

Oral Presentations

Friday, 27 September 2013

Hall & Meeting Room, Kanazawa Bunka Hall

Friday, 27 September		
Time	Meeting Room	
09:00-09:10	9:00	AAI-01
09:10-09:20		Invited
09:20-09:30		A. Chatt
09:30-09:40		AAI-02
09:40-09:50		Invited
09:50-10:00		T. Miura
10:00-10:10	10:00	Coffee Break
10:10-10:20		
10:20-10:30	10:20	AAO-01
10:30-10:40		General J.H. Moon
10:40-10:50	10:40	AAO-02
10:50-11:00		General Y. Toh
11:00-11:10	11:00	AAO-03
11:10-11:20		General K. Ninomiya
11:20-11:30	11:20	AAO-04
11:30-11:40		General M. Fukushima
11:40-11:50	11:40	AAO-05
11:50-12:00		General N. Shirai
12:00-12:10	12:00	Lunch Time
12:10-12:20		
13:20-13:30	13:20	API-03
13:30-13:40		Invited
13:40-13:50		Y. Hamajima
13:50-14:00		13:50
14:00-14:10		General C. Gautier
14:10-14:20	14:10	APO-05
14:20-14:30		General T. Yoshimura
14:30-14:40	14:30	APO-06
14:40-14:50		General J.D. Despotopoulos
14:50-15:00	14:50	Coffee Break
15:00-15:10		
15:10-15:20	15:10	Closing Ceremony
15:20-15:30		
15:30-15:40		
15:40-15:50		
15:50-16:00		
16:00-16:10		
16:10-16:20		
16:20-16:30		
16:30-16:40		
16:40-16:50		
16:50-17:00		
17:00-17:10		
17:10-17:20		
17:20-17:30		
17:30-17:40		
17:40-17:50		
17:50-18:00		
18:00-18:10		
18:10-18:20		
18:20-18:30		
18:30-18:40		
18:40-18:50		
18:50-19:00		
19:00-19:20		
19:20-19:40		
19:40-20:00		
20:00-		

Simultaneous Analysis for As, Sb, and Se Species in Water by Chemical Separation and Neutron Activation

W. Menendez Sanchez, Y. Shi, and A. Chatt

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, NS, B3H 4J3, Canada

Abstract – APSORC'13 Abstract

Keywords – solid-phase extraction, solvent extraction, HPLC, INAA, speciation analysis, arsenic, antimony, selenium

I. INTRODUCTION

Arsenic speciation analysis has become an increasing health concern since the toxicity of the element depends upon the chemical species. Inorganic arsenic species are more toxic than their organic counterparts. Among the inorganic forms, As(III), the major arsenic species present in fresh water systems, is considered to be more toxic than As(V). It is well known that As(III) and As(V) undergo interconversion in aqueous solutions depending on pH, temperature, oxygen content, microorganisms, *etc.* Co-contaminants such as species of antimony and selenium in water can also affect arsenic speciation. There exists a need for simultaneous analysis of all these species.

Simultaneous speciation neutron activation analysis (SSNAA) technique has been developed in our laboratory over the last 20 years or so. This technique can now be used for the simultaneous determination of not only various species of a single element but also species of other elements present in the same sample. Almost all speciation techniques consist of two steps. The first step involves the separation of species from a sample followed by the second step of element-specific detection. Neutron activation analysis (NAA) methods in combination with high-performance liquid chromatography (HPLC) were developed first for the determination of low levels of five arsenic species, namely As(III), As(V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and arsenobetaine (AsB) in water samples. Organically bound arsenic (OBAs) and total arsenic levels were measured. These methods were then extended to include the determination of arsenic, antimony and selenium species, namely As(III), As(V), AsB, OBAs, MMA, DMA, Sb(III), Sb(V), and Se(IV), in natural water samples by solvent extraction and solid-phase extraction (SPE).

II. EXPERIMENTAL

In the HPLC method [1], OBAs was first separated by solid phase extraction using a C₁₈ silica column. Next DMA and AsB were separated in a cation exchange column followed by injection into HPLC with 10 mM NH₄H₂PO₄/(NH₄)₂HPO₄ buffer as the mobile phase. The effluent

containing MMA, As(III), and As(V) species was then injected into HPLC with 75 mM NH₄H₂PO₄/(NH₄)₂HPO₄ buffer at pH 5.5.

An independent solvent extraction method was developed to separate soluble As(III) and As(V) compounds in water using APDC/MIBK [2].

In the SPE method [3], As(V), MMA, and DMA were separated and preconcentrated by an Alltech strongly anion exchange (SAX), namely Extract-Clean SPE SAX, column and strongly cation exchange (SCX), namely Extract-Clean SPE SCX, column in tandem while As(III) remained in the effluent. Once the columns were physically separated, acetate buffer at pH 3.4 was used to elute MMA from the SAX column. Then 5 mL of 1 M nitric acid was used to elute As(V). The SCX column was also eluted with 5 mL of 1 M nitric acid for DMA determination. This SPE method was further extended to separate As(III), As(V), AsB, OBAs, MMA, DMA, Sb(III), Sb(V), and Se(IV) in natural water samples [4].

All samples were irradiated in the Dalhousie University SLOWPOKE-2 Reactor facility at a neutron flux of either 5 or $2.5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. Samples were counted using either a conventional or a Compton suppression gamma-ray spectrometer. The 559.1-keV γ -ray of ⁷⁶As ($t_{1/2} = 26.3 \text{ h}$) was used for arsenic determination.

III. RESULTS AND DISCUSSION

The detection limits (ng mL⁻¹) of the HPLC-NAA method were found to be 0.005 for OBAs, 0.02 for AsB, DMA, MMA, As(III), and As(V) and 0.12 for total arsenic. The detection limits of As(III) and As(V) in the solvent extraction methods were 0.007 for fish/shellfish, 0.005 for As(III) and 0.006 mg kg⁻¹ for As(V) in plants. The detection limits (ng mL⁻¹) were 0.9, 1.7, 1.6, 3.8 and 16 for As(III), As(V), MMA, DMA and total arsenic, respectively.

References

- [1] Y. Shi, R. Acharya, A. Chatt, *J Radioanal Nucl Chem*, 262(2004) 277-286.
- [2] R. Zwicker, B.M. Zwicker, S. Laoharajanaphand, A. Chatt, *J Radioanal Nucl Chem*, 287(2011)211-216.
- [3] W. Menendez Sanchez, B. Zwicker, A. Chatt, *J Radioanal Nucl Chem*, 282(2009)133-138
- [4] W. Menendez Sanchez, Ph.D. Thesis, Dalhousie University, Halifax, NS, Canada, 2009.

Precise Determination of Bromine in PP Resin Pellet by Instrumental Neutron Activation Analysis using Internal Standardization

Tsutomu Miura¹, Ryo Okumura², Yuto Inuma², Shun Sekimoto², Koichi Takamiya², Masaki Ohata¹,
Akiharu Hioki¹

¹National Metrology Institute of Japan, AIST

²Kyoto University Research Reactor Institute

Abstract – Instrumental neutron activation analysis with the internal standardization was applied the precise determination of bromine in PP resin. Gold was used as an internal standard. The analytical results of Br were in excellent agreement with the values obtained by ID-ICPMS. The relative expanded uncertainty ($k=2$) was 1.9 %, and it was comparable to that of ID-ICP-MS.

Keywords – Neutron activation analysis, Bromine, certified reference material, Uncertainty

I. INTRODUCTION

National Metrology Institute of Japan is responsible for developing certified reference materials (CRMs) and for establishing the traceability of SI (The International System of Units) on chemical metrology in Japan. To establish SI traceability, the primary method of measurements should be applied to the characterization of the CRMs. Recently, neutron activation analysis (NAA) using comparator standard is recognized as a potential primary ratio method [1]. Despite the potential of NAA as primary ratio method, the evaluation of the measurement uncertainty is required in any analysis. In general, there are three main components of uncertainty in NAA, that is, sample preparation uncertainty, neutron flux homogeneity, and gamma ray measurement uncertainty. Usually, flux monitor is used to correct the neutron flux in-homogeneity. However, although the flux monitor can correct the neutron flux variation using the count rate of the known amount of the monitor nuclide, it does not reflect the neutron flux of the actual sample. The most practical method to eliminate neutron flux in-homogeneity and to improve gamma ray measurement uncertainty is an internal standard method [2]. In this paper, we presented that notable capability of internal standardization in NAA for determination of Br in polypropylene (PP) resin pellet as a candidate CRM.

A. Instruments and methods

The PP resin pellet candidate CRM was produced by a mixing machine. The calibration solution was prepared from NMIJ primary Bromide standard solution. The Au solution for the internal standard was prepared from a high purity metal. The calibration solutions contained Br and Au. One hundred mg of the PP resin pellet samples was used for Br analysis. The Au solution was added to the samples before neutron irradiation. The neutron irradiations were performed by KUR (Kyoto University Research Reactor) PN-3(thermal neutron flux: $4.6 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$) for 10 min and TCPn (thermal neutron flux: $8.0 \times 10^{10} \text{ cm}^{-2}\text{s}^{-1}$) for 30 min. The γ ray

measurement system consisted of a Canberra GC4070-7500 Ge detector and a Laboratory Equipment Corporation MCA600.

B. Results and discussions

It was found that the neutron flux varied according to the sample position in the irradiation capsule. The relative standard uncertainty of the in-homogeneity was estimated to be about 5.1 % by ¹⁹⁸Au sensitivity (cps/ μg) at 411 keV of the internal standard ($n=19$). The uncertainty related to the neutron flux homogeneity significantly contributes to the overall uncertainty, if an internal standard is not applied. The calibration curve linearity was also improved by internal standardization. The calibration curves of ⁸²Br showed good and sufficient linearity. The relative uncertainty related to the calibration curve linearity was improved to 0.97 % from 2.0 % for ⁸²Br by using an internal standardization. The analytical results of Br by proposed method were in excellent agreement with the values obtained by Isotope dilution-Inductively Coupled Plasma Mass Spectrometry (ID-ICPMS). The relative expanded uncertainty ($k=2$) was 1.9 %, and it was comparable to that of ID-ICP-MS.

APSORC'13 HEADING (WITHOUT NUMBER)

- [1] Greenberg, R., Bode, P., De Nardi Fernandes, E., *Spectrochim. Acta B*, 66 (2011) 193-241.
- [2] Miura, T., Chiba, K., Kuroiwa, T., Narukawa, T., Hioki, A., Matsue H., *Talanta*, 82 (2010) 1143-1148.

Analysis of most popular and/or consumed fish species by neutron activation analysis in six Asian countries

J. H. Moon¹, B. F. Ni², R. M. Theresia³, N. A. Abd. Salim⁴, B. Arporn⁵, C. D. Vu⁶

¹Korea Atomic Energy Research Institute, Daejeon, Korea

²China Institute of Atomic Energy, Beijing, P.R. China

³National Nuclear Energy Agency, Serpong, Indonesia

⁴Malaysian Nuclear Agency, Bangi, Kajang, 43000 Selangor, Malaysia

⁵Thailand Institute of Nuclear Technology, Bangkok, Thailand

⁶Vietnam Atomic Energy Agency, Dalat, Vietnam

Abstract – Since 2000, collaborative studies for applying NAA have been performed through the Forum for Nuclear Cooperation in Asia (FNCA) sponsored by the Japanese Government. Fish were selected as a common target sample for a collaborative study in 2011. Six Asian countries, China, Indonesia, Korea, Malaysia, Thailand, and Vietnam, are greatly concerned about the composition of arsenic, heavy metals, and essential trace elements and took part in this work. Fish samples were purchased from commercial markets and prepared by following a protocol that had been proposed for this study. Samples were analyzed by their own NAA systems. Each country has determined toxic and/or essential elements. These data will be very helpful in the monitoring of the levels of food contamination and to evaluate the nutritional status for people living in Asia.

Keywords–Neutron Activation Analysis, FNCA, Fish Species, Toxic Metals

I. INTRODUCTION

Since 2000, collaborative studies applying a neutron activation analysis (NAA) have been carried out as one of FNCA (Forum for Nuclear Cooperation in Asia) projects for the application of nuclear technology for socio-economic development. Six Asian countries, China, Indonesia, Korea, Malaysia, Thailand, and Vietnam agreed to participate in the analysis of the most popular and/or consumed fish species as a sub-theme of the NAA project in 2011. The aims of this study were to determine the inorganic elemental contents in fish species of six Asian countries by NAA and to evaluate the dietary intake levels of nutritional and toxic elements for population of the participating countries.

II. EXPERIMENTAL

Each participating country selected six to ten fish species and purchased them from the commercial market for this study. Analytical samples were prepared by cutting the edible parts of the fish, cleaning, grounding, freeze-drying, and homogenizing fish samples. The samples prepared by each country were analyzed using their own NAA facilities. Samples were activated by short and long irradiation to detect short-, median- and long-lived nuclides. To detect the gamma-rays emitted from the irradiated samples, HPGe detectors coupled to multichannel analyzers were used. The elemental content was determined by relative method and/or k_0 -method.

III. RESULTS

China determined 14 elements from 10 fish species and most element concentration from the sea fish is higher than freshwater fish. Indonesia determined 17 elements from 6 types of fish samples, and As concentrations in sea fish is higher than in freshwater fish and Hg is contained in all types of fish. In Korea, 17 elements including As, Cr, and Hg were analyzed from 7 fish species. Malaysia determined Cr, Hg, Se, and Zn on eight species of marine fish, and the level of mercury in several fish showed a high value in dietary intakes levels compared to the EPA guideline value. Thailand analyzed As, Cd, Co, Cr, Fe, Hg, Rb, Sb, Sc, Se and Zn in 10 fish species As in all fresh water fish species does not exceed the standard recommended (2ug/g) but exceeds it in all marine fish species, while Hg in two fresh water fish species and three marine fish species exceed the standard recommended (0.5ug/g). Vietnam analyzed 18 elements in 10 samples of 6 sea fish species and As from Scad fish in the Vinh Hai district is higher than the WHO tolerable value.

ACKNOWLEDGEMENT

This research has been carried out by the support of the Ministry of Education, Culture, Science and Technology of Japan.

REFERENCES

- [1] Ebihara M, Chung YS, Chueinta W, Ni BF, Otoshi T, Oura Y, Santos FL, Sasajima F, Sutisna, Wood AKBH (2006) J. Radioanal. Nucl. Chem. 269(2): 259-266
- [2] World Health Organization (2006) Trace elements in human nutrition and health. Geneva, WHO, Belgium

Current status and future perspective on time-of-flight prompt gamma-ray analysis combined with gamma-ray coincidence technique

Y. Toh¹, M. Ebihara², K. Hara¹, A. Kimura¹, H. Harada¹, S. Nakamura¹, M. Koizumi¹, K. Furutaka, F. Kitatani¹

¹ Research Group for Applied Nuclear Physics, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

² Graduate School of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan

Keywords – Prompt gamma-ray analysis (PGA); Time-of-flight (TOF); Coincidence method; Pulsed neutron; High-purity Ge detectors

Prompt gamma-ray analysis (PGA) is a rapid, non-destructive and a nuclear analytical technique which can perform both qualitative and quantitative multi-element analysis of elemental and isotopic compositions. The multiple gamma-ray detection method, also known as the coincidence method, is widely used in nuclear spectroscopy. By applying the multiple gamma-ray detection method to PGA, called MPGA (multiple prompt gamma-ray analysis), the signal-to-noise ratio (S/N) can be improved. The kinetic energy of a neutron can be measured with the time-of-flight (TOF) technique at a pulsed neutron source by measuring the time it takes a neutron to reach a sample. The neutron capture cross sections of most nuclides exhibit strong variations with the energy of neutron. Therefore, the energy of the neutron obtained by TOF method can be used for identification of nuclides (elements). For further improvements of the S/N and sensitivity, we have developed a time-of-flight prompt gamma-ray analysis combined with multiple gamma-ray detection method (TOF-MPGA).

The Accurate Neutron-Nucleus Reaction Measurement Instrument (ANNRI) has been designed and developed for PGA, nuclear cross-section data and nuclear astrophysics (See Fig.1). ANNRI is located at the beamline No. 04 at the Material and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC). MLF is high intensive pulsed neutron facility, which operates at

approximately 300 kW proton beam power, and will be increased up to 1 MW in the near future. The germanium detector-array, which consists of two cluster-Ge detectors, eight coaxial-Ge detectors and BGO Compton suppression detectors surrounding cluster-Ge and coaxial-Ge detectors, was installed at the flight length of 21.5m in ANNRI. It is designed to provide high gamma-ray energy resolution and high detection efficiency. The typical time resolution of Ge detector is rather poor but this is not a disadvantage because of the proton beam pulse width of approximately 100ns (100ns double pulse, bunches separated by 600 ns). Frame overlap occurs when fast neutrons from a given pulse can catch-up with slower neutrons from a succeeding pulse. Whenever there is frame overlap there is a problem because the neutron energy cannot be unambiguously determined. Disk choppers consisting of a neutron absorbing disk are placed upstream of the Ge detectors. The disc choppers are used to prevent frame-overlap problems by limiting the neutrons which arrive at a sample. The rotation frequency of the choppers is the same as the source repetition rate (25Hz) under normal operation.

We present some remarks regarding the current status of experiments in TOF-MPGA development and its future perspective. The results of some standard sample measurements are discussed. These are compared with the results of the experiments of MPGA at Japan Research Reactor-3, and the similarity and difference are also discussed.

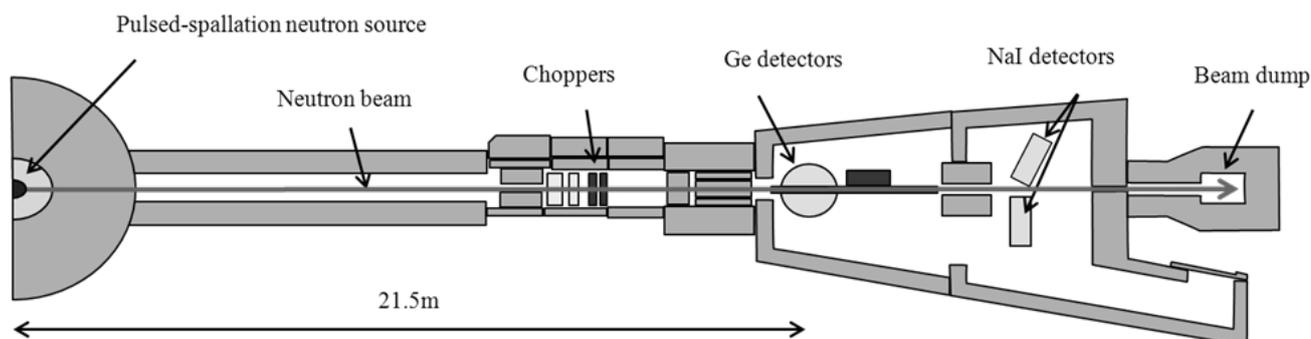


Figure 1 The Accurate Neutron-Nucleus Reaction Measurement Instrument (ANNRI)

Simultaneous and Multielemental Analysis by Muonic X-rays for Inside Japanese Bronze and Gold Coins

K. Ninomiya¹, M. K. Kubo², T. Nagatomo³, G. Yoshida¹, M. Inagaki¹, A. Shinohara¹, T. Suzuki²,
N. Kawamura³, P. Strasser³, K. Shimomura³, Y. Miyake³, Y. Kobayashi⁴, W. Higemoto⁵, S.
Sakamoto⁵,
T. Saito⁶

¹Graduate School of Science, Osaka University

²College of Liberal Arts, International Christianity University

³Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK)

⁴Nishina Center for Accelerator-Based Science, RIKEN

⁵J-PARC Center, Japan Atomic Energy Agency (JAEA)

⁶National Museum of Japanese History

Abstract – A nondestructive, quantitative and multielemental analysis method for bulk samples was developed, which was based on the measurement of high-energy muonic X-rays emitted from muonic atoms inside material after muon irradiation. We demonstrated quantitative determination of the elemental composition inside archaeological artifacts without sample destruction.

Keywords – Elemental Analysis, Muonic Atom, Muonic X-ray

I. INTRODUCTION

Quantitative elemental analysis is one of the most important themes in the field of natural science. In particular, non-destructive elemental analysis for inside material is very useful in the field of archeology. The archeological sample surface is usually oxidized and coated. The destructive analysis methods are never applied to the very valuable sample. The elemental analysis methods inside bulk material are strongly desired.

In this paper, we report the development of a non-destructive, position-sensitive, quantitative and simultaneous multielemental analysis method for bulk samples by muonic X-ray measurements [1]. Muonic atom is the exotic atoms that has one negatively charged muon in its atomic orbital. When a muon is stopped in material, a muonic atom is formed, and characteristic X-rays (muonic X-rays) were emitted from the muonic atom. Because the mass of a muon is 207 times larger than that of an electron, the energies of muonic X-rays are very high. Therefore muonic X-ray can penetrate a bulk sample layer and the muonic X-rays from inside sample are detectable. In addition, this elemental analysis method has position sensitivity; the depth of muonic atom formation in the sample is controllable by adjusting the incident muon energy.

II. EXPERIMENTAL

We performed muon irradiation experiments at Muon Science Establishment (MUSE) in J-PARC (Japan). We measured muonic X-rays emitted from an old Japanese bronze coin (tempo-tsuho) and an old Japanese gold coin (tempo-koban) using high purity germanium detectors. For

quantitative analysis, we also carried out muon irradiation for some standard alloys to obtain the relation between their elemental compositions and the muonic X-ray intensities.

III. RESULTS AND DISCUSSION

Muonic X-ray spectrum of the tempo-koban is shown in Figure 1. Muonic X-rays originated muon capture in Au and Ag atoms were identified. We easily determined that tempo-koban was alloy made from Au and Ag, and the compositions of the other elements were low. We also found incident muon momentum dependence of muonic Au X-ray intensity for the tempo-koban. This result showed that elemental composition of tempo-koban changed as its depth. The elemental composition inside the tempo-koban (> 5 μm in depth) was quantitatively determined (Au: 56%, Ag: 44%). Our result well reproduced the previous analysis result with destructive method [2]. The details will be reported in our presentation.

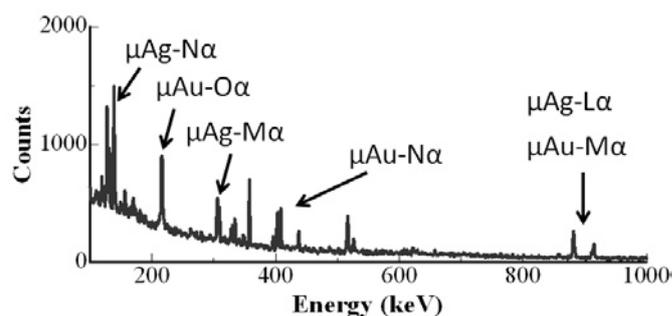


Figure 1: Muonic X-ray spectrum for old Japanese gold coin (tempo-koban). Muonic Au and Ag X-rays were clearly detected and no X-ray peaks originated from the other elements were identified.

[1] K. Ninomiya et. al., *Bull. Chem. Soc. Jpn.*, **85**, 228 (2012)

[2] M. Ueda et. al., *IMES Discussion paper series*, 96-E-26 (1996)

Rapid Analysis for Selenium in Urine Samples using the 17.4-s Neutron Activation Product ^{77m}Se

Michiko Fukushima¹, Amares Chatt², Yoshitaka Nakamura³, Megumi Haga⁴,
Seiko Hoshi⁵, Takashi Sakata¹

¹ Ishinomaki Senshu University, Ishinomaki, Miyagi, Japan;

² Dalhousie University, Halifax, NS, Canada;

³ Meiji Co., Ltd., Odawara, Kanagawa, Japan;

⁴ formerly at Shokei Gakuin University, Natori, Miyagi, Japan;

⁵ Shokei Gakuin University, Natori, Miyagi, Japan

Abstract – APSORC'13 Abstract

Keywords – Selenium, urine samples, NAA, short half- life nuclide

I. INTRODUCTION

Selenium is an essential trace element for humans. Selenium deficiency causes dysfunction of various organs, including skeletal and cardiac muscles. The recommended dietary allowance (RDA) levels for Se in Japan [1] are 10 and 15 $\mu\text{g d}^{-1}$ for 1-2 and 3-5 years old children, respectively. Although Se intake levels can be estimated by directly analyzing foods and diets [2], some researchers prefer to use bodily fluids or excretions as a better reflection of body burden of Se. For example, Dael *et al.* [3] used stable isotopes, namely ^{76}Se as selenate and ^{74}Se as selenite as supplements given to infants, analyzed their urine samples, and reported total Se intake of $60.8 \pm 4.6 \mu\text{g}$ per 72 h, apparent Se absorption of $45.6 \pm 5.2 \mu\text{g}$ per 72 h, and total urinary Se excretion $21.0 \pm 4.2 \mu\text{g}$ per 72 h.

The techniques commonly used for the determination of Se in biological fluids are atomic absorption spectrometry (AAS), inductively-coupled plasma (ICP) atomic emission spectrometry (AES), and ICP mass spectrometry (ICP-MS). All of these techniques are suitable but time-consuming. The objective of the present project was to investigate a rapid method for the quantitative determination of Se in urine samples of children. We have developed an instrumental neutron activation analysis (INAA) method for this purpose using the short-lived nuclide ^{77m}Se (half-life = 17.4 s).

II. EXPERIMENTAL

24-h urine samples were collected from 75 healthy 3-5-year-old children by their families in their own houses living in two different cities of Miyagi Prefecture, Japan. The average total volume of urine was 503 mL d^{-1} . The urine samples were kept in cold and dark place for two days. After bringing the samples to the laboratory, they were frozen until the analysis.

Prior to analysis the urine samples were defrosted and 1 mL of each sample was transferred to a pre-cleaned polyethylene irradiation vial using a calibrated Eppendorf pipette. These vials were pre-cleaned using the following steps: soaking overnight in 2 mL of 4 M HNO_3 , washing

them with tap water followed by distilled water, and drying them in an oven. About 0.7 g of pure sucrose was added to each vial containing 1 mL urine and dried under IR lamp overnight in a fumehood. The vials were then heat-sealed. Comparator standards, for calculating Se concentrations in urine samples using the relative NAA method, were prepared by adding 1 mL of the Se standard solution containing 0.2, 0.5, or 1.0 μg of Se to 0.7g of sucrose using the same procedure as the urine samples. Samples, comparator standards and various reference materials were irradiated for 10 s in a neutron flux of $5 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$ at the Ghana Research Reactor-1 (GHARR-1). After a 10-s decay time the samples were counted for 30 s using a conventional gamma-ray spectrometer. The Se levels were assayed using the 161.9-keV gamma-ray of ^{77m}Se . It is evident that the INAA part of the analysis can be accomplished within 60 s which is quite rapid.

III. RESULTS AND DISCUSSION

To evaluate the accuracy of the INAA method developed here the following standard reference material (SRM) and certified reference material (CRM) were used: NIST SRM 2670a Toxic Elements in urine (Freeze Dried), NIST SRM 1549 Non-Fat Milk Powder, NIST SRM 1577b Bovine Liver, and NRC DOLT-3 Dogfish Liver. Our values agreed within $\pm 10\%$ of the certified values. Out of the 75 urine samples analyzed by the INAA method described above, only 4 samples were below the detection limit of 10 ng mL^{-1} . The average level of 71 samples was $79.2 \pm 46.8 \text{ ng mL}^{-1}$ with the highest value of 242 ng mL^{-1} .

References

- [1] Ministry of Health, Labour and Welfare of Japan. Dietary Reference Intakes for Japanese, 2010.
- [2] Reiko Yamamoto, Rie Okita, Akane Hiruta, Tosiko Konno, Research Reports of Shohkei Gakuin College 52 (2006) 205-218.
- [3] Peter Van Dael, Lena Davidsson, Rafael Munoz-Box, Laurent B. Fay, Denis Barclay, British J. Nutrition 85 (2001) 157-163.

Neutron activation analysis of iron meteorite

Naoki Shirai¹, Yoshihiro Hidaka¹, Shun Sekimoto², Mitsuru Ebihara¹, Hideyasu Kojima^{3,4}

¹Tokyo Metropolitan University

²Kyoto University Research Reactor Institute

³National Institute of Polar Research

⁴Graduate University for Advanced Sciences

I. INTRODUCTION

Iron meteorites are made of Fe-Ni metal phases with such minor minerals as schreibersite, troilite, cohenite and other Fe-Ni carbides [e.g., 1]. As most iron meteorites are believed to be samples of the metallic core of asteroidal parent bodies, petrological, mineralogical and chemical studies of iron meteorites are fundamental for unraveling the process of planetary differentiation.

Based on structure, iron meteorites were classified into hexahedrites, octahedrites and ataxites. Hexahedrites and ataxites are nearly made of kamacite and taenite, respectively. Octahedrites consist of kamacite and taenite and they are further divided into six subgroups on the basis of the width of the kamacite from finest (<0.2 mm) to coarsest (>3.3 mm). Almost all iron meteorites are classified into octahedrites. Therefore, it is difficult to determine representative elemental abundances of iron meteorites due to their heterogeneity. Bulk elemental abundances for iron meteorites have been obtained by using neutron activation analysis (NAA) [e.g., 2]. Other analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS) have not been very often applied to iron meteorites [3, 4]. As subgroup IVB iron meteorites are made of ataxites and these chemical compositions are highly homogeneous, Campbell and Humayun [3] applied laser ablation with ICP-MS (LA-ICP-MS) to this subgroup. However, other subgroups have not been analyzed by using LA-ICP-MS for determination of their bulk chemical compositions. D'Orazio and Folco [4] analyzed iron meteorites by using solution nebulization ICP-MS. However, elements having smaller mass number than 80 significantly suffered spectral interferences caused by molecular ions such as FeO⁺. There is a possibility of vaporization of Ge as GeCl₄ during the digestion of iron meteorites. Kong et al. [5] developed the INAA procedure for iron meteorites by using a TRIGA Mark II reactor at the Institute for Atomic Energy, St. Paul's University. In this study, Kyoto University Research Reactor was used for determination of elemental abundances of iron meteorites and the analytical capability was evaluated in comparison with the procedure of Kong et al. [5].

II. EXPERIMENTAL

As the Canyon Diablo iron meteorite was used for control sample in considering that it has been vigorously analyzed and its elemental abundances were well established. A piece of Canyon Diablo was cut into square plates weighing 33 and 41 mg by using a ISOMET Low Speed Saw. In INAA, samples were firstly irradiated for 10 sec at

a neutron flux of $4.6 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$ at KURRI for determination of Cu, Ge and Rh. The samples were reirradiated for 4 hrs at a neutron flux of $5.6 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$ at KURRI and were measured for gamma rays several times with different cooling intervals. JB-1 and the Allende meteorite were also analyzed for reference samples. In addition, chemical standard samples were prepared for the determination of Cu, Ga, Ge, Mo, Ru, Rh, Pd, Sb, W, Re, Os, Ir, Pt and Au. The analytical procedure used in this study is basically similar to that described by Kong et al. [5].

III. RESULTS AND DISCUSSIONS

In short irradiation of Canyon Diablo, ^{60m}Co, ⁶⁵Ni, ⁶⁶Cu, ⁷⁵Ge and ¹⁰⁴Rh could be detected. Among these elements, Cu, Ge and Rh contents were calculated and shown in Table 1, where literature values were also indicated for comparison. Our values are in good agreement with literature values [2,6].

The plots of Ni vs. Ga, Ge and Ir can separate iron meteorites into about 12 subgroups. Usually, Ge has been determined by using radiochemical NAA [2] and Ni data have been obtained by INAA with long irradiation. Considering that short-irradiation INAA is able to determine both Ni and Ge. Therefore, our INAA procedure is simple and effective in classification of iron meteorites.

Reference: [1] Goldstein J. I. et al. (2009) *Chemie der Erde*, 69, 293-325. [2] Wasson J.T. and Kallemeyn G. W. (2002) *GCA*, 66, 2445-2473. [3] Campbell A. J. and Humayun M. (2005) *GCA*, 69, 4733-4744. [4] D'Orazio M. and Folco L. (2003) *Geostand. Newsl.*, 27 (3), 215-225. [5] Kong P. et al. (1996) *Anal. Chem.*, 68, 4130-4134. [6] Nichiporuk W. and Brown H. (1965) *J. Geophys. Res.*, 70 (2), 459-470.

Table 1. Cu, Ge and Rh abundances (in ppm) of Canyon Diablo in comparison with literature.

	This work		Literature
Cu	136 ± 11	154 ± 10	148, 150 ^[2]
Ge	329 ± 22	314 ± 21	323, 330 ^[2]
Rh	1.33 ± 0.11	1.08 ± 0.10	1.5 ^[6]

What has been revealed in the Low-Level Radioactivity Measurement?

- Low Level Gamma-Ray Counting in Ogoya Underground Laboratory -

Yasunori Hamajima
Kanazawa Univ. LLRL.

Abstract – In Ogoya Underground Laboratory, low-level radioactivity measurement is performed. We have 18 low background Ge detectors and all detectors provide excellent counting efficiency. We report recent results.

Keywords – low-level counting, underground laboratory, well-type Ge detecto

I. INTRODUCTION

In gamma ray measurements, it is important to reduce the background noise of detectors and activation of shielding materials derived from secondary cosmic ray components (muons and neutrons). It is difficult to reduce these components by conventional shield at aboveground. The intensity of secondary components decreases with the depth of overburden at the underground facility. Ogoya Underground Laboratory (OUL) is in a 546 m tunnel of the former Ogoya Copper Mine. It is located 270 m from the tunnel entrance, where the overburden is 270 mwe. The background count rates of OUL detectors are about 1/100 of the aboveground ones.

II. DETECTORS AND SHIELDING IN OUL

OUL has 11 well, 6 planar, and 1 coaxial Ge detectors, as shown in Table 1. In order to measure a wide energy range from 20 keV to about 3 MeV, the planar type detectors have large diameters and thicknesses and the well type detectors have also large diameters. For most of detectors, ultra low-background aluminum was used for the end-cap. The cryostat is the J-type and/or U-type and the preamplifier is located outside of the lead shield. The lead shield is 15 to 25 cm thick, and its upper part is covered by 10 to 15 cm of iron. The inner 3 to 5 cm of the lead shield is made of lead refined 200 years ago. The space near the detector head is filled with Hg shield encapsulated in a polyethylene bag and nitrogen gas from the Dewar is blown to the top of the end cap.

III. RECENT RESULTS IN OUL

Some significant measurements have been made at OUL such as the detection of low level cosmogenic nuclides,

natural radio nuclides, fission products and activated nuclides induced by environmental neutrons and fission neutrons.

In the recent results of extraterrestrial science, “Neutron Activation Analysis of a Particle Returned from Asteroid Itokawa” was in Science, 333, 1119-1121, (2011), and “Radar-Enabled Recovery of the Sutter’s Mill Meteorite, a Carbonaceous Chondrite Regolith Breccia” was reported in Science 338, 1583-1587, (2012).

In those of Oceanography, “Surface pathway of radioactive plume of TEPCO Fukushima NPP1 released ^{134}Cs and ^{137}Cs ” was reported in Biogeosciences, 10, 3067-3078, (2013), and “Cross equator transport of ^{137}Cs from North Pacific Ocean to South Pacific Ocean (BEAGLE2003 cruises)” was in Progress in Oceanography, 89, 7-16, (2011).

Table 1. Specifications of Ge crystals and background counting rates.

Ge	Type (Al end cap)	Relative Eff, (size)	BG (min^{-1})
I	planar	18%(28cm ² x 2cm)	0.48
J	planar	34%(38cm ² x 3cm)	0.57
K	planar	34%(38cm ² x 3cm)	0.52
L	planar	18%(28cm ² x 2cm)	0.57
M	planar	22%(28cm ² x 2.8cm)	
N	planar	22%(28cm ² x 3cm)	
C	well(10φx40mm)	37%(61φx56mm,)	0.9
D	well(21φx62mm)	56% (72.0φx74.8mm)	2.51
A	well(21φx62.5mm)	56% (72.0φx75.0mm)	2
B	well(21φx62.5mm)	56% (72.0φx74.7mm,)	1.93
G	well(21φx66.5mm)	71.5%(74.0φx79mm)	2.83
H	well(21φx66.5mm)	71.7%(74.0φx80mm)	2.09
W	well(21φx60mm)	65% (75.1φx81mm)	1.72
X	well(21φx68mm)	73.4%(74.3φx80mm)	1.69
Y	well(21φx68mm)	70.5%(74.3φx80mm)	1.4
E	well(21φx60mm)	68%(74.06φx80mm)	1.7
F	well(21φx55mm)	56%(75φx55mm)	2.1
U	coaxial	94% (78.9φx81mm)	1.12

BG: integrated count rate (50 – 2000 keV)

Zr and U determination at trace level in simulated deep groundwater by Q ICP-MS using TRU-based and TODGA-based extraction chromatography

C. Gautier¹, M. Coppo¹, C. Caussignac², I. Laszak², P. Fichet¹, F. Goutelard¹

¹Operator Support Analyses Laboratory, Atomic Energy Commission, CEA Saclay, DEN/DANS/DPC/SEARS/LASE, Building 459, PC171, 91191 GIF SUR YVETTE CEDEX, FRANCE

²Nuclear, Isotopic Elementary Analytical Development Laboratory, Atomic Energy Commission, CEA Saclay, DEN/DANS/DPC/SEARS/LANIE, Building 391, PC33, 91191 GIF SUR YVETTE CEDEX, FRANCE

Abstract – APSORC'13 Abstract

In the past decades, metallic fuels, such as UZr metallic alloys, were used as nuclear fuels. Direct disposal in deep geological repository can be an option for the long-term management of spent nuclear fuels. In the framework of such an issue, it is necessary to develop a source-term model for the release of radionuclides from the spent nuclear fuels. The validation of the dedicated model requires the implementation of leaching experiments in the conditions of a deep geological repository. For the spent UZr fuels studied in France, the leaching and the release of two major radionuclides, ²³⁵U and ⁹³Zr, have to be investigated in the reference groundwater which is planned to be a deep clayey Callovo-Oxfordian groundwater containing high concentrations of salts (alkali and alkaline earth metals). Given the expected concentrations of ²³⁵U and ⁹³Zr isotopes ($< 10^{-6}$ mol L⁻¹ or < 0.2 mg L⁻¹) in leaching solutions, Q ICP-MS can be considered as the most promising technique for their simultaneous measurements. However, due to the groundwater composition, sample dilution has to be applied before ICP-MS analysis to avoid matrix effects. This option is incompatible with our requirements in terms of detection limits. Consequently, a full analytical procedure was implemented to determine Zr and U at trace level in a simulated deep Callovo-Oxfordian groundwater by Q ICP-MS.

Separation procedures based on extraction chromatography were developed to eliminate the high salt contents and to concentrate Zr and U simultaneously. Since U and Zr display different chemical behaviors in solution, their speciation was first discussed. Theoretical and experimental speciation studies showed the importance of adjusting the medium to HNO₃/HF (0.5M/0.005M) to guarantee the stability over time of the analytes before removal of the matrix. Two preconcentration methods based on TRU® and TODGA® resins were optimized for the simultaneous isolation of Zr and U prior to Q ICP-MS measurements. Using TRU resin, alkali and alkali earth metals contained in the deep groundwater were removed with 2M HNO₃ whereas Zr and U were recovered with a HNO₃/NH₄HC₂O₄ (0.02M/0.05M) medium. For the separation protocol based on TODGA resin, alkali and alkali earth metals were eliminated with 3M and 11M HNO₃ while Zr and U were simultaneously stripped with a HNO₃/HF (0.5M/0.2M) medium. The procedure optimized on TODGA resin was the only one validated with the French AFNOR NF T90-210 standard by studying linearity, limits of quantification (LOQ) and separation yields. The LOQ was determined to be 0.008 µg L⁻¹ for Zr and U after the separation. Both analytes were recovered quantitatively. Compared to a direct Q ICP-MS analysis after sample dilution, the developed preconcentration method allowed improving the sensitivity up to a

20 fold factor for Zr and U measurements at trace level by Q ICP-MS.

The leaching experiments are requested to be performed in hot cells of the LECI laboratory (Laboratory for Studies on Irradiated Fuel) at CEA (French Alternative Energies and Atomic Energy Commission) Saclay. Blank samples (containing 0.5M HNO₃ + 0.005M HF) were introduced during one week in the selected hot cell where spent fuels are usually handled. The solutions were analyzed by Q ICP-MS to check whether the atmosphere of the hot cell induces problems of blank contamination for Zr and U measurements at trace level. The measured concentrations were lower than the limits of quantification validated at 0.008 µg L⁻¹ after separation, which proved the feasibility of the scheduled experiments.

The developed procedure was demonstrated to be very efficient for this application but it could be also used for many other issues concerning analysis of trace amount of radionuclides contained in high salt matrix.

Photoluminescence of Five- and Six-coordinate Tetracyanonitridotchnetium(V) and –rhenium(V) Complexes

Takashi Yoshimura¹, Hayato Ikeda², Akitaka Ito³, Eri Sakuda³, Noboru Kitamura³, Tsutomu Takayama⁴
Tsutomu Sekine⁵, Atsushi Shinohara²

¹Radioisotope Research Center, Osaka University

²Department of Chemistry, Graduate School of Science, Osaka University

³Department of Chemical Sciences and Engineering, Graduate School of Chemical Sciences and Engineering, Hokkaido University

⁴Department of Chemistry, Daido University

⁵Center for Advancement of Higher Education, Tohoku University

Abstract – Six-coordinate tetracyanonitrido Re(V) and Tc(V) complexes with a volatile organic compound (VOC) and five-coordinate complexes were synthesized and characterized. Reversible luminescence switching between six- and five-coordinate Re(V) complexes and between the relevant six-coordinate Re(V) complexes was achieved by exposing them to VOC vapor in the solid state at room temperature. Luminescence changes were observed from the five-coordinate Tc(V) complexes in a MeOH vapor atmosphere in the solid state. In contrast, no vapochromic luminescence was observed from the five-coordinate and six-coordinate complexes in an acetone vapor atmosphere.

Keywords – Technetium, Rhenium, Photoluminescence

I. INTRODUCTION

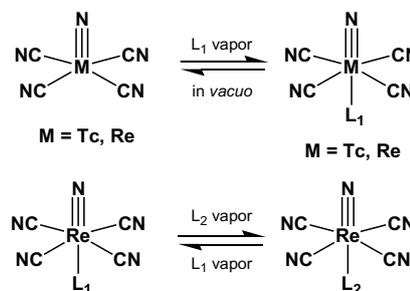
Among the Group 7 metal ions, a very small number of technetium complexes have been reported to show photoluminescence. In coordination compounds, molecular sensing can be done based on the color change of a complex through changes in the coordination environments and/or direct interaction of the metal ion with a molecule to be sensed. In contrast, molecular sensing based on the vapochromic luminescence through a ligand substitution reaction and the coordination number of a metal ion in the solid state has been rarely reported. We report novel six-coordinate nitrido Re(V) and Tc(V) complexes and their five-coordinate square pyramidal complexes without an axial ligand. The present study demonstrated for the first time that the nitrido Tc(V) complex showed luminescence in the solid phase at room temperature. We demonstrate for the first time interconversion between the six-coordinate Re(V) complexes through a solid state substitution reaction upon exposure to VOC vapor, and between the five-/six-coordinate complexes by a solid state ligand coordination/elimination reaction.[1]

II. RESULTS AND DISCUSSION

Six-coordinate Re(V) and Tc(V) complexes with a VOC, $(PPh_4)_2[MN(CN)_4L]$ ($M = Re, L = MeOH, EtOH, acetone, or MeCN$; $M = Tc, L = MeOH$), and five-coordinate $(PPh_4)_2[MN(CN)_4]$ ($M = Re or Tc$), were synthesized and their spectroscopic and photophysical properties were investigated. Results demonstrate that the tetracyanonitrido

Re(V) and Tc(V) complexes were bistable between the five-coordinate square pyramidal and six-coordinate octahedral coordination environments. All of the five-coordinate square pyramidal and six-coordinate octahedral complexes showed photoluminescence in the solid state at room temperature. The emission spectra and photophysical data of the five-coordinate $[ReN(CN)_4]^{2-}$ were significantly different from those of the relevant six-coordinate complexes.

Vapochromic luminescence between the bistable five- and six-coordinate Re complexes with the VOCs (MeOH, EtOH, acetone, or MeCN) and between the six-coordinate complexes was investigated. We found unique reversible coordination and elimination of a VOC at the axial site of the Re complex in the solid state that gave rise to changes in the emission maximum wavelength, demonstrating photoluminescence switching and sensing of VOC by the present Re(V) complexes at room temperature. Upon exposure of MeOH vapor to the five-coordinate Tc complex, the emission spectrum changed to that of the MeOH coordinate complex. The coordinating MeOH molecule can be removed by evacuation of the complex in vacuo. In contrast, the emission band shapes of the five-coordinate Tc complex remained unchanged even upon exposure of acetone vapor. The emission spectrum of MeOH coordinate Tc complex changed to that of the five-coordinate complex by exposure to acetone vapor. This suggests that the coordinating MeOH molecule in the Tc complex was eliminated under acetone vapor atmosphere, but acetone was not incorporated and did not coordinate at the axial site in the Tc complex.



Scheme 1.

- [1] H. Ikeda, T. Yoshimura, A. Ito, E. Sakuda, N. Kitamura, T. Takayama, T. Sekine, A. Shinohara, *Inorg. Chem.*, **51**, 12065-12074 (2012).

Studies of Flerovium and Element 115 Homologs with Macrocyclic Extractants

John D. Despotopulos^{1,2}, Narek Gharibyan¹, Roger A. Henderson¹, William Kerlin², Kenton J. Moody¹,
Dawn A. Shaughnessy¹, Evgeny Tereshatov¹, Ralf Sudowe²

¹Lawrence Livermore National Laboratory, Chemical Sciences Division, Livermore, California 94551, USA

²University of Nevada Las Vegas, Las Vegas, Nevada 89154, USA

Abstract – Recent studies of the chemical behavior of Copernicium (Cn, element 112) and Flerovium (Fl, element 114) together with the discovery of isotopes of these elements with half-lives suitable for chemical studies have spurred a renewed interest in the development of rapid systems designed to study the chemical properties of elements with $Z \geq 114$ [1,2]. Due to the short half-lives of the transactinide elements, fast and efficient separations are necessary to evaluate their properties, such as ionic radii and chemical speciation, by comparing to their lighter homologs. Separations based on extraction chromatography resins using macrocyclic extractants show promise for achieving the short separation times, large extraction yields, and high separation factors required for transactinide studies. In this study the potential of different macrocyclic extractants for their future application to a Fl and element 115 chemical system has been investigated.

Keywords – Transactinide, homolog, element 114/115, separations

I. INTRODUCTION

Studies of the chemical properties of superheavy elements (SHE) pose interesting challenges due to their short half-lives and low production rates. Chemical systems must have extremely fast kinetics to be able to probe the chemical properties of interest, such as chemical speciation, before the SHE decays to another element. To achieve chemistry on such time scales (~ seconds), the chemical system must also have the potential to be easily automated. The transactinides (elements with $Z > 103$) are predicted to exhibit changes in their chemical behavior compared to that of their lighter homologs (elements in the same chemical group) or pseudo-homologs (elements with the same oxidation state and similar ionic radii) due to relativistic effects [3].

II. EXPERIMENTAL

A. Extractants and Resins

Crown ethers and their derivatives show high selectivity for metal ions based on their size compared to the cavity of the ether. Di-t-butylcyclohexano-18-crown-6 (fig. 1) is known to show high affinity for the Pb^{2+} ion.

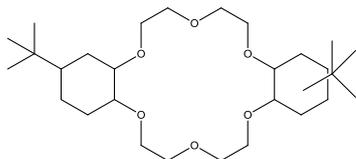


Fig. 1: Di-t-butylcyclohexano-18-crown-6.

LLNL-ABS-631618

Eichrom's commercially available Pb resin is based on the di-t-butylcyclohexano-18-crown-6 extractant sorbed to the resin backbone in isodecanol. Consequently, this resin exhibits high selectivity for Pb^{2+} [4]. Thiacycrown ethers, which replace the oxygen atoms with sulfur, act as softer Lewis bases compared to traditional crown ethers [5]. This unique property of thiacycrowns should make them even better extractants for softer metals such as Pb. Hexathia-18-crown-6 (fig. 2) was synthesized and investigated.

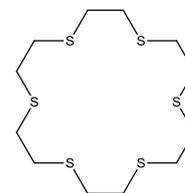


Fig. 2: Hexathia-18-crown-6.

B. Extraction Studies

Batch experiments were performed for the direct homologs of Fl (Pb and Sn) and element 115 (Bi and Sb) using the Eichrom Pb resin. Promising results were obtained from HCl/KI matrices as well as from simple mineral acid matrices. Column studies were performed to assess these extractions under dynamic conditions. Liquid-liquid extractions were also performed using hexathia-18-crown-6 to determine its suitability and compare it to that of the standard crown ether.

Acknowledgment: This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. This work was funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 11-ERD-011.

REFERENCES

- [1] R. Eichler *et al.*, Chemical characterization of element 112, *Nature*, **2007**, 447, 72-75.
- [2] R. Eichler *et al.*, Indication for a volatile element 114, *Radiochim. Acta*, **2010**, 98, 133-139.
- [3] P. Pykko, Relativistic effects in structural chemistry, *Chemical Reviews*, **1988**, 88, 563-594.
- [4] E. P. Horwitz, *et al.*, A lead-selective extraction chromatographic resin and its application to the isolation of lead from geological samples, *Analytical Chemistry*, **1994**, 292, 263-273.
- [5] E. Sekido, *et al.*, Liquid-liquid extraction of some class b metal ions with thiacycrown ether 1,4,8,11-tetrathiaclotetradecane, *Analytical Sciences*, **1985**, Vol. 1, 363-368.