word: Electrochemical redox derivatization; Electrolytic flow cell; Electrochemically modulated liquid chromatography; Secondary chemical equilibrium

1 Introduction

HPLC is always demanded to acquire new separation selectivity in order to achieve better separation and determination of trace levels of compounds in complex matrix samples. Use of a chemical reaction specific for target compounds as a pre-column or on-column derivatization is one of the efficient ways for enhancement of separation selectivity of HPLC. We recently presented two redox derivatization techniques, on-line derivatization using double separation columns and one redox derivatization unit [1, 2] and on-column derivatization via electrochemically modulated liquid chromatography (EMLC) [3]. It will be shown in this paper that on-line and on-column electrochemical redox derivatization techniques provide intriguing pathways for realizing a highly selective separation of redox active analytes.

2 Materials and Methods

The electrolytic flow cell used for the on-line electrochemical derivatization was a Model 5020 guard cell (ESA, USA), which contained a porous graphite working electrode, a palladium counter electrode and a palladium-hydrogen reference electrode (Pd/H₂). All potentials described for this cell are given vs. Pd/H₂.

The EMLC column consists of a Nafion cation-exchange membrane in tubular form (Perma Pure Inc., USA) placed inside a porous stainless steel cylinder (Mott Metallurgical Corp., USA) [4]. The Nafion tubing serves as a container for the porous graphitic carbon (PGC) stationary phase (3.5 μm BTR carbon, Biotech Research, Japan). PGC also functions as the working electrode. The porous stainless steel cylinder prevents deformation of the Nafion tubing under the high pressure of chromatographic flow and is also used as the counter electrode. An Ag/AgCl reference electrode (saturated NaCl) is placed in an electrolyte reservoir that surrounds the stainless steel counter electrode.

3 Results and Discussion

The on-line electrochemical redox derivatization HPLC system consists of two separation columns and a small electrolytic flow cell placed between them [2]. A redox derivatization reaction proceeds in the electrolytic flow cell so that an analyte compound migrates as its original form in the first column, while as its oxidized or reduced form in the second column.

The selective separation of an analyte compound can be achieved because redox reactions specific for the analyte in the electrochemical derivatization unit can be controlled by alteration of potential applied to the cell. There are three requisites for the cell to be used for the on-line redox derivatization HPLC: (1)the cell should withstand high pressure; (2)the inner volume of the cell should be small; and (3)the efficiency of electrolysis should be 100 %. We substantiated that the electrolytic cell we adopted meets the first two requisites; the maximum operating pressure of the cell shown by the manufacturer is 422 kgf/cm² and the inner volume of the cell we determined is 44 μ L. We also evaluated the electrolysis efficiency of the cell using Co(II)-EDTA and Co(III)-EDTA as model compounds and found that Co(II)-EDTA was oxidized to Co(III)-EDTA by the electrolytic cell at 0.1 V or above, while Co(III)-EDTA was completely converted to the Co(II)-EDTA at -0.6 V or below. The electrolysis efficiency is approximately constant independent of the flow rate in the range of 0.02 to 0.10 mL min⁻¹. We applied this on-line electrochemical redox derivatization system to determination of trace amount of cobalt in a stainless steel sample after chelation with EDTA. The cobalt complex eluted in the first column as Co(II)-EDTA and was separated from the trivalent metal complexes including Fe(III), while after oxidation by the electrolytic cell it was completely separated from the other divalent metal ions during elution in the second column. The cobalt concentration determined by the present method was in good agreement with the recommended value.

Using catalytic redox activity of PGC packings, we presented a new type of secondary chemical equilibrium (SCE) for enhancement of selectivity in HPLC [5]. This technique is based on redox equilibria and may become much more useful if the equilibria can be controlled electrochemically. We have thus developed an on-column electrochemical redox derivatization method using EMLC technique [3]. We examined dependence of the retention factor and peak area of hydroquinone, resorcinol, catechol, tyrosine, and dopa on potential applied to the EMLC column and found out that hydroquinone and catechol migrate through the column as equilibrium mixtures of their oxidized and reduced forms and the heterogeneous rates for these redox reactions are much higher than the rate of mass transfer between the mobile and stationary phases. This indicates that these redox reactions can be used as secondary chemical equilibria so that the corresponding equilibrium mixtures elute as single peaks and their retention times can be controlled by alterations in the potential applied to the PGC stationary phase. All five compounds were reasonably separated at +300 mV, whereas both catechol and resorcinol and dopa and L-tyrosine co-eluted at 0 mV. These data point to the ability to enhance EMLC-based separations via on-column electrochemical transformations of the analyte. Factors that influence efficiency in EMLC will also be reviewed from a chromatographic perspective.

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Preparation, Characterization, and Analytical Applications of a Novel Hybrid Organic-inorganic Material Used as Chromatographic Stationary Phase

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So far, columns of packed particles have still been the most popular and core devices for chromatographic separations and detections because of their great utility, excellent performance and wide variety. In order to overcome the defects of traditional column packing, such as fragile under extreme pH and not rigid enough under high pressure, a novel hybrid organic-inorganic material used as chromatographic stationary phase has been synthesized, which maintains the advantages of both organic polymers and inorganic supporters.

According to the excellent mechanical and thermal properties, carbon nanotubes with a concentration between 0.1~5% (wt%) of monomers have been incorporated into polystyrene-divinyl benzene microspheres to form homogeneous packed particles ranging from 2 μm to 8 μm . Three different ways have been tried to synthesize polystyrene-divinyl benzene-carbon nanotubes (PS-DVB-CNT) hybrid particles. One is to intermingle carbon nanotubes which is purified by mixed acids with monomers simply, another is to copolymerize modified carbon nanotubes with other monomers, and the third is to modify the surface of polystyrene-divinyl benzene with pretreated carbon nanotubes. After optimization of the synthetic conditions, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermal-gravimetric analysis (TGA), elemental analysis and Fourier transform Laman spectroscopy (FT-Laman) have all been used for the characterization of this novel stationary phase. And the results prove that carbon nanotubes have been incorporated into the matrix of polystyrene-divinyl benzene definitely.

Besides, the chromatographic properties of the stationary phase have been investigated by reversed-phase high-performance liquid chromatography with alkylbenzenes, pyridines, anilines and phenols as probes. After comparison with pure PS-DVB particles, the hybrid stationary phase owns better hydrophilicity and the chromatographic peaks are more symmetric, which may help to separate non-polar compounds on organic polymer supporters. And with wide pH endurance, this stationary phase can be utilized in extreme mobile phases to separate different kinds of acids and alkalis. Meanwhile, it is suitable to be used in ion-pair chromatography to separate organic and inorganic acids for its longer life compared with silica gel columns. As a result, the incorporation of carbon nanotubes has enhanced the rigidity of the packed particles and improved the porous structure of the microspheres with better selectivity, resolution and wider applications.

Biography

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His current research is focused on ion chromatography, new stationary phase for liquid chromatography, and sample pre-treatment for ionized species. He is the author and co-author of 150 original research papers published in international journals, 5 reviews, 4 books and 10 patents.

Use of ion-exclusion/adsorption chromatography to evaluate quality of TiO₂ photocatalytic materials in water

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Summary

In our laboratory, ion-exclusion/adsorption chromatography of dimethylsulfoxide (DMSO) and its derivatives, i.e., methanesulfinic acid (MSI), methanesulfonic acid (MSA), and sulfuric acid (SA), was employed to test the quality of TiO₂ photocatalyst in water. DMSO was separated by hydrophobic adsorption, and MSI, MSA, and SA were separated by ion-exclusion using a weakly acidic cation-exchange resin column with 20 mM succinic acid as the eluent. Among the separated species, DMSO and MSI were detected by UV at 195 nm and MSA and SA were detected by conductivity. This method was used to monitor the decomposition of DMSO with OH radicals generated by the UV irradiation of TiO₂-coated materials. The concentration of DMSO by OH radicals was found to decrease through the stoichiometric reaction in the order of MSI, MSA, and SA.

Keywords: Ion-exclusion; adsorption; chromatography; photocatalyst; dimethylsulfoxide; OH radicals

1 Introduction

Recently, the use of TiO₂ photocatalyst has attracted from the viewpoint of applications in advanced oxidation technologies for the purification of air and water. Therefore, many TiO₂-coated materials have been developed by researchers, and they have been employed commercially in the manufacture of tiles, floors, walls, roads, glass, etc.

In order to establish a quality test for photocatalytic materials in the liquid phase, we used dimethylsulfoxide (DMSO) as a test sample. DMSO is well known as a scavenger that can be used to indirectly determine active oxygens such as OH radicals generated during a biological reaction [1]. By the oxidative decomposition of DMSO with OH radicals, MSI, MSA, and SA are formed on the basis of stoichiometric reaction. In this study, we developed an ion-exclusion/adsorption chromatography of DMSO and its derivatives as an analytical method for evaluating the artificial decomposition of DMSO by a photocatalytic material.

2 Materials and Methods

Ion-exclusion chromatographic system

We used the Tosoh IC-2001 ion chromatograph; it consists of a dual pump (0.6 ml/min), an online degasser, an auto-sample injector (30 μ l), a column oven (40 °C), and a conductivity detector, and the Tosoh UV 8020 UV-vis detector was inserted between the separation column and the conductivity detector. We used the Tosoh TSKgel Super IC-A/C as a separation column; this is a polymethacrylate-based weakly acidic cation-exchange resin of H⁺-form that is packed with 3- μ m particles, and it has 0.1 mequiv./ml cation-exchange capacity (150 mm \times 6 mm i.d.). Among the species separated by the column, DMSO and MSI were detected by UV at 195 nm and MSA and SA were detected conductivity.

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Photocatalytic reaction system

A schematic of the acryl-resin-based photocatalytic oxidation reactor ($290 \times 108 \times 110$ mm) used in this system is shown in **Fig. 1**. The tested TiO_2 -coated materials were placed in the photocatalyst area of the reactor. A 500-ml solution containing 10 ppm DMSO was poured into the photocatalytic reactor. An anatase-type TiO_2 -glass beads BL2.5DX coating $1 \mu\text{m}$ thickness of TiO_2 on a 2.5mm \varnothing of silica-glass bead was purchased from Photocatalytic Materials Inc. (Aichi, Japan). 50 g of photocatalyst-coated beads were used in one experiment. The TiO_2 photocatalyst was a commercial BLB light ($\lambda_{\text{MAX}} = 350$ nm). The solution in the reactor was circulated by a pump at a flow rate of 500 ml/min. During the photocatalytic reaction, a 10-ml sample solution was collected every 30 min. The concentrations of DMSO and its products in the solution were determined by the ion-exclusion/adsorption chromatography technique developed in this study.

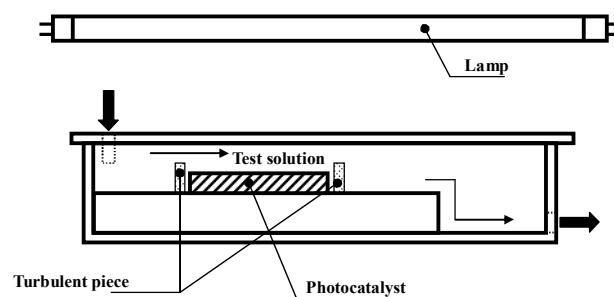


Fig. 1. Schematic illustration of the present photocatalytic reaction system

3 Result and Discussion

Ion-exclusion/adsorption chromatography of DMSO and its derivatives using a weakly acidic cation-exchange resin in the H^+ -form with succinic acid as the eluent was optimized in terms of the retention times and the peak resolutions of each analyte with UV and conductivity detections. In ion-exclusion/adsorption chromatography, the retention mechanism is hydrophobic adsorption onto the cation-exchange resin for organic solvents such as DMSO [2]; in contrast, the mechanism is ion-exclusion for fully ionized species such as MSI, MSA, and SA [3]. As a result, a well-resolved chromatogram was obtained with the combination of a weakly acidic cation-exchange resin column and 20 mM succinic acid.

The photooxidation of DMSO by anatase-type TiO_2 -coated glass beads in water was investigated by using the photocatalytic reaction system developed in this study. The test solution with 10 ppm DMSO was poured into the reactor and circulated for 4 h under UV irradiation. As shown in **Fig. 2**, the remaining DMSO decreased gradually with the time-dependence of UV irradiation; in contrast, the intermediates were produced in the order of MSI, MSA, and SA with irradiation. As shown in **Fig. 3**, the plots indicated that the concentrations of sulfur atoms in the remaining DMSO and the intermediate products formed were found to be stoichiometric oxidation by OH radicals from the TiO_2 material irradiated with UV light.

In Japan, one part of this analytical method was adopted as a standardized evaluation method for TiO_2 photocatalytic materials in water (JIS R1704), and at present, it is awaiting ISO certification (ISO/CD10676 Fine ceramics - advanced ceramics, advanced technical ceramics).

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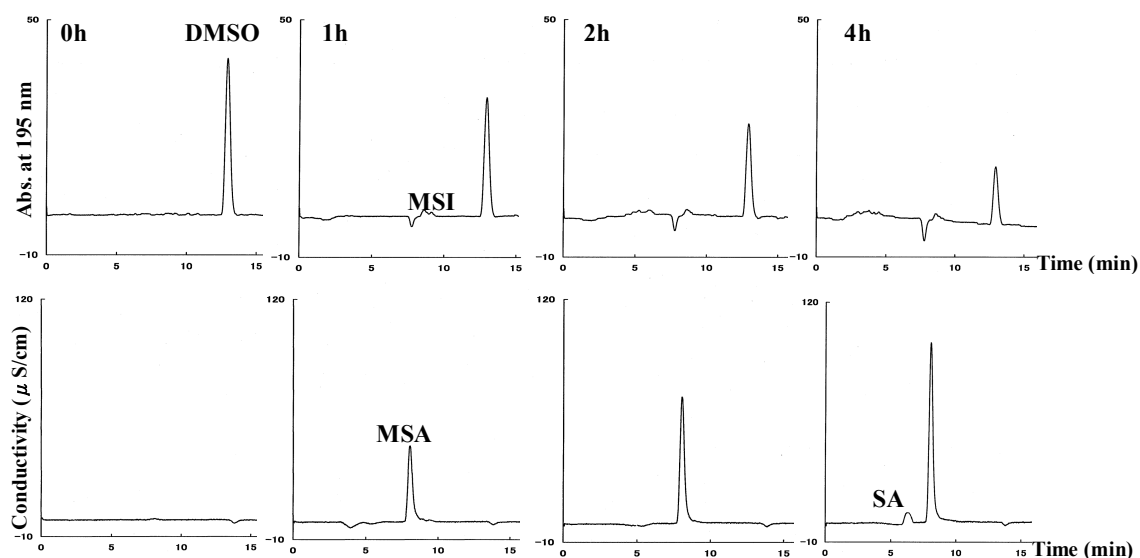


Fig. 2. Peak profiles of decomposed DMSO and the products formed by the TiO₂ photocatalyst with UV irradiations. Ion chromatographic and photocatalytic conditions are described in Materials and Methods (i.e., Sec. 2).

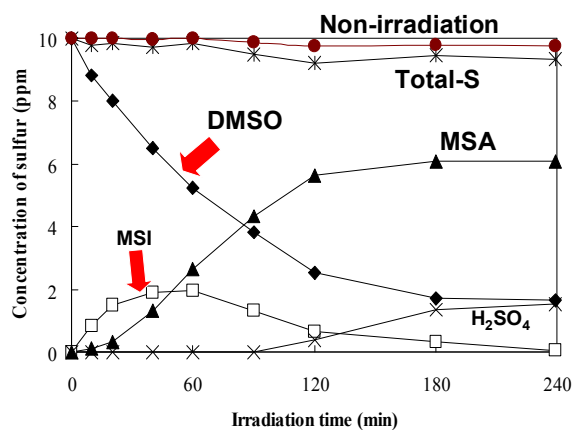


Fig. 3. Changes of sulfur atom concentrations in the DMSO and its decomposed products with and without UV-irradiation

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Analysis of Amino Acid and Peptide Biomarkers by CEC-ESI-MS and HPLC-ECD

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Some amino acids and peptides are regarded as biomarkers which are associated with human diseases. For examples, amyloid- β (A β) polypeptides is targeted as the potential biomarker for Alzheimer's disease (AD) [1]. The oxidized tyrosine derivatives including 3,4-dihydroxytyrosine (L-DOPA), dopamine, dopamine quinone are relevant in Parkinson's disease [2]. Therefore, the analytical techniques for analysis of multiple amino acids and peptides are needed as a new paradigm in disease prognosis and drug development. Hyphenated separation techniques like liquid chromatography (LC), capillary electrophoresis (CE) and electrochromatography (CEC) coupled to mass spectrometric (MS) and electrochemical detections (ECD) offer high separation selectivity and excellent detection sensitivity.

In recent years we focus one of our works on the development of hyphenated separation techniques CE/CEC/LC with MS and ECD detections [3-5]. The recent progress on analysis of amino acid and peptides by CEC-ESI-MS and LC-ECD in my group will be presented in this talk. The main contents include (1) a novel sheathless nanoelectrospray interface for hyphenating CE/CEC to electrospray (ESI)-MS [3], (2) Lupamin-coated column technology for analysis of amino acids and peptides by CEC-ESI-MS [3,4], (3) analysis of small molecular peptides with same amino acid composition but different sequence by CE and LC-MS [5], and (4) analysis of amino acid biomarkers of tryptophan and kynurenine by LC-ECD with carbon nanotubes-modified electrodes.

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Acknowledgments

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Advance of capillary electrophoresis/electrochromatography coupling with electrospray ionization mass spectrometry based on monolithic columns in doping analysis

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In recent 30 years, capillary electrophoresis/electrochromatography (CE/CEC) have attracted considerable attention due to high separation efficiency, low sample consumption and short analysis time. Compared with ultraviolet detector, which used mostly in CE/CEC instruments, mass spectrometry (MS) has some inherent advantages. Firstly, MS can provide both molecular mass and structural information. Secondly, MS enables to extract analytes signals from a high background noise. Thirdly, MS can provide high selectivity and sensitivity. These are of particular importance when it is necessary to positively identify analytes in complex samples such as biological fluids.

Monolithic column technique is an emerging column preparation technique, and attracted more and more attention due to good permeability, fast mass transfer property, high stability and easy modification. Monolithic columns can be classified into two categories: silica-based and organic polymer-based monoliths. Silica-based monoliths usually offer the advantages of high mechanical strength, heat stability and resistance to organic solvent. In comparison with silica-based beds, polymer-based monoliths exhibit more potential advantages, involving simple preparation and the possibility of controlling their properties of porous and surface chemistries.

In our laboratory, some novel CE/CEC-ESI-MS methods based on different kinds of columns, which including bare fused capillary, chemically modified fused silica capillary, silica-based and polymer-based monolithic column, have been developed for rapid and sensitive analysis of doping. A rapid, high-resolution and effective new method for simultaneously analyzing 12 diuretics by CE-ESI-MS was demonstrated in our laboratory [1]. To reduce adsorption and provide fast separation ability, a coated capillary was prepared and applied to rapid analysis of peptides and amino acids in CE-ESI-MS system [2]. Based on silica-based monolithic columns, a pressure-assisted CEC-MS method for rapid and sensitive analysis of narcotics was established. Under the optimum conditions, the tested five narcotics could be completely separated within 10 min with the detection limit in the range of 2.0–80 nmol/L [3]. A method for rapid separation and sensitive detection of β -blockers by pressure-assisted CEC-ESI-MS using silica-based monolithic column were within 11 min with detection limits in the range of 0.15–0.80 ng/mL (defined as S/N= 3). The real samples from some male volunteers were successfully analyzed and confirmed with the proposed method [4]. Also, to overcome limitation of silica-based monolithic columns, a novel porous polymer-based monolithic column was prepared [5] and applied to analysis of β_2 -agonist and narcotics [6]. These novel CE/CEC-ESI-MS methods present many superiority compared with traditional GC-MS or LC-MS methods, which include higher separation efficiency, shorter analytical time, and lower sample and organic solvent consumption.

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Prof. Lan Zhang was born in March 1963. She received her M.S. PhD degree in Analytical Chemistry from East China Normal University. She has been a teacher of Fuzhou University in 1995 and now she is head of the Fuzhou University Detect Center. Her research interests cover the pharmaceutical analysis, bioelectrochemistry, capillary electrophoresis, Chromatographic Technology, Chromatography and mass spectrometry combined technology, etc. Prof. Lan Zhang has gained the brilliant academic achievements in pharmaceutical analysis, modern separation and detection technology, etc. More than 70 papers have been published in the international Journals such as *Electrophoresis*, *J. Chromatogr. A*, *Talanta*, *Anal. Chem. Acta*, etc. and gained much citation. In 2002, Prof. Lan Zhang was elected for the Fujian Provincial Project of "Talent Project". In 2006, Prof. Lan Zhang was inducted into "the Plan of University New Century Outstanding Talented Man of Fujian Province". Then Prof. Lan Zhang received the Second Prize of Fujian Provincial Scientific-Development Award in 2004 and 2006 respectively. Now Prof. Lan Zhang continue her scientific career as the Director of University Analytical and Testing center of Fujian Province and a main member of the Ministry of Education Key Laboratory of Analysis and Detection for Food Safety. She immersed in the research of the key technology for food safety capillary electrophoresis and capillary electrochromatography, chromatography and mass spectrometry combined technology, the separation and analysis of natural medicinal effective compounds and bioactive compounds, etc.

Representative paper:

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Break through point of micro GC and future image of advanced GC

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Miniaturized and microfabricated instruments for GC are of interest because of their very small size, weight, and resource requirements and are intended for on-site analysis [1]. These instruments are under development in several laboratories and some of them are commercially available. The advantages of micro GC for monitoring volatile and semivolatile organic compounds, relative to conventional sorbent tube or whole-air sampling methods followed by laboratory analysis, include the following: reduced sample handling, which minimizes loss, degradation, or contamination; greater sample throughput; and the potential for more timely responses to measurement results [2]. Where nonspecific detectors are employed, qualitative analysis is based solely on retention time. Instruments employing GC with more sophisticated detectors, such as mass spectrometers or ion mobility spectrometers, can provide more definitive identification of eluting species at the cost of increased size, power, complexity, and cost.

In our research, a compact GC by applying microfabrication and inkjet technologies for flow control, on-chip column separation [3] and liquid sample injection [4,5] was developed. A small pencil-sized atomic emission detector (AED) using a helium radio-frequency microplasma was also employed for the GC system [6]. This AED is capable of operating using a radio-frequency board of up to 3W of applied power or with only carrier (helium) gas, and performed high selectivity and sensitivity by using a USB-driven CCD spectrometer. The detection limits of chlorine, bromine, sulfur and phosphorus were obtained to be pg/sec levels. These GCs have a possibility of becoming more compact and further improvements of their performance, robustness and usability will be effective for saving of time, space, electrical power and cost for on-site and in-laboratory GC analyses.

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Microfluidic chip for cell analysis

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Cell is the basic unit of life. To reveal cell function and its underlying molecular mechanism has been highly focused for a long time. With the development of cellular biology, new approaches are greatly demanded for better understanding more and more sophisticated cell phenomena both in qualification and in quantification. Therefore, cell analysis becomes a major challenge for bioanalytical chemist to innovate the techniques. Microfluidic chip, or also referred to as lab-on-a-chip is a new concept technology and is recognized as the next-generation platform for chemical and biological analysis, due to its advantages of miniaturization, integration, automation and high throughput. Because the size of microchannel in microfluidic chip is quite compatible with the dimension of a regular cell, microfluidic chip is an ideal tool for cell analysis, which has been recently paid much attention.

In this work, we are trying to develop advanced microfluidic chips for multiple purposes of cell analysis. 1) Microfluidic chip for cell sorting: regularly, cell sorting is performed using flow cytometry. However, conventional flow cytometry is applicable only for a large amount of cells. Thus, we attempted to develop a microfluidics-based cell sorter for sorting a small amount of cells. By using novel on-chip pressure gating technology, the purity and recovery of sorting particles and cells are over 90%, revealing a better performance than previous reports. 2) Cell stimulation on a microfluidic chip: Cell can give reply with various stimuli. Investigation on stimulation-reply can obtain valuable information about cell function. In our work, we developed a microfluidics-based and time-controllable platform for cell stimulation. Cells were cultured inside the microchannels. By using on-chip pressure gating-pinching technique, cell could be stimulated and washed with a minimum time of 20 ms, and made the concept of the-same-cell-analysis very applicable. Examinations of cell stimulations with ATP and histamine implied that our method is simple, stable, accurate and reliable. 3) Microfluidic chip for cell clamping. We demonstrated a sidewall clamping technique in microchannel, which could realize high throughput cell clamping, hence paved a new approach for high throughput and automatic patch clamping. 4) Microfluidic chip for cell-to-cell communication. When cells were cultured inside the microchannel, a cell could be stimulated by chemicals while other cells could not because of laminar flow effect in microchannel. With this way, we successfully visualized the calcium waves among cells due to cell-to-cell communication by gap junction. To a conclusion, microfluidic chip is suitable platform for cell manipulation and analysis. Further applications of lab-on-a-chip technology on cell analysis are greatly promising.

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His research focuses on systems biology-oriented analytical science in the areas of micro separations, microfluidics and molecular imaging. He is the author and co-author of over 50 original research papers and 9 invited reviews published in international journals.

Studies on Microfluidic High-Speed Capillary Electrophoresis

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In 2008, we developed a microfluidic picoliter-scale sample introduction technique based on a short capillary and translational spontaneous injection technique. With the novel approach, a high-speed capillary electrophoresis (HSCE) system was built to achieve high-speed separations of FITC-labeled amino acids [1]. The HSCE system was composed of a short capillary and an automated sample introduction system with slotted sample and buffer reservoirs and a computer-programmed translational platform. The inlet end of the capillary was mechanically ground into a tapered tip. Translational sample introduction was performed by linearly moving the platform, allowing the capillary inlet to enter the sample solution, and then remove from it to achieve spontaneous sample introduction by capillary action. The platform continuously moved to allow the capillary inlet to enter the buffer solution, and CE separation was performed by applying high voltage between the buffer and waste reservoirs. With the HSCE system, five FITC-labeled amino acids including arginine, phenylalanine, glycine, glutamic acid and aspartic acid were separated within 5.5 s in 15 mm separation length. High separation efficiencies ranging from 0.40 to 0.46 μm plate height were obtained.

Recently, we applied this HSCE system in the separation of DNA fragments and proteins under capillary gel electrophoresis mode. In the HSCE system for DNA fragments separation, ΦX 174-Hae III digest DNA Marker was separated within 100 s using an effective separation length of 2.5 cm. Theoretical plate number of 603 bp fragment was 3.2×10^6 /m. In the HSCE system for protein separation, five protein standards including myoglobin, egg albumin, BSA, phosphorylase b and myosin were separated in 60 s with an effective separation length of 1.5 cm.

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When prion drop into the picnic basket of analytical chemist's: Surprising properties of optical isomers of proteins and novel detection methods

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Prior to the discovery of prion, it was thought that all pathogens of diseases used nucleic acids to direct their replication. However, the "protein-only hypothesis" which was based on the conversion of a normal cell-surface glycoprotein (PrP^C) into a conformationally altered isoform (PrP^{Sc}), proposed that a protein structure can replicate without the use of nucleic acid.¹ This was initially controversial as it contradicts the so-called "central dogma of molecular biology", which describes nucleic acid as the only central form of replicative information. That is why prion has attracted great attention of biologists in recent years.² However, what will happen when prion was highlighted by analytical chemists?

Our present work is composed of three parts, namely discussion the properties of optical isomers of prion proteins, exploitation the novel detection methods, development of a variety of labeling and imaging techniques for prion protein in living cells.

It has stimulated long-standing endeavors to understand homochirality in life and the production of enantiomeric excess in prebiotic organic molecules. We took prion protein as a model to design a simple experiment to discuss the instinctive relationship between protein configuration and the stirring direction of their culture medium. It was surprisingly to find that the configuration of the cellular prion protein is dependent on the stirring direction (clockwise or anticlockwise). By simply controlling the stirring direction, we have obtained prion protein with distinctive properties of optical isomers corresponded with the stirring directions, and D-amino acid was speculated to be concluded in the protein of cultured by anticlockwise direction. These results occur us to further explore the mysterious homochirality in life exactly how and where in the cell the optical isomers of proteins occur.

To develop the high selective and sensitive methods for prion proteins detection, a aptamer-participated haprin structure was designed by employing cellular prion protein (PrP^C) as a model protein, and thus an aptamer-mediated turn-on fluorescence assay for proteins was developed. The designed aptamer-participated haprin structure consists of three segments. Namely, an aptamer sequence located in the loop, three guanine bases at 3'-terminal, and a fluorophore modified at 5'-terminal. It was found that the guanine bases at the 3'-terminal could quench the fluorescence of the fluorophore such as tetramethyl-6-carboxyrhodamine (TAMRA) at the 5'-terminal about 76.6% *via* electron transfer if the guanine bases are close enough to the fluorophore, and the quenched fluorescence could get restored when the target protein is present since the interaction, which could be confirmed by measuring fluorescence lifetime, between TAMRA-aptamer and the target protein forces the guanines away from TAMRA so that TAMRA-modified aptamer changes into turn-on state. We also developed a new ultra-sensitive prion protein detection strategy that based on the fluorescent resonance energy transfer (FRET) between PrP^C functionalized quantum dots (QDs) and nanometer-sized gold particle (AuNPs) labeled with Anti-PrP^C aptamer. The detection limit was low to 1.0 fg/mL.

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Aptamer adapted gold/silver nanoparticles (Apt-G/SNPs) probes with both stability and biocompatibility were developed as a novel optical probe for labeling and imaging of prion protein, wherein G/SNPs act as illuminophore and aptamer as biomolecule specific recognition unit, respectively. It's further application demonstrates that the caveolae-related endocytosis is likely a necessary pathway for Apt-G/SNPs labeling PrP^c internalization in SK-N-SH cells. The integrated capability of Apt-G/SNPs to be used as light scattering and TEM imaging agents, along with their potential use for single particle spectral analysis, makes them a great promise for future biomedical imaging and diseases diagnosis. For real time labeling and imaging of prion protein in living cells, aptamer conjugated QDs as an optical probe was also designed by employing aptamers as “underdiscovers”. The utility of this probe has been demonstrated in real time tracking of cellular prion protein.

Keywords: prion, optical isomers, aptamer, detection methods, optical imaging probes

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A Study of Gold-Coated Magnetic Nanoparticles for Solid-Phase Immunoextraction:
Determination of Epitestosterone in Urine by High-Performance Liquid
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A solid-phase immunoextraction method for quantitative analysis of epitestosterone (ET) in urine samples by high-performance liquid chromatography (HPLC) has been developed based on gold-coated magnetic nanoparticles. In this method, half-IgG fragments of anti-ET monoclonal IgG antibodies were covalently immobilized onto magnetic core-shell Fe₃O₄@Au nanoparticles. The magnetic nanoparticles (MNPs) were used as a solid phase for extracting epitestosterone in spiked human urine samples. An external magnetic field was applied to recover the MNPs which were then washed with distilled water followed by eluting with absolute methanol to obtain ET as the analyte. The obtained extraction solution was analyzed by HPLC with UV detection (244 nm) within 12 min. The standard calibration curve obtained for ET showed good linearity in the range of 20-200 ng/mL in phosphate-buffered saline

(PBS) solutions with acceptable accuracy and precision results. This method has an enrichment factor of 100-fold to fulfill the need for measuring analyte with its concentration 100 times lower than the limits of quantification ($S/N = 10$). The results obtained by the present method for spiked urine samples were in good agreement with those from indirect competitive enzyme-linked immunoadsorbent assays (ELISAs). The approach described here is high specific, fast, easy to operate and is likely to have the advantage of conventional immunoaffinity column technique.

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Development of advanced ion chromatography applied to developing countries

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A Novel Approach for Aroma Components Analysis Using Monolithic Material Sorptive Extraction method."MonoTrap"

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Summary

Monolithic Material Sorption Extraction (MMSE) is a novel approach for sample adsorption and extraction using a monolithic hybrid adsorbent -MonoTrap. MMSE has several advantages such as effective pretreatment with simple operation and high-efficiency adsorption capacity. In this study, Various Aroma components were analyzed by MMSE and SBSE method.

Key word: MMSE, MonoTrap, Aroma, juice, Food, Coffee.

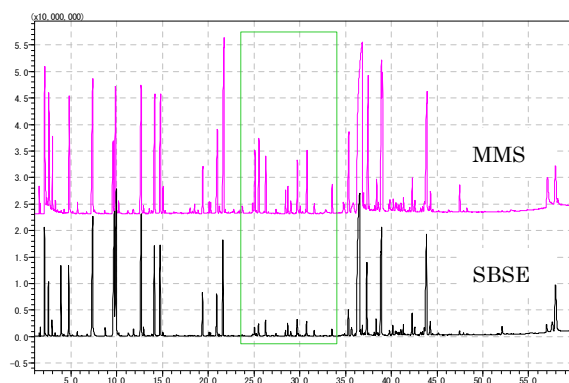
1 Introduction

A Conventional media for sample adsorption and stir bar sorptive extraction (SBSE) and solid-Phase micro extraction (SPME) are coated with an extracting polymer phase, for example, polydimethylsiloxane (PDMS). Disadvantages of conventional media are their small surface area and thin polymer phase coating resulting in low recovery and need for a long extraction time and long conditioning time. The newly introduced product, MonoTrap is a new generation media for adsorption and extraction developed by using silica monolith technology. The state-of-the-art silica monolith technology allows us to manufacture an innovative hybrid adsorbent of silica and activated carbon (graphite carbon) having a large surface area bonded with octadecyl silane (C18). This C18 bonded hybrid medium shows quite effective adsorption capability to a wide variety of compounds. In this study, the aroma component of peach juice were analyzed by MMSE and SBSE methods.

2 Materials and Methods

Instrumentation. Analyses were performed GC2010 and GCMS, QP2010 (Shimadzu), Thermal desorption unit (T-Dex) and GC Capillary Column IC-PureWAX (30mX0.25mm.i.d., df=0.25um), MonoTrap-TD^(*2)(graphite carbon) (GLSciences).

3 Result and Discussion



As a result, it was confirmed that MMSE has the capability of the Adsorption the Some Aroma components far better than SBSE method.

An component with high sensitivity is described below.

- 1; beta-Linalool
- 2; gamma-Caprolactone
- 3; alpha-Terpineol
- 4; Benzyl acetate

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5 Biographical Sketch

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Record :

The recent trend of analysis method for food safety in China

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In recent years, public and scientific concern about food contaminations has been increased seriously due to their potential risks to human health. The monitoring of the contaminants such as pesticides and antibiotics in agricultural products and process foods, and intentional addition of illegal hazardous substances such as melamine and cyclamate etc. in food stuff must be carried out before these products are released to the market. However, high throughput analysis is biggest challenge to these products since freshness of these products are necessary. Moreover, the cost of analysis is also one of important considerations for development of the new analytical method. Although the performances of the analytical instrument for ultra fast determination have rapidly been improved in recent years, the sample pretreatment procedures remain the bottleneck for rapid analysis. Therefore, economical and effective pretreatment methods to eliminate matrix interferences, to achieve high throughput are demanded.

Recently, solid phase extraction (SPE) is getting most popular technique as a replacement of classical liquid-liquid extraction (LLE) in China, since SPE has the advantages of quick treatment and affordable cost. Most of the latest analytical methods such as residual pesticides analysis or melamine analysis are including this SPE procedure. However, the cost of SPE tube is not really cheap for the routine analysis purpose. Therefore, we have introduced matrix solid-phase dispersion (MSPD) for the determination of residual pesticides in vegetable and fruits. Same sorbents used for SPE can be dispersed to homogenized matrices for solid sample or liquid sample for extraction and clean-up. In order to improve the extraction efficiency for polar compounds, large amounts of Na_2SO_4 are usually added in this procedure. The combination of MSPD and on-line sample pretreatment GCMS instrument such as GPC-GCMS hyphenated system is quite acceptable in China market due to low cost and quick determination for residual pesticides.

In this report, the recent trend of analysis method for food safety in China including latest Chinese official method, residual pesticides analysis and melamine analysis will be introduced.

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Dr. Hashi graduated from Dept. of Chemistry, Osaka University, Osaka, Japan in 1986. At the same year, he joined Shimadzu Corporation, analytical instrument division to develop HPLC instrument 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, LCMS and GCMS for the enhancement of analysis efficiency. Based on this research work, he has received a Ph.D. degree from Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences in 2009. Currently, he is interested in the multi-dimensional GC/GCMS system for expansion of applicability. Application area is not only for food safety but also, for pharmaceutical, environmental and life science such as 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.

Food Regulation and Analytical Method for the Food Safety in KOREA

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Food safety issues have been attracting a big concern in every country, becoming global problems in a very short period soon after its outbreak. Over the past 10 years, a lot of food safety issues have been attracting the national and international interest. The consumers require eating the safe and wholesome food, while the government, producers, manufacturers and research institute endeavor themselves to find the best way providing the safe food to the people. Based on our past experience, providing safe food to the consumers is considered to be one of the most difficult tasks to be solved.

Safe food must be free from the following hazards to health; Biological Hazards (Pathogenic bacteria, virus, parasites, worms); Chemical Hazards (Natural toxins, agricultural chemicals, environmental contaminants, food additives); Physical Hazards (Stones, metal fragments, bone shards)

To provide the safe food to the consumers, the effective food control system is required in governmental and private sectors. Where food safety is concerned, most countries share the objectives of protecting consumers from health hazards and commercial fraud. Achieving these objectives require a food control system based on a fundamental food law, accompanied by detailed regulations and administered by an efficient food control organization. Therefore when food legislation is enacted the importance of consumer participation must be recognized, as this will enhance consumer confidence in the national food control system.

On the other hand government food control agencies tend to avoid consumer organisations, which they view as antagonistic and not representative of the true concerns of the individual consumer within the country. In the eyes of the of government officials the issues raised by consumer groups seems irrelevant and even when they are viewed as important there may not be enough resources to deal with the issues that were raised.

Analytical method to ensure the food safety, food sanitary law related with food and food additives in Korea include the food code, functional food code and food additive code. In the food sanitary law, the analytical methods for proximate components, hazardous materials, nutrients, functional compounds, food additives and other components. In the presentation, food regulation and analytical method in the view point of food safety has been discussed.

韓国の環境政策と環境分析研究の最前線

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Summary

This paper describes the historical development of Korean environmental analysis research, and the environmental issues and policy in Korea. In 1950s, DDT and synthetic chemical compounds were used during the Korean War. 1960s and 1970s were the time of industrialization in Korea, which began to bring up the pollution issues. The government and people of Korea started to experience the change in their concept of environmental issues between 1980s and 1990s. In 21st century, environmental policy and laws were prepared as counter plans for the global environmental issues.

The Environmental Analysis field showed the change in trend from criteria pollutants to toxic compounds like Hazardous Air Pollutants (HAPs) and Persistent Organic Pollutants (POPs), and to trace level analysis and environmental problems.

The monitoring data of environmental analysis is the important scientific evidence of risk assessment of humans and ecosystems. The results of these monitoring data are being used to reduce the human and environmental risk, to create safe living environment and to find solutions for the global environmental issues. Thus, it can be concluded that “Sources and Environment Budget System Approach”, which begins from the discovery of the source to the environmental media, should be completed for the future environmental analysis research.

Key word: Dioxins, Emerging POPs, HAPs, Sources Inventory, Environ Budget System

環境汚染究明と環境分析化学

地球環境 5 6 億年の変化の中で人類が生き残るため活動してる中で作り出した化学物質の種類を明確に答えることは出来ないと思われる。近年、環境問題は地域的問題ではなく、また、一つの国に留まる問題でもない地球規模の問題として取り上げられている。それは産業発展と共に作り出した化学物質の製品だけではなく、製品の生産などの過程で非意図的に発生した化学物質が環境汚染物質として越境移動している問題を乗り越え両極地までの影響を与える状況である。これらの現状を分かるようになった科学的な研究成果の基盤は化学分析研究者の努力に伴う分析技術の発展の成果の一つである。その歴史の中で地球環境 5 6 億年の生命誕生のMillerの地球大気再現実験などの科学的根拠を作り出したこともクロマト分析化学であり、成層圏のオゾ

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ン破壊問題を指摘していたRowland 教授とMolina博士の研究の基盤にはECD-クロマトグラフの開発のより1970年代のLovolock博士による大西洋大気中のCFCsの分析結果によることである。また、近年の環境ホルモンの問題、ダイオキシン類の問題、残留性有機汚染物質 (POPs)等その出発と原因の解明、対応など研究の中心にはクロマト分析技術が大きな役割を果たしてきたと言われることが出来る。

全世界におけるこれらの分析技術の発展の中で、特に、環境分析研究は一般の化学分析とは異なり極微量であり、環境媒体からの数多くの化学物質の中での目的成分の同定の分析技術の研究能力が要求されていた状況であった。これは環境分野研究における特殊性の一つであり、環境モニタリングは発生源、大気などの環境プロセス過程の媒体、水、土壌、低質、生物などの環境収容体と人における暴露の過程までの喪失と濃縮の繰り返し現状を持ち、自然の中での複雑な過程の解明作業である。これらの特殊性を持つ環境試料の分析結果は国の政策と社会的ないろいろな面との関係を持っている。その結果は政策に対し一つの尺度的であるため科学的な根拠を持ちいる事が要求されていると共に法律的、行政的実行の根拠として用いられ環境管理の政策の作りと実行の科学的な出発が環境分析の位置付けである。

韓国¹⁾の歴史的な環境問題と環境政策の法律的根拠

韓国の場合でもこれらの環境分析の地位と言うものは世界共通のことである。韓国の環境管理の政策も同じく、近年の国際レベルの分析技術に基づいて科学的な根拠により法律と行政実行の流れを持ち行けるように成りつつある。

そして、韓国の環境管理の政策において法律的な根拠は以下のようなことにある。

- 憲法第35条: すべての国民は健康で、快適な環境で生活できる権利を持ち、国家と国民は環境保全に努力すべきであると述べられている。
- この意味は広義では、環境政策基本法第3条1項において規定している“自然環境と生活環境”に関わる関連の法律である。しかし、狭義では、政府の組織の環境部に関わる事として自然環境と生活環境の保全と環境汚染防止に関する法律である。

このことで、韓国の環境問題に対する政策の歴史的な流れを見ると、まず、1950年6月25日に起きた韓国戦争は国土環境と経済の破壊、苦しい国民環境生活などの様々な問題問題が生じていた。それに対し、国の再建設のため産業の発展は国家最大の目標でもあった。1950年代の韓国戦争はまず、生活衛生問題を起こし、合成化学物質に依存するきっかけになり、最近のPOPsの一つであるDDTという化学物質の本格的な使用の始まりであったかも知らない。韓国においての忘れられない6. 25の韓国戦争はDDT使用による“奪われし未来”の出発であったかも知らない。韓国戦争が終わり、国家の再建設は国の第一の目標であり、工業を中心とした産業経済活性化の第1次経済開発5階年計画による工業化の推進が行ったのが1960年から70年代であった。それに伴ない公害対策として環境管理の政策の始まりが1960年代韓国の環境政策は公害対策であった。

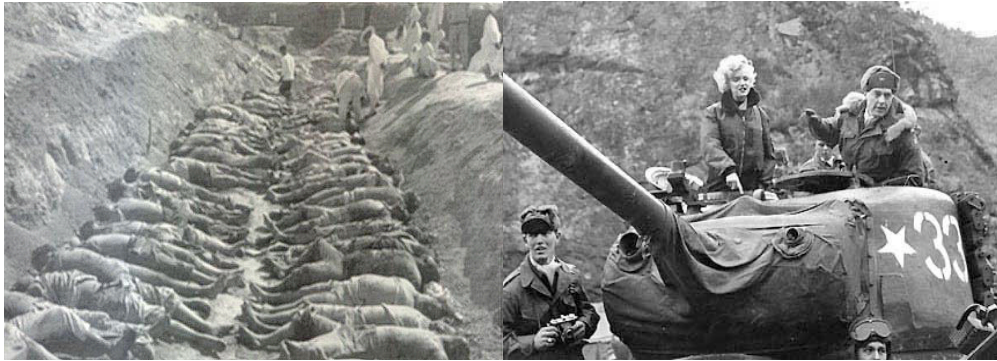


図 韓国戦争の被害と女優のマリリンモノロのアメリカ軍人の慰問講演の訪問



図 アメリカ軍による北朝鮮軍と子供にDDTの散布

- ‘第1次経済開発5階年計画による工業化の推進が1963年に公害対応の環境基本法である「公害防止法」が制定・公布された。
- しかし、公布された公害防止法は予算を含め実施に伴う法律がまとまらなく、その役割は微々の状況であった。
- 1960年代と70年代に掛け繊維、衣類、製鉄、化学、造船など重化学工業を中心とした経済開発が本格的に行い蔚山—温山地域などで発生した環境汚染問題は恩山病の名前が付けられ大きな社会問題として取り上げられていた。

韓国の産業公害から環境問題までに関わる環境分析の話題

韓国の産業発展とこれらの公害汚染問題からの分析対象の汚染物質は主に、重金属、窒素酸化物質(NOx)、黄酸化物(SOx)、塩化水素(HCl)などが発生源と環境中の主なモニタリングの対象物質であった。特に、大気汚染のモニタリングではダストージャ方法で亜硫酸カスのモニタリングをしたり、発生源の煙突排ガスの測定のため一日4個位の煙突を昇った記憶がある。そして、機器分析は主にAAとUVが使用されていた。

また、温山の公害問題以前の70年代半ばには、海洋汚染の一つとして国レベルで大きく取り上げられた分析研究結果としては当時、韓国釜山水産大学の元ジョンフン教授により韓国の南海岸

の水産物の重金属汚染の研究結果が日本の“ぶんせき”学会論文に報告され、韓国の水産物の日本に輸出が出来なくなることの事件が起きた。その時代の韓国経済成長に水産分野の役割は大きく、それに影響を与えたことで朴大統領から大学は重い責任をとることが指摘されたが研究者を育つことも大切であったことも認めたとするエピソードがあった時期でもある。しかし、その時代、朴大統領は韓国国土の緑化、し尿などを用いエネルギー化など最近の地球温暖化問題に対応出来る環境政策を世界一に取り上げ未来を設計していた政治家であったと思う。

1970年代後半、「公害防止法」が廃止され、この代わりに「環境保全法」が1977年12月31日制定・公報され環境基準及び排出基準、環境監視制度、防止施設の設置の義務化と環境影響の評価などの一連の根拠が作り出された環境政策の基盤が出来た時期であった。

1980年から1990年代は韓国の産業の発展がもっと進められ従来の産業汚染と自動車排ガス、都市地域の下水、ごみ問題、自然生態系の破壊を始め生活消費と関係する環境問題が大きくなり始めていた。

1990年から2000年には本格的に公害汚染から環境汚染の問題へに転換されると共に汚染の対象物質は無機から有機の汚染物質の問題が取り上げられるようになった。特に1990年代に入り都市大気の大気質の悪化、有害化学物質の使用の増加、廃棄物排出の増加などにより埋立地などの最終処分場の確保の問題の発生から廃棄物の焼却によりダイオキシン問題が1995年本格的に取り上げられるようになった。その事で国レベルで、1996年環境部からの研究依頼を受け廃棄物焼却によるダイオキシンの排出実態の調査と排出ガイドライン作りの研究が釜慶大学の私の研究室で本格的に始まることになり、ごみ焼却からのダイオキシン対策に対する政府政策が取りまとめられた。

2000年代に入り、環境政策は事前予防の原則（Precautionary Principle）に伴ない政策を検討するようになっており、環境部が管理する関連法律は46に拡大された。また、大気と水質に関して汚染物質の環境排出に対し総量の管理制度が導入されると共に、水に関しては使用者の負担原則と廃棄物管理においては生産者責任の制度が実行される時代になった。

特に、2000年には釜慶大学ダイオキシン研究センターの黄砂中ダイオキシンモニタリング研究結果からダイオキシン類の越境移動している問題が最初に取り上げる事にもなり春の黄砂の環境問題が社会問題として関心を高まることになった。

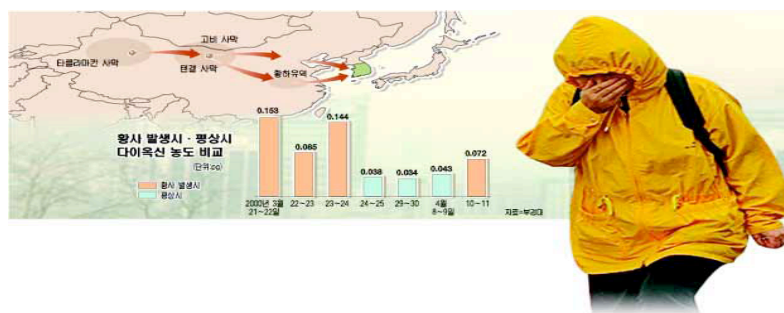


図 黄砂とダイオキシン類の越境移動

そして2000年代での環境政策はグローバル化が進んであり、残留性有機汚染物質（POPs）管理を目的として2007年 残留性有機汚染物質（POPs）管理法が制定された。

韓国のダイオキシン類などPOPsの対策とモニタリング

これらの法律を行かせるためには まず、発生源の目録化により排出量を把握する必要があり、2001年にダイオキシン類（PCDD/DFs及びCo-PCBs）に対し、国レベルのダイオキシンインベントリのカテゴリ分類など方法を環境部から依頼され釜慶大学ダイオキシン研究センターと環境管理公団が共同に開発し2001年から発生源のモニタリングが始まり2005年に排出量がまとまるようになった。図に韓国のダイオキシンインベントリ推進の概要を表した。韓国のダイオキシン類のインベントリ分類カテゴリは発生量が大きく予想される順位になっており、それに伴ない発生源のモニタリングの優先順位と削減対策の優先順位の位置付けが決まる事になった。

Inventory research process

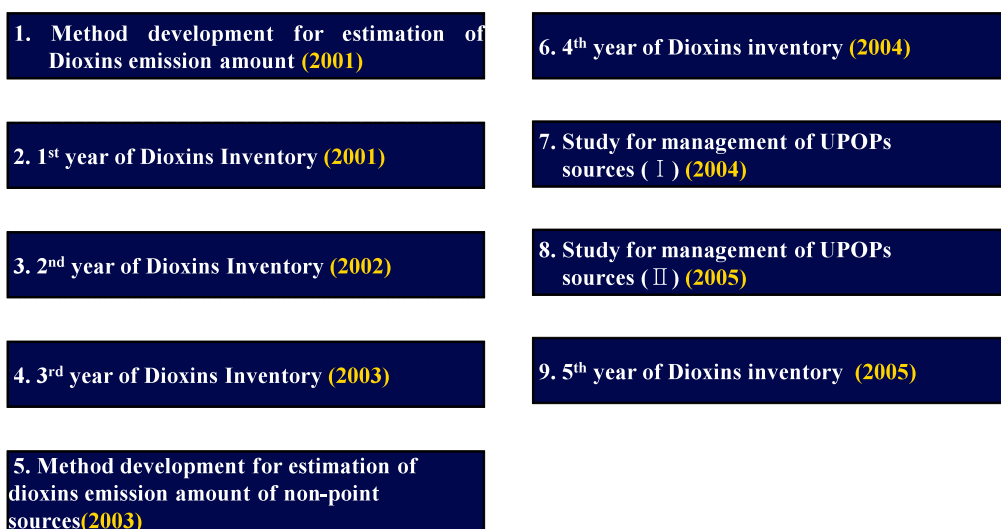


図 韓国のダイオキシンインベントリ推進の概要

また、韓国と外国とはの違いのもう一つの特徴は発生源の中での火葬場において外国には廃棄物のカテゴリに分類されているが、韓国の場合は廃棄物とは区別し、別のカテゴリに分けることにした。これは人間尊重の韓国の精神と文化の哲学の概念を用いる事にしたのが理由である。これらのインベントリ計画により発生源のモニタリングが実施されダイオキシン類の削減戦略が本格的に実行されることになった。

表 韓国のダイオキシン類のインベントリの分類カテゴリ

Categories		
Main	Semi-sub	Sub
1. Waste Treatment	Waste Incineration	Municipal, Industrial, Hazardous
	Landfill	Controlled, Non-controlled
2. Ferrous Metal Production	Iron and Steel Production	Sinter Furnace, Electronic Arc Furnace, Alloy
	Foundries	Pig-iron, Steel Casting
3. Non-Ferrous Metal Production	Smelting, Refining and Alloy	Copper, Aluminum, Lead and Zinc
	Rolling, Compressing and elongating	Copper, Aluminum, Other
	Non-Ferrous Metal Foundries	Aluminum, Copper, Other
4. Production of mineral Products	Glass	Flat Glass, Industrial Glass
	Ceramic	Refractory, Non-refractory
	Cement and Lime	Cement, Lime
	Other	Asphalt
5. Production of Chemicals	Chloride Compounds	EDC, VCM, PVC
	Pulp and Paper Manufacturing	Pulp and Paper
6. Power generation	Power generation	
	Area heating Facility	
7. Combustion of Manufacturing Industry	Furnace of Process	
8. Heating	Commerce and Public Facility	
	Residence facility	
9. Transport	Gasoline, Diesel, LPG	
10. Others	Crematory, Forest Fire, Fire accident, Tobacco	

そして、2005年にはダイオキシン類以外の農薬類POPsの公定試験法が環境部からの依頼を受け検討されるようになった。その対象の環境媒体は まず、大気、水、土壌、低質を中心にし、試料の採取方法を含む、高分解ガスクロマトグラフ・高分解質量分析機（HRGC/HRMS）を用いた試験法が制定された。

韓国の環境中のPOPsの中でダイオキシン類はすべての環境媒体から検出されているが、農薬類のPOPsはダイオキシン類に比べ検出頻度はかなり少なく、農薬類POPsの中ではDDTとLindanが別の化合物に比べ検出される頻度があるが、その濃度レベルも外国に比べかなり低いことも確認された。

また、海洋汚染に対しては韓国の西海の低質からのダイオキシン類の調査の結果が1999年発表された以降、海洋汚染の現状の把握のため海洋水産部からの研究計画を作り環境ホルモンとPOPsに関する調査研究が2002年から始まりダイオキシン類を中心に全国モニタリングが行っている。これらの一連の研究結果らは2006年国レベルで環境残留と環境暴露評価の報告がまとめられ、焼却からの発生は250～257 g WHO-TEQ/year、製鉄などを含む非焼却源からは154 g WHO-TEQ/yearで推算された。また、一般の生活環境において食品を含め環境

経路からの暴露のレベルは0.505 pg WHO-TEQ/kg/dayとして推算された。

また、近年UNEPは12グループのPOPs以外、PBDEsなど9種のEmerging POPsが追加された。韓国でも有害汚染物質管理及び残留性有機汚染物質（POPs）における政策はダイオキシン類を出発にして Emerging POPs としてのPBDEs、PFOS/PFOAなどのモニタリングが行われている。その結果を見ると先端IT産業の環境問題が新しい局面の状況にあると考えられる。

大気中の有害化学物質のモニタリング

もう一つの環境問題は化学物質の移動及び排出の概念であるTRIからの情報と国際的な管理が要求されているREACH(Regulation on the registration, evaluation, authorisation and restrictions of chemicals)などからも新しいアプローチが要求されている。

そして、有害大気汚染物質（HAPs; hazard air pollutants）により人のリスクの削減の対策が要求され、2008年HAPsインベントリを検討し化学関連の産業施設を始めHAPsの発生源からのモニタリングを行っている。

HAPsインベントリのモニタリングには対象になる化合物の種類が53化合物であり、無機と有機化合物に対する試料の採取と分析が必要である。このモニタリングにおいて試料の採取方法と分析方法は5グループ以上が要求されている。特に、分析にはガス状の試料を吸着材等を用い直接に機器分析に対応できるGerstel-TDS システムとGC/MSDを組み合わせ分析などが主に用いられた。

また、2001から2002年には温室ガス対策のため排出インベントリも検討された。分析の対象化学物質は主にCO₂, CH₄, N₂Oが取りあげられているが一般的には電気化学センサーの連続ガス分析とガスクロマトグラフィーのGC-FIDとGC-ECDが用いられたが、それと共に我々は特に N₂O に対してはGC-MSDを用い確認と分析結果の精度を上げる事になっていた。

終わりに

最近の韓国での環境に対する分析の対象は微量で、毒性が強く、人をはじめ生態系に与える悪影響を及ぼす可能性が高い化学物質の研究が活発に行われるようになった。また、環境分析はただの規制基準に基づいたことでなく、環境の管理に事前対応出来、新しい化学物質の管理に必要な科学的な解明の研究が進んでおり、その中の中心に微量で、制度よい環境媒体を対象にしている化学分析の役割が存在し、環境媒体の微量化学物質の分離と同様にクロマト分析の大切さが目立っていると言われる。

その環境分析結果はただの濃度と規制の意味ではなく、人と環境生態系の管理とリスクアセスメントの大切なパラメーター作りの資料としての活用につながっている。人と環境のリスクアセスメントを行うためには発生源から環境媒体のプロセス全般と食品、生物、人の暴露試料まで分析が要求されている。

したがって、空から海の下まで分析は幅広くアプローチをし“**Sources and Environ Budget System Approach**”の研究シナリオによる環境研究は必要であると思う。

The Analytical Chemistry Division on Chinese Chemical Society and Recent Research Topics in China

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The Chinese Chemical Society (CCS) is an academic organization formed by Chinese Chemists of their own accord and aiming at uniting Chinese Chemists at home and abroad to promote the development of chemistry in China.

The CCS was founded in Nanjing (Nanking) on August 4, 1932. Since then sixteen Boards of Directors had been elected by 1949 with more than 3000 individual members and 150 group members. In 1959, the CCS merged with the Chinese Chemical Engineering Society to become the Chinese Chemical and Chemical Engineering Society, but was split up again into two separate organizations, the Chinese Chemical Society and the Chinese Chemical Engineering Society in 1963.

At present, there are more than 55000 registered individual members, some foreign members and 58 group members. Under the CCS there are 7 Academic Committees, 15 Specialized Committees and 7 working Committees. The CCS has established a close relationship with some chemical organizations in the countries from Europe, America, and Asia. Since 1983, the CCS has set up 11 kinds of awards, including Young Chemists Award, Professor Wang Baoren's Award for accomplishments in the field of polymer science, Professor Liang Shuquan's Award for accomplishment in basic research in analytical chemistry, Chuangxin Award for Polymer Science etc.

The Analytical Chemistry Division is one of the 15 specialized committees of CCS. Prof. Erkang Wang is the chairman. Prof. Jin-Ming Lin and other six professors from different universities or institutes are the associate chair for the division. Each three years, we have once national symposium on analytical chemistry. This year during October 29 to November 2, the 12th National Symposium on Analytical Chemistry will be held at Yangzhou City. More than 1000 analysts and students will attend this symposium. Liang Shuquan's Award and the Awards for the Excellent Research Papers published in *Fenxi Huaxue* (Chin. J. Anal. Chem.) during 2005-2007 will be announced at the conference. Beside this symposium, each year there are many different meetings for the different research topics, for example, life analytical chemistry, luminescence, capillary electrophoresis, μ -TAS, spectrometry, electroanalytical chemistry, chromatography, mass spectrometry, environmental analytical chemistry, sensor, etc. In the present presentation, I shall introduce the function of the Analytical Chemistry Division of CCS and the recent research topics in China. I hope to be as a bridge between China and Japan in the research area of analytical chemistry.

Biography

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Professor Jin-Ming Lin was born in 1963 in Fujian, China. He received his BA degree in 1984 and received a PhD degree in analytical chemistry at Tokyo Metropolitan University in 1997. He had studied and worked in Showa University and Tokyo Metropolitan University during 1992-2002. He is currently a full professor of Tsinghua University since 2004. He is a vice chairman of the Division of Analytical Chemistry, Chinese Chemical Society, and a member of council of Chinese Society for Chromatography Science. He is a contributing editor of Trends in Analytical Chemistry, a guest editor of Talanta for special issues of China-Japan-Korea Environmental Analytical Chemistry and editorial boards of Talanta, Luminescence, Eurasian Journal of Analytical Chemistry, J. Flow Injection Analysis, International Journal of Analytical Chemistry and seven Chinese journals. He received several awards for his contributions in chemiluminescence and separation science: Outstanding Young Chemist Award (Chinese Chemical Society, 1992), Young Analyst Award for Flow Injection Analysis (Flow Injection Section, Japan Society of Analytical Chemistry, 2000), Kanton New Century Award (Japan Society of Analytical Chemistry, 2001), National Science Fund for Distinguished Young Scholars of China (National Natural Science Foundation of China, 2002), FIA Award for Science (Flow Injection Section, Japan Society of Analytical Chemistry, 2008) and GC Contribution Award (GC Discussion Group, Japan Society of Analytical Chemistry, 2008)

His current research is focused on sample pretreatment, chemiluminescence, capillary electrophoresis and microfluidic device. He is the author and co-author of 218 original research papers published in international journals, 21 reviews, 3 books and 31 patents.

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- 1985-1989 Department of Chemistry, Liaoning University,
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- 1994-1998 Faculty of Science, Shenyang Pharmaceutical University,
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Professional Experience

- 1998, 04-1998, 11 Visiting Scholar Department of Chemistry, Northeastern University, Shenyang
- 1998, 11-1999, 11 Postdoctoral Research Assistant Department of Chemistry, Hong Kong Baptist University
- 1999, 12-2003, 12 Associate Professor Department of Chemistry, Zhejiang University, Hangzhou
- 2003, 12-present Professor Department of Chemistry, Zhejiang University, Hangzhou

Research Activities

- 1989-1997 Applications of flow injection analysis (FIA) in pharmaceutical analysis
FIA liquid-liquid extraction system.
Microdialysis sampling-FIA system for in vivo monitoring.
- 1998, 04-1998, 11 H-channel microfluidic capillary electrophoresis system.
- 1998, 11-1999, 11 On-line cloud-point extraction FIA system
Applications of cloud-point extraction in extraction of ginsenosides from
Chinese herbal medicine
- 1999, 12-present Researches on microfluidic analysis:
Microfluidic sample introduction and pretreatment
Microfluidic FIA, capillary electrophoresis and droplet analysis
Spectral detection techniques for microfluidic systems
Development of integrated microfluidic analyzer
Application of microfluidic systems in bioanalytical chemistry, clinical diagnosis and single
cell analysis.

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Title : The development of advanced ion chromatography applied to developing countries

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Summary

Water pollution in the developing country get more serious. When thinking about such a water quality, important items are inorganic anions , alkali metal ions , ammonium ion, alkaline-earth metal ions and silicas ,etc. In general , the spectrophotometric , the electrode method, and the atomic absorption method, etc. are used for the analysis of such an ion. The ion chromatography is can measure these important items at a time, and excellent methods of analysis in reproducibility and the sensitivity. As this application , we tried the simultaneous analysis method of the anions and the cations , the analyses of the hydrogen ion, and other methods.

Key word:4 to 6

Ion chromatography , water quality , simultaneous analysis of the anions and cations , analysis pf the hydrogen ion

1 Introduction

In the developing country, aggravation of water quality is serious with economic rapid development. Environmental aggravation has brought about not only destruction of an ecosystem but residents' health impairment. Especially the living environment preservation item accompanying centralization of the population to a city is important, must always monitoring, and must prevent declining water quality. In a living environment preservation item, measurement of nutrient matter, such as nitrogen, phosphorus, silica, salt, a hardness, etc. is also important besides base items, such as BOD, COD, DO, and pH.

Since the ion chromatography can measure more items simultaneously by comparatively easy pretreatment and operation, it came to be used in the place of recent years many. Then, the analytical method developed as the latest application (ex. the simultaneous analytical method of an anions and a cations, a hydrogen ion and , cations, silicate ion and a phosphoric acid ion) was applied to the environmental analysis, and analysis suitable for a developing country was considered.

2 Environment in Developing Country, and Analytic Present Condition

In a developing country, the population concentration to a city is remarkable and an antipollution measure is an important item. For effective countermeasures against pollution, measurement of a water pollutant is indispensable. The present condition is grasped by analysis, the effect of a measure is verified, and it supervises being maintained. For this reason, staff reservation of a analytical operators is indispensable and needs to maintain that operation level more than fixed. However, it is difficult for training of talented people not to meet the deadline, but for there to be a locality gap of the analysis level, and to always acquire the right measured value in a developing country.

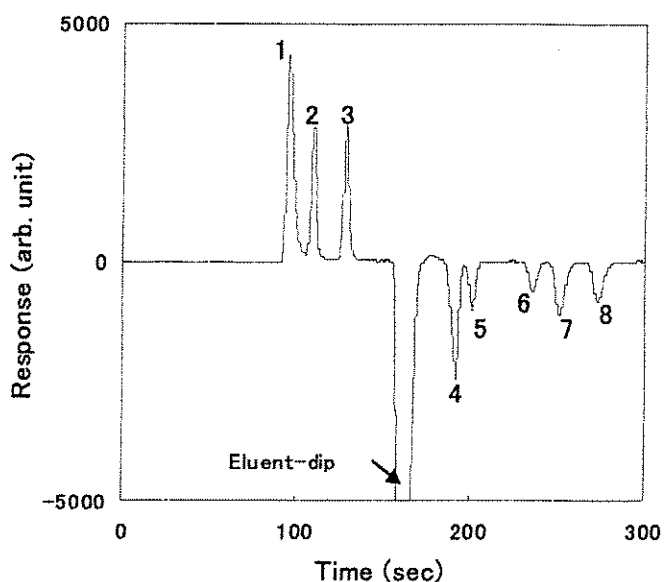
If based on such the present condition, the simple instrument excellent in operativity will be more desirable than an high-performance and expensive instruments. Moreover, the coincidence measurement of more items is more desirable than measurement of a single item.

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Therefore, it is necessary to use simple measurement and precise measurement properly and to try achievement for the purpose of measurement. Though operation is simple, it is high precision and quantity sensitivity, and since the coincidence measurement of two or more items is possible for ion chromatography, it is the analytical method excellent in measurement under such environment.

3 Environmental analysis by Ion Chromatography

In environmental analysis, measurement of anions and cations are important and these measurement is indispensable. These days, the simultaneous analytical method which combined ion exclusion and ion exchange is developed as a measuring method of an anion and a cation. Show the analytical conditions and the chromatograms of standard solution.



Separation Column : TSKgel Super IC-A/C
 Eluent : 6 mmol/L tartaric acid /3 mmol/L 18-crown-6-eter
 Flow rate: 1.0 mL/min
 Standard Solution: Na₂SO₄, KNO₃, NH₄NO₃, MgSO₄, CaCl₂ (0.1 mmol/L each)
 Injection Volume : 30 μL
 Detect : Electric Conductivity
 Peaks : 1= SO₄²⁻; 2= Cl⁻; 3= NO₃⁻; 4= Na⁺; 5= NH₄⁺; 6= K⁺; 7= Mg²⁺; 8= Ca²⁺

Thereby, an important environmental analytical value can be once known by operation. Moreover, the coincidence measurement of a hydrogen ion and a cation is also possible in ion chromatography. Such coincidence measurement becomes possible by using cation exchange for separation. These days, there is also an announcement which uses this method for measurement of alkalinity. Ion exclusion is used for separation of weak acid, such as silicate ion and a phosphate ion. What uses an electric conductivity meter, and the thing which uses spectrophotometer are used for these detection. In the case of using an electric conductivity meter, since weak acid has not dissociation on pH conditions of the eluent, a response signal is small. For this reason, it mixes with pH adjustor after separation, and high sensitivity becomes possible by performing dissociation of weak acid. When using spectrophotometer, it mixes with a color coupler after separation. The high sensitivity analysis of the case of the coincidence measurement of silicate ion or a phosphate ion becomes possible with the combination of post column labeling and the molybdenum blue method. These days, ascorbic acid which is a reducing agent is used as an eluent, and the method aiming at simplification is also announced.

4 Conclusion

The environmental analysis using ion chromatography is a very useful, and since operation is also easy, many things used by the way are expected. However, a problem remains on maintenance of a column or the problem of analytical cost. There is also a method which can perform use of a comparatively cheap column, and development of new analytical method is expected

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these days. It is possible to guess also about a quality control by the ion balance of an anions and a cations, the ratio of the electric conductivity calculated from the total ion to the electric conductivity obtained from survey, etc. Moreover, using this, a worker's skill can be presumed and improvement in technology can be aimed at by performing fixed education.

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