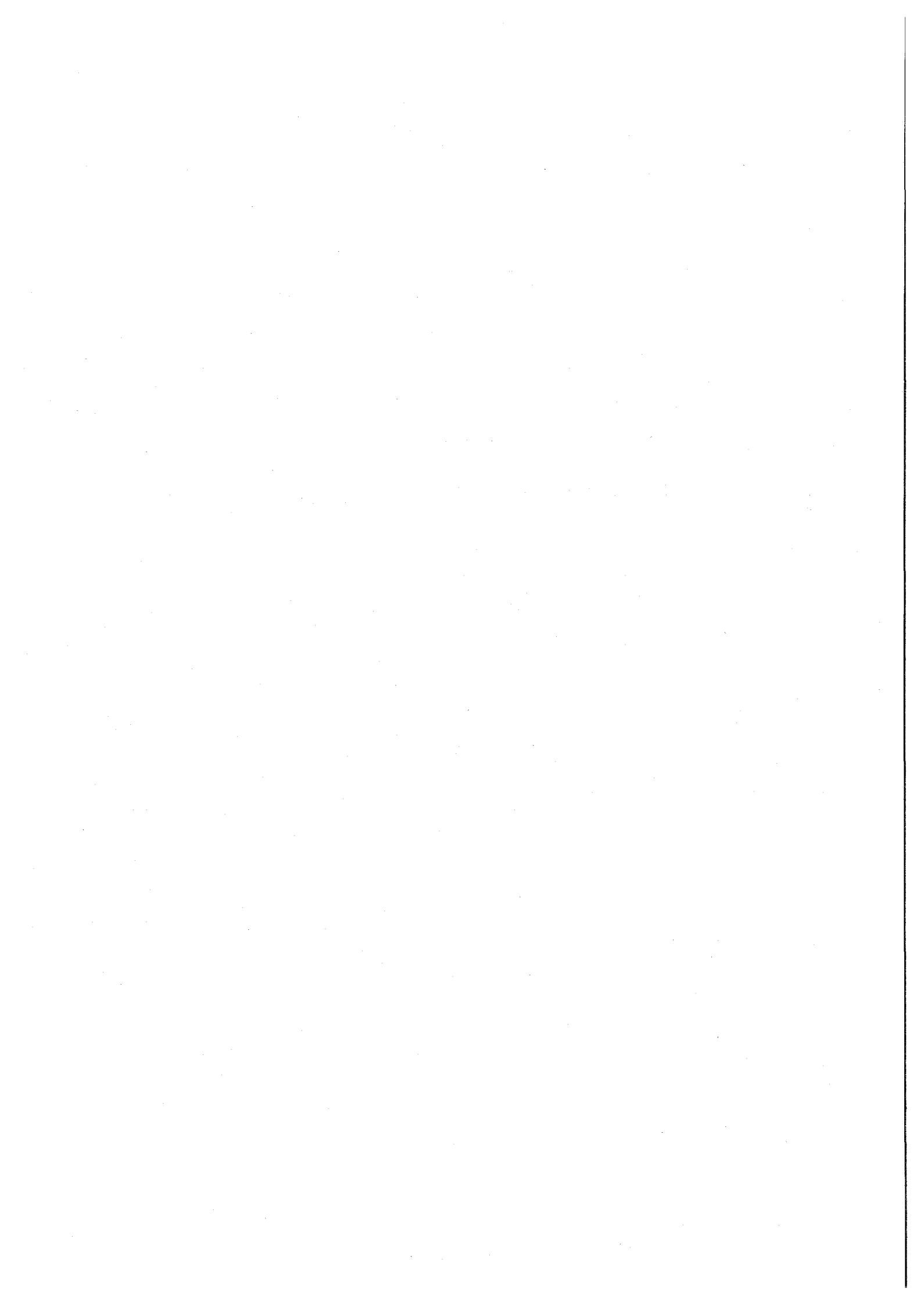


PLENARY LECTURER'S ABSTRACTS



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A review is given of the present knowledge of the chemical properties of the heaviest elements which can only be produced one-atom-at-a-time in heavy-ion reactions. The experimental techniques capable of doing single-atom chemistry are introduced. We also comment on the accompanying theoretical work in which the electronic structure of the transactinides and of their lighter homologs is calculated with relativistic molecular-orbital codes.

In the gas phase, volatile halides, oxyhalides, oxide-hydroxides, and oxides have been observed for elements 104 through 108 and their absorption enthalpies on quartz surfaces have been determined based on a microscopic model of gas-solid interactions in open column.¹ These are compared with absorption enthalpies of carrier-free tracer activities of the lighter homologs preferably studied under identical experimental conditions.

In the liquid phase, liquid-liquid extractions, extraction chromatography, and ion-exchange chromatography have been performed with halide complexes, oxyhalides, hydroxides, and chelates of elements 104 through 106, and their distribution coefficients have been determined. Again, these are compared with values of carrier-free tracer activities of the lighter homologs determined under identical conditions.² The sequences of distribution coefficients are consistent with theoretical predictions if the latter take explicitly into account complex formation and the competition by hydrolysis reactions.³ It is often found that the chemical properties of the transactinide elements do not follow straightforward extrapolations within the Periodic Table but that trends in a given group are reversed when going from the 5d- to the 6d- element

1. I. Zvara, *Radiochim.Acta*, 38, 95 (1985).

2. J.V. Kratz, in *Heavy Elements and Related New Phenomena*, eds. W. Greiner, R.K. Gupta, World Scientific, Singapore, Vol. 1, 129 (1999).

3. V. Pershina, B. Fricke, *ibid.*, 194 (1999).

Accuracy and Uncertainty in Radiochemical Measurements: Learning from Errors in Nuclear Analytical Chemistry

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"Knowledge increases...not by the direct perception of truth but by a relentless bias toward the perception of error."¹

Recently, the ISO² and other international bodies have formalized the measurement and statement of uncertainty. Quantitative uncertainty calculations require that all errors be examined and specified, as a consequence of which the significant sources of uncertainty are exposed for improvement. A characteristic that sets radioactivity measurements apart from most other kinds of spectrometry is that the precision of a single determination can be estimated from Poisson statistics. Remarkably, measurements can be made that are limited chiefly by counting statistics, even when that precision is very good. This easily calculated counting uncertainty permits the detection of systematic errors by comparison of observed with *a priori* precision.³ The redundancy often present in radiochemical measurements provides still more built-in quality control: multiple gamma rays, multiple isotopes, and repeated counts after decay may all be available to verify a result.

A good way to test the many underlying assumptions in radiochemical measurements is to strive for high accuracy. Three measurements in our group, for example, have revealed inadequacies in our procedures at first, and then led to improvements that have been incorporated into routine work. A measurement some years ago by instrumental neutron activation analysis (INAA) of gold film thickness in Rutherford backscattering standards⁴ revealed the need for pulse pileup correction, even at modest dead times. Once we understood the phenomenon,⁵ we were able to achieve an average of 0.3% agreement in a blind comparison with gravimetric measurements. Later we determined aluminum in fly ash, verifying our methods by measuring the stoichiometry of single-crystal Al₂O₃ to within 0.2% of the theoretical value.⁶ Because this measurement used 2.3-minute ²⁸Al, it was necessary to understand in detail the interaction of radioactive decay and system dead time.⁷ Recently, in the certification of ion-implanted arsenic in silicon (Standard Reference Material 2134) by INAA, we were able to achieve an expanded (95% confidence) uncertainty of 0.38% for 90 ng of arsenic.⁸ This work revealed another difficulty: a published half-life appears to be substantially in error. Because a complete, quantitative error analysis was performed, this As measurement meets the metrological standard of a primary ratio method as defined by the Consultative Committee on the Quantity of Material.

1. K. E. Boulding, *Science*, **207**, 831 (1980).
2. *Guide to the Expression of Uncertainties in Measurement*, 1995, International Standards Organization, Geneva.
3. K. Heydorn, *Neutron Activation Analysis for Clinical Trace Element Research*, CRC Press (1984).
4. R. M. Lindstrom, S. H. Harrison, J. M. Harris, *J. Appl. Phys.*, **49**, 5903 (1978).
5. A. Wyttenbach, *J. Radioanal. Chem.*, **8**, 335 (1971).
6. R. F. Fleming, R. M. Lindstrom, *J. Radioanal. Nucl. Chem.*, **113**, 35 (1987).
7. R. M. Lindstrom, R. F. Fleming, *Radioact. Radiochem.*, **6(2)**, 20 (1995).
8. R. R. Greenberg, R. M. Lindstrom, D. S. Simons, *J. Radioanal. Nucl. Chem.*, **245**, 57 (2000).

PL3 Atomic and Molecular Motion in Iron Organometallics

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The temperature-dependence of the area under a Mössbauer effect resonance curve can be related to the corresponding temperature-dependence of the recoil-free fraction, and hence to the mean-square-amplitude-of vibration (msav) of the metal atom in iron organometallics, by making use of a transmission integral fitting procedure for samples showing appreciable absorption effects, and a Lorentzian fitting procedure for optically thin samples. This analysis has been validated for ferrocene [(η^5 -C₅H₅)₂Fe] by reference to single crystal X-ray U_{ij} values at a number of different temperatures, and the resulting data, coupled with an analysis of the Gol'danskii-Karyagin asymmetry of the doublet spectra, yield a msav of the metal atom parallel and perpendicular to the principal symmetry axis of the ferrocene molecule. At room temperature [$\langle x_{\text{para}}^2 \rangle$]^{1/2} = 0.226±0.008 Å, while [$\langle x_{\text{perp}}^2 \rangle$]^{1/2} = 0.179±0.010 Å. This vibrational anisotropy is also observed in a number of structurally related ferrocenoid molecules, and can be related to the molecular level architecture of these diamagnetic solids and will be discussed in detail.

PL4 APPLICATIONS OF ¹⁴C-AMS IN BIOMEDICAL SCIENCE

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Accelerator mass spectrometry (AMS) is an ultrasensitive measure for tracing ¹⁴C -labeled molecules *in vivo* or detecting the biomarker for assessment of carcinogenesis. Basic principles, wide applications and some new progresses of ¹⁴C-bio-AMS have been introduced. It is a state-of-the-art tool for measuring the adduction of large biological molecules with xenobiotics, including carcinogens, drugs etc..

A catalogue of xenobiotics has been studied by AMS as follows: 1) carcinogens: MeIQx, PhIP, benzene, trichloroethylene etc.. 2) therapeutic drugs: tamoxifen, toremifene etc.. 3) agrochemicals: pirimicarb, malathion, atrazine etc.. 4) tobacco toxicants: nicotine, NNK. 5) nutrients: folic acid, beta-carotene.

We have committed to study the genotoxicity of smoking specific nicotine and its nitrosamine derivative NNK since 1994. The DNA-nicotine/NNK adduction as well as histones and blood proteins Hb/SA adductions with nicotine/NNK have been positively measured. We arrived at an important point that nicotine is not only a smoking addiction factor, but also a potential carcinogen *per se*.

In recent years, AMS techniques have been well coupled to other analytical methods, e.g., HPLC, GC, Liquid Scintillation Counting etc., thus greatly improving the potentiality of this technique. Another important trend is to carry out AMS study directly in humans instead of the conventional animal tests. The safety of radiation dose to human body has been specially discussed.

1. Y. F. Liu, Z. Y. Guo, X. Q. Liu et al., *Pure and Applied Chemistry*, **66**, 305(1994).
2. K. W. Turteltaub, J. S. Vogel, *Current Pharmaceutical Design*, **6**, 991(2000).

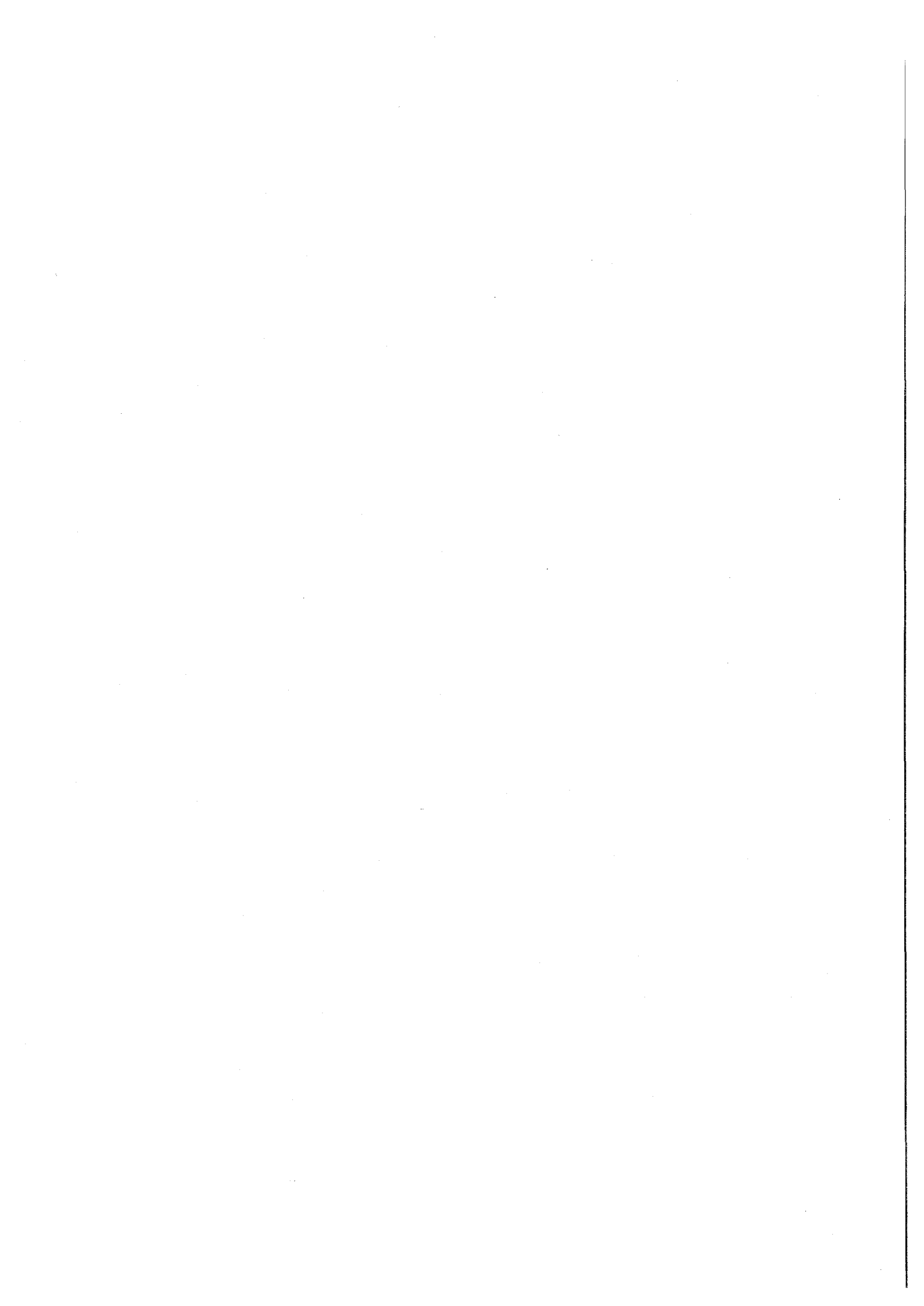
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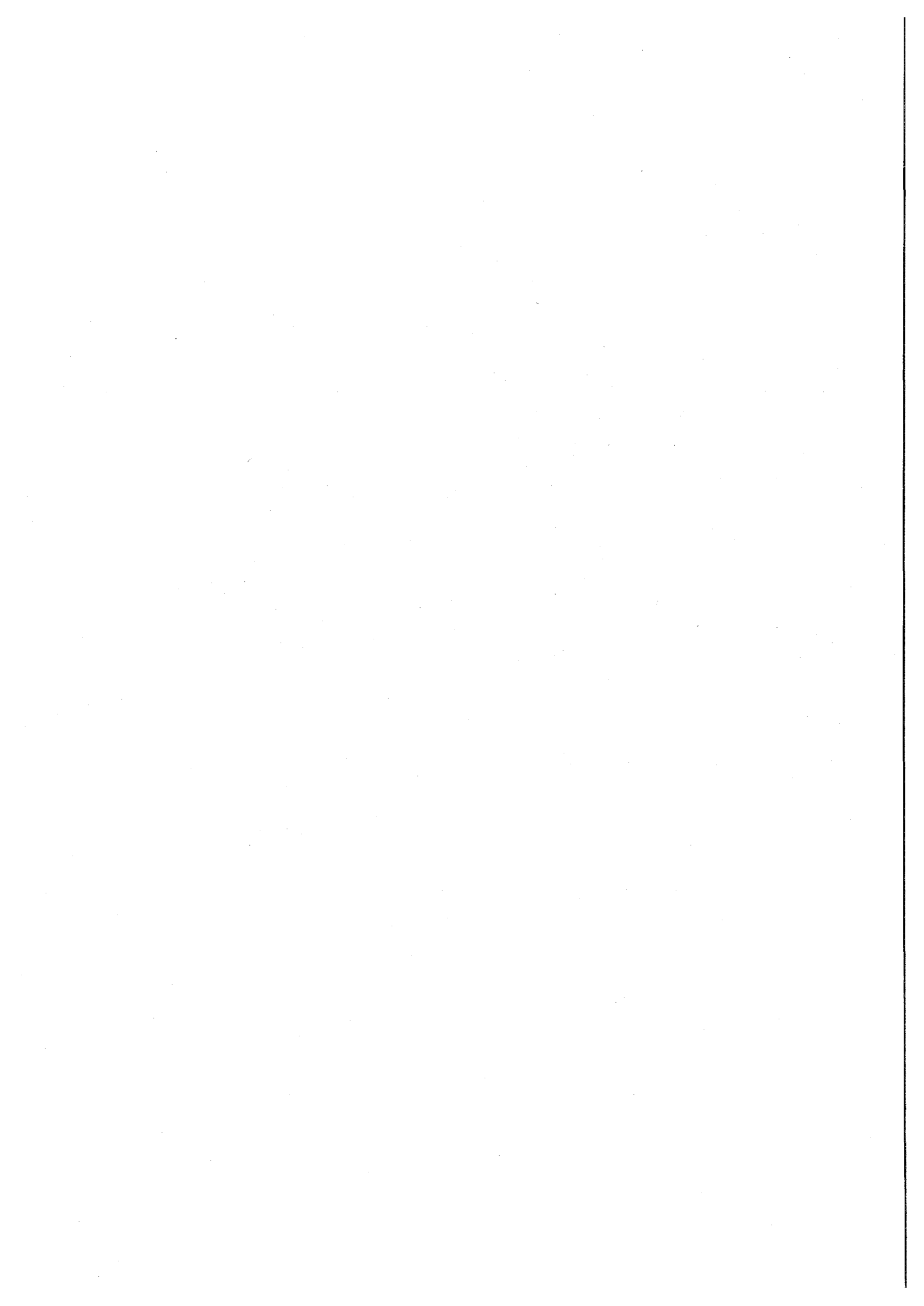
Comprehensive understanding of the hypervalent bonding is a subject of current interest. For a molecular system with covalent bonds of light elements, the octet rule states that the most stable species is formed when eight electrons are shared in the valence shell. All of the hydrides of elements in the second- and third-row of the periodic table obey the rule. However, replacement of hydrogen atoms by lithium atoms in such hydrides as CH_4 , NH_3 , H_2O and H_2S changes the feature of bonding. In fact, experiments with Knudsen-effusion mass spectrometry (KMS) by our research group as well as theoretical work by Schleyer *et al.* have shown the existence of thermodynamically stable polyolithiated molecules with nine or more valence electrons; e.g., Li_3O , Li_3S and Li_4P with nine valence electrons and Li_6C , Li_4O and Li_4S with 10 valence electrons. Despite their unusual stoichiometries, these Li_nA ($\text{A} = \text{C}, \text{O}, \text{S}, \text{P}$) molecules are thermodynamically more stable than the corresponding octet molecules like CLi_4 , Li_2O and Li_2S . These molecules are called "hyperlithiated" or hypervalent molecules. In the hyperlithiated molecules, the excess valence electron is delocalized over the lithium atoms and contribute to the formation of a Li_n^+ cage with Li-Li bonds. The electronegative central atom (A^{m-}) is embedded in the Li_n^+ cage, and the electrostatic attraction between Li_n^{m+} and A^{m-} would enhance the stability of neutral Li_nA molecules.

Further KMS experiments gave evidence for another type of hyperlithiated or hypervalent molecules M_2CN ($\text{M} = \text{Li}, \text{Na}, \text{K}$), in which the bonding situation was apparently different from Li_nA . Each of M_2CN molecules has several structural isomers with a global minimum. The most stable isomer in the planar structure with C_s symmetry is the hypervalent molecule in which the excess valence electron is delocalized over the two lithium atoms forming a M_2^+ cation. The molecule is stabilized in the form of M_2^+CN^- . The linear isomers of M_2CN , less stable than the planar isomer, are complexes described as $\text{M}^+\text{CN}^- \cdot \text{M}$ and $\text{M} \cdot \text{CN}^- \text{M}^+$; these are "electronomers" or electronic isomers.

All of the structures of Li_nA and M_2CN ($\text{M} = \text{Li}, \text{Na}, \text{K}$) have been derived only from theoretical calculations with *ab initio* MO methods and the density functional theory (DFT). Recently, however, we have experimentally verified the structures of newly detected hyperlithiated molecules Li_2F and Li_2OH as well as Li-rich clusters $\text{Li}_n\text{F}_{n-1}$ ($n = 3 - 5$) and $\text{Li}_n(\text{OH})_{n-1}$ ($n = 3 - 6$) existing in supersonic beams from a laser ablation source. Namely, the structures of these species were determined from precise measurements of the ionization efficiency curves (IEC) by photoionization time-of-flight (TOF) mass spectrometry in combination with simulations of IEC based on Franck-Condon factors for ionization processes. Furthermore, the analysis of IECs with the aid of theoretical calculations of the potential energy curves for both neutral and cationic Li_3O gave the first experimental evidence for an "electronomer" of Li_3O , the structure of which was fluctuating both in D_{3h} and C_{2v} symmetries.



INVITED LECTURER'S ABSTRACTS



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Mössbauer spectroscopy is a dynamic field with applications ranging from physics to biology. This paper gives a review of Mössbauer spectroscopy activities carried out by different groups in China. About thirty of such groups are founded and distributed all over China for both fundamental and practical aspects. In-beam Mössbauer setup was established at HIRAC accelerator in Lanzhou, and the nuclear scattering facility has already been planned at Shanghai Synchrotron Radiation light Source. In this review, some developments and achievements are discussed, as the examples: (1) Brownian motion in anisotropic media, (2) Applications to archaeology, and (3) Molecule-based magnetic materials

1. Y. Hsia and H. Huang, *Mössbauer Effect Reference and Data Journal* **23(4)**, 141 (2000)
2. J. G. Stevens, A report from MEDC in *ICAME' 99*
3. Y. Hsia, N. Fang, H. M. Widatallah, D. M. Wu, X. M. Lee and J. R. Zhang, *Hyp. Int.* **126**, 401 (2000)
4. Z. Y. Gao, S. H. Chen, X. J. Pan and G. D. Li, *Nucl. Tech.* (in Chinese) **13 (9)**, 533 (1990).
5. You song, *Ph. D. Dissertation*, Nanjing University, 2000.

Recent Development of Environment Radiochemistry in China

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Abstract

Environmental radiochemistry is a relatively newer subject in China. Recent years environmental radiochemistry has widely been studied and applied. It mainly involves radionuclide migration study, environmental measurement and analysis as well as other tracing techniques. The purposes of these activities are to understand the pollutant movement behavior of both radioactive and nonradioactive and to find the better ways for environmental protection. Comparatively, the bigger developments are achieved in the study of nuclide migration than in the study of nuclide speciations in environment media and in study of mutual interactions among nuclides and environment media. This paper describes recent China's progress of environmental radiochemistry in nuclide migration, oceanology and tracing studies.

1 B3

Radioactivity Measurement and Standardization
in Thailand

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ABSTRACT

This paper is divided into two parts. In the first part I describe the work on absolute measurement for disintegration rates of radioisotopes by 4π beta-gamma coincidence counting systems and 4π beta-gamma coincidence absorption method. Absolute activity of Co-60 sample was determined by the counting systems of Japan and Thailand. The absolute activity of Mo-99 sample was also determined. In the second part I describe the work on radon gas measurement and standardization. The radon chamber was constructed and employed for the comparative measurements by pulse-counting ionization chamber and environmental-level scintillation cell. Background radon concentration of the chamber was also determined.

FORMATION AND CHEMICAL REACTIONS OF POSITRONIUM STUDIED BY AMOC MEASUREMENTS

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The application of the AMOC (*age-momentum correlation*) technique developed at an MeV positron beam^{1,2} to the field of "positronium chemistry" is reported. Correlated measurements of the individual positron lifetimes (= positron *ages*) and of the *momenta* of the annihilating positron-electron pairs (*age-momentum-correlation*, AMOC) have become a powerful tool to study the evolution of the different positron states in the time domain. In this way direct, time-dependent observations of transitions and chemical reactions of positrons and positronium (Ps) have been made feasible. The time scales which can be observed are in the order of 10 ps to 10 ns, depending on the lifetime of the distinct positron and positronium states (examples see below).

The slowing-down of positronium could be analyzed in detail by beam-based AMOC measurements^{1,2}: The initial kinetic energies of positronium at its formation and its slowing-down times have been determined for the first time. The slowing-down times vary from 10 ps to 40 ps in liquids and solids where optical phonons are present. In liquid and solid rare gases where optical phonons are absent and energy can be transferred to acoustical phonons only, much higher positronium slowing-down times (up to 400-600 ps) are found.

The AMOC technique is also extremely useful to differentiate between distinct reactions of positrons and positronium³. It enables us to monitor transitions between the different positron states rather directly. In the field of "positronium chemistry" AMOC allows the study of chemical and other reactions of the hydrogen like positronium "atom" with molecules of the host material. Examples are oxidation, as well as spin conversion and inhibition of the positronium formation. Furthermore, bound states between positrons (e^+) and halide ions could be investigated. In all cases, AMOC allowed the determination of lifetimes of all positron states as well as the transition rates between them. For instant the formation rate of the positron (e^+) - halide bound state in the system 0.01 M NaBr in water was found to be $K_M = 0.33 \cdot 10^9 \text{ s}^{-1}$.

1. H. Stoll: *MeV Positron Beams*, in: *Positron Beams and their Applications*, ed. P.G. Coleman, (Word Scientific, Singapore, 2000) pp. 237-257
2. H. Stoll, P. Bandzuch, and A. Siegle, *Materials Science Forum* **363-365**, 547-551 (2001)
3. P. Castellaz, J. Major, C. Mujica, H. Schneider, A. Seeger, A. Siegle, H. Stoll, and I. Billard, *J. Radioanal. Nucl. Chem.* **210**, 457-467 (1996)

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The environmental radiation/radioactivity monitoring program in Korea can be categorized as i) nationwide radioactive fallout monitoring and ii) environmental radiation/radioactivity monitoring of the areas around the nuclear facilities.

The former, which is conducted at twelve regional monitoring stations all across the country by the Korea Institute of Nuclear Safety (KINS), aims to quickly detect any abnormal situations in environmental radioactivity. It includes measurement of the gross beta and gamma radioactivities and the activities of H-3, Sr-90, Pu-isotopes and Cs-137 in airborne dust, fallout, rainwater, livestock products, farm products, soil, drinking water, milk. It also measures the background radiation levels throughout the nation using TLDS.

The latter, which is carried out by the facility operators, has the goal of evaluating the radiological influence of the operation of the nuclear facilities. It includes measurement of the gross beta and gamma activities and the activities of H-3, C-14, Co-60, Sr-90, I-131, Pu-isotopes and Cs-137 and in the samples of air particulates, land samples (soil, pine needles), water samples (seawater, underground water, precipitation), seabed samples (sediment, benthos), and food samples (milk, fishes and shellfish, cereal, egg, seaweed). Also measured are gamma dose rates and collective absorbed doses using TLDs.

All the data collected are available to KINS and the Korea Ministry of Science and Technology through the Integrated Environmental Radiation Monitoring Network. In 1997, KINS began to inform the public the results of nationwide environmental radiation monitoring on real-time basis through the Internet web site: <http://iernet.kins.re.kr>. In order to assure the accuracy of the monitoring, KINS implements a quality control program which includes the standardized surveillance procedures, the standard operating procedures for sample collection and analysis, instrument calibration and verification and etc. KINS also implements some R&D programs to improve the monitoring techniques, such as study on the methodology of C-14 analysis in biological samples, development of the analytical method for determining Rn-226 in drinking water and ground water, and exposure rate mapping of the areas around the nuclear power plants.

2AB

Application of Radioactive Tracer Method to Copper Migration in Semiconductor Lithography

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ABSTRACT

The radioactive tracer technique of ⁶⁴Cu was applied to investigate the migration of Cu impurity from ArF and KrF photoresists onto silicon-based underlying substrates of Si(100), Si(110), Si(111), poly-Si, SiO₂ and Si₃N₄. The effects of polymer constituent of photoresist and baking temperature were studied. Our results indicated migration ratios of Cu from ArF photoresist was always higher than that from KrF photoresist, irrespective of the substrate types and baking temperatures. The migration-adsorption model was proposed to explain the pathway of Cu migration in the photoresist layers. In the bulk region of photoresist layer, part of Cu collided and coordinated with residual solvent. In the interface region, the effects such as electronegativity, surface adsorption site, interfacial Cu concentration and the interfacial pH condition were responsible for the migration ratios. A correlation function was proposed to modify the diffusion coefficient. The mathematical differentiation on the diffusion coefficient could explain the migration ratios of Cu impurity in ArF and KrF photoresist layers under various baking temperatures.

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SUMMER SCHOOLS IN NUCLEAR AND RADIOCHEMISTRY

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This successful educational program for advanced undergraduate students to make them aware of the many challenges and career opportunities in nuclear science will be described. Perhaps it can serve as a model for similar programs in other countries where there is continuing need for trained personnel in the various areas of nuclear science. The story of its founding at San Jose State University (SJSU) in 1984 will be summarized, along with the establishment of a second site at the Brookhaven National Laboratory (BNL) in 1989.¹ Funding now from the U. S. Department of Energy supports 24 fellowships for participation in the simultaneous, intensive, six-week summer schools. Students are provided transportation to and from the school site, lodging and food, text and reference books, laboratory supplies, and tuition for six units of transferable college credit through the American Chemical Society (ACS) accredited chemistry programs at SJSU or the State University of New York at Stony Brook.

The instructional program consists of lectures and laboratory exercises that cover the fundamentals of nuclear theory and radioactive decay, radiochemistry, nuclear instrumentation, radiological safety, and applications in research, medicine, and industry. Guest lecturers and seminar speakers cover their own specialties and broaden the students' exposure to the various aspects of nuclear science. Emphasis is placed on making the students aware of the many challenges and career opportunities available, as well as the needs for personnel at various degree levels to work in the universities, national laboratories, nuclear power industry, medical facilities, and in environmental clean-up and waste disposal and management activities. Both sites employ field trips to nearby nuclear facilities to show the students first-hand some potential work environments and to facilitate their interaction with nuclear science practitioners. This obvious recruiting mechanism has been successful in attracting students into at least considering further education and training in some aspect of the nuclear sciences, if not actually pursuing it and becoming a nuclear science practitioner themselves.

Graduates of the summer school who request it are given assistance in the following year(s) to join a research project at a university or national laboratory, and also, in their applications to graduate or professional school. Building on the knowledge gained during the summer school, they are strongly encouraged to pursue a hands-on activity in some aspect of nuclear science that interests them during a following term or summer. Keeping them involved with nuclear science increases the chances that they will continue their education and training toward a career in some aspect of it. This is aided by the networking that naturally occurs and the continued mentoring, advice, and encouragement from the summer school staff.

Each school site identifies its Outstanding Student, and these two students are rewarded with an expense-paid trip to the fall national meeting of the ACS. They are encouraged to attend the scientific sessions, participate in the society's programs for undergraduate students, and network with other chemists and nuclear scientists. This summer school program has attracted a number of students into careers in nuclear science and medicine. In addition it has produced academicians, physicians, researchers, and industrial scientists who have been made aware of the many benefits of nuclear science and some of its challenges. Additional information about the summer school program and its student participants can be found at URL <http://www.cofc.edu/~nuclear/nukess.html>

1. J. R. Peterson, *J. Radioanal. Nucl. Chem.*, **219**, 231(1997).

1 A5 **Some Recent Activities of the International Atomic Energy Agency in the Field of Nuclear Data**

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Din D. Sood and Andrej Trkov

Nuclear Data, PGNA, Medical Radioisotopes, Dosimetry, Cross Section Standards

Results of recent IAEA activities related to assembly, maintenance and verification of databases of relevance to radiochemistry are presented. These include: i) integral and differential nuclear constants for prompt gamma neutron activation analysis, ii) excitation functions for cyclotron production of medical radioisotopes using proton, deuteron and alpha particle projectiles, iii) data for dose calculations in radiation medical treatment/diagnosis and iv) nuclear cross section standards.

ORGANIC COFFEE DISCRIMINATION WITH INAA AND DATA MINING TECHNIQUES: NEW PERSPECTIVES FOR COFFEE TRADE

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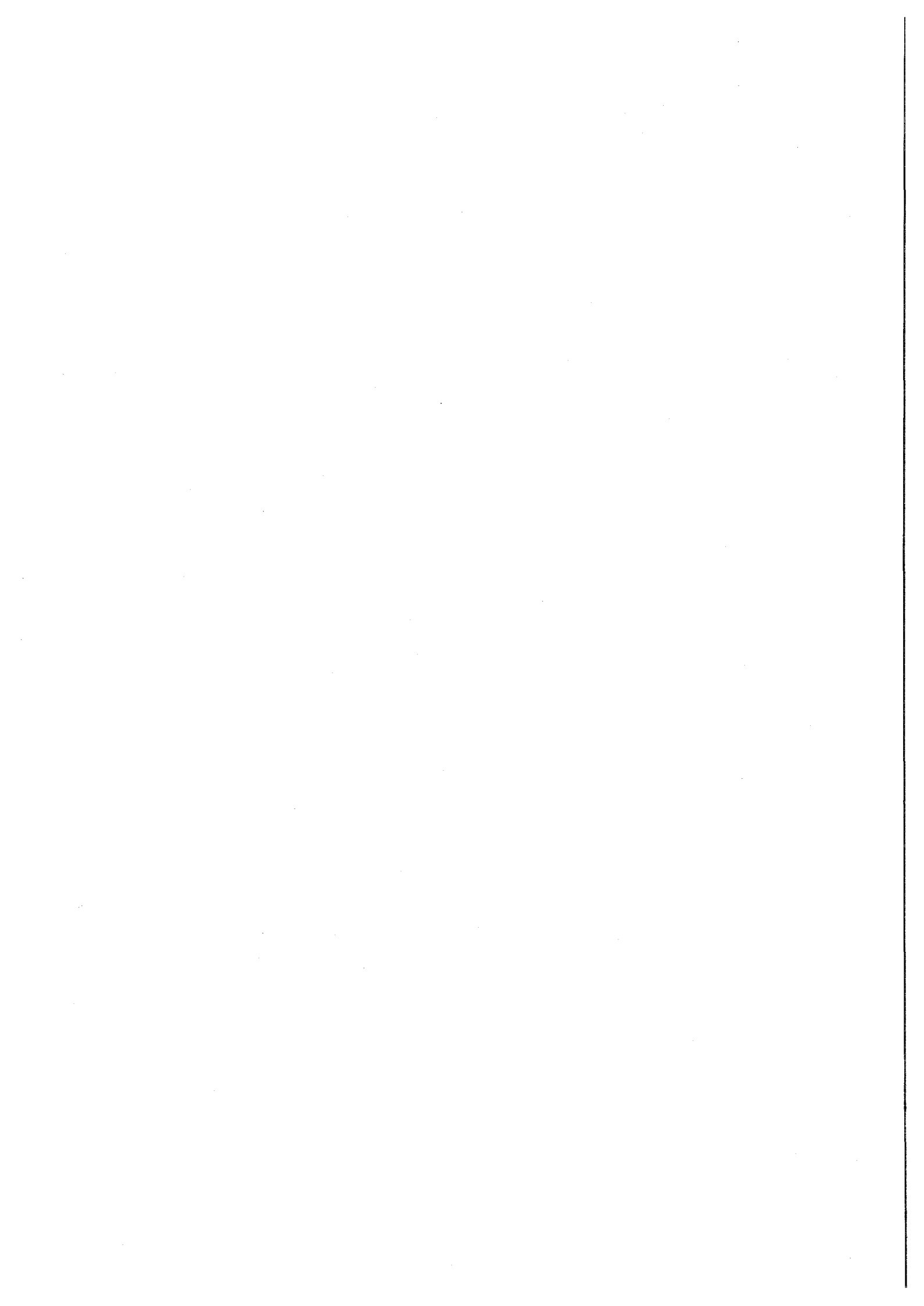
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The interest for organically cultivated coffee has grown during last years because of increasing consumer concerns related to environment and food safety. Organic coffee production is enhancing gradually to meet the demand of strong economical markets like the EC, Japan and the USA. Due to the more laborious production process and fair trade principles, the price of organic coffee is higher than the conventionally produced coffee.

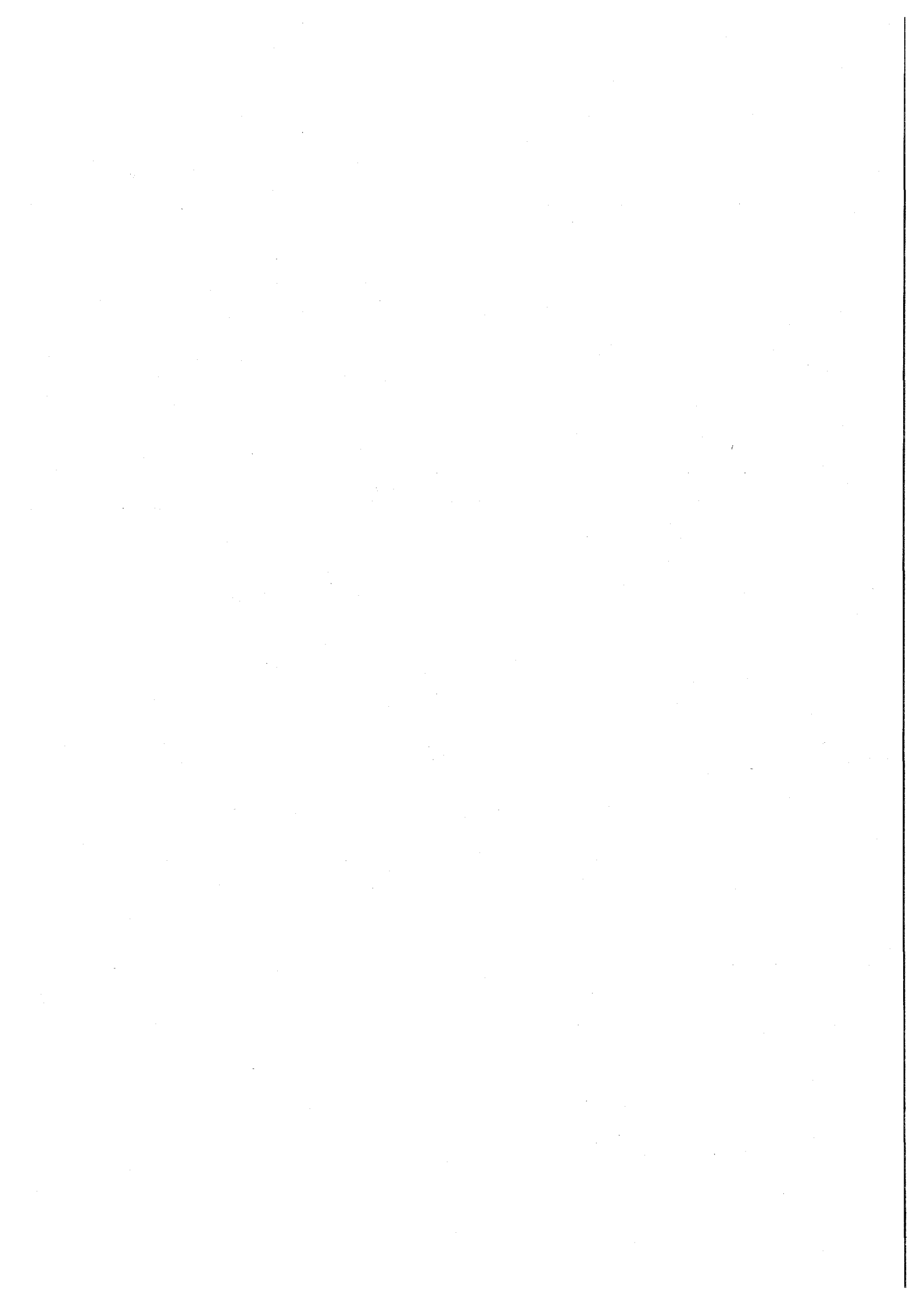
Importers, however, are facing numerous problems in the discrimination of organic coffees from other coffees in order to discover and avoid frauds. Because higher international market prices are achieved by organic coffee and current discrimination strongly relies on "designation" certificates, there is an incentive in the market to sell conventional coffees or mixed coffees as being pure "organic." Appropriate identification of organic coffee means protection to producers and consumers, as well as new perspectives for international trade. This identification may be based on the determination of the agrochemical compounds and residues, which is to some extent troublesome due to the high costs of the associated standards and to the fact that only very few such standards are available. Therefore it has been assessed if the elemental compositional characterization of organically and conventionally produced coffee could serve the same purpose.

This work is an attempt to establish "fingerprints" of original organic coffee, aiming at "demonstrating" that a product is what the seller "claims" it to be. In order to achieve this objective, samples of Brazilian coffee beans produced by organic and conventional methods were taken from farms in the Minas Gerais State, Brazil, and elemental concentrations determined by instrumental neutron activation analysis (INAA). INAA is an advantageous technique for this kind of study since it is considered a primary ratio-method used for validation purposes without matrix-matching multi-element standard.

The available information for each sample – including details on production methods and elemental concentrations – was organized in a data base and explored by a data mining approach, based on pattern recognition, multidimensional graphics and advanced statistical techniques. This procedure resulted in a minimum set of fingerprints (elemental concentration ranges) and rules, organized in a classification tree, which allowed full discrimination of organic and conventional coffees in the samples considered in the data base. In spite of being a preliminary finding, which can be better understood and refined by considering a larger number of coffee samples from other regions, these results suggest positive perspectives for discrimination methods based on elemental concentrations.



SPECIAL LECTURER'S ABSTRACT



SL

JAPANESE PIONEERS IN THE FIELD OF NUCLEAR AND RADIOCHEMISTRY

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This talk will review the life and work of the great Japanese pioneers in the field of nuclear and radiochemistry: Dr. Satoyasu Iimori (1885-1982) and Prof. Kenjiro Kimura (1896-1988).

Dr. Iimori was born in Kanazawa City, Japan. He graduated from Tokyo Imperial University in 1910. After working at the University for a while, he moved to England in 1919. From 1920 to 1921 he stayed at Oxford University to study radiochemistry under Prof. F. Soddy. In 1921 he returned home to join the Institute of Physical and Chemical Research in Tokyo (abbreviated as RIKEN). This institute was founded in 1917 as a center of advanced research for natural science in Japan.

Iimori contributed to radiochemistry in the area of both research and education. He proposed a new technical term, **DOIGENSO**, as a Japanese version of **ISOTOPE**. He also gave the first lecture of radiochemistry entitled "Chemistry of Radioelements" at the Department of Chemistry, Tokyo Imperial University in 1922. The lecture continued for 22 years until 1943. His research activities at RIKEN, include extensive radiogeochemical studies on radium, uranium, thorium in minerals and radon in natural waters. It is worth noting that radon in geochemical samples was analyzed by means of IM Fontactoscope which Iimori invented in 1931. The fontactoscope has been employed by many Japanese geochemists for measurements of radon.

Prof. Kimura was born in Utsunomiya City, Japan. His academic study at Tokyo Imperial University began in 1917. After finishing university education in 1920, he worked under Prof. Yuji Shibata for a few years. During that period, Kimura published his first paper co-authored with Y. Shibata, which reported on chemical analyses of Japanese radioactive minerals. From 1925 to 1927 he stayed at the Copenhagen Institute of Theoretical Physics in order to study radiochemistry and related subjects under Prof. N. Bohr and Prof. G. Hevesy. He met Dr. Yoshio Nishina, a prominent Japanese physicist, there. Soon they became very close friends and studied X-ray spectroscopy together. In July 1927, Kimura came back to rejoin Prof. Shibata's laboratory. In 1933, He was appointed Professor of Tokyo Imperial University in charge of analytical chemistry.

For more than three decades from 1930s, Kimura and coworkers conducted extensive studies on naturally occurring radionuclides in rocks, minerals, sediments and mineral springs in Japanese islands. In these studies, some emphasis was placed on the determination of radium and radon in many mineral springs. One of the interesting achievements in their research is radiochemical interpretation of radioactive disequilibria between radon and its decay products. In 1937, Dr. Nishina installed the first Japanese

cyclotron (65 cm, 23 tons) in RIKEN. At the invitation of Nishina, Kimura and coworkers began a series of experiments with artificial radioactivities produced by the cyclotron.

During the period of 1939-1941, they bombarded uranium targets with fast neutrons from the cyclotron.

After tremendous efforts, Nisina, Kimura and their physics and chemistry groups discovered U-237, a new uranium isotope, and new fission products of seven elements.

In 1954, Kimura and coworkers were heavily involved in the radiochemical survey of radioactive debris from the nuclear explosions in Bikini islands. As a result of their investigations, not only fission products but also U-237 and Pu-239 were detected. The presence of U-237 in the debris provided a definite evidence that atomic bombs of 3F type were exploded in Bikini islands.

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Neutron activation analysis (NAA) is a well-established analytical technique for the simultaneous determination of multielement concentrations. Although various forms of NAA are generally used for measuring the total concentrations of elements, NAA methods involving chemical separations prior to irradiations can be developed to determine the species of an element. The technique can then be called speciation NAA (SNAA). Since the toxicity of an element depends heavily on its physico-chemical form, there is an increasing interest in studying its speciation. Several analytical techniques can be used for elemental speciation; however, SNAA offers a number of advantages including the possibility of simultaneous speciation of several elements. We have developed SNAA methods for assaying various arsenic species, namely arsenite, arsenate, dimethylarsonic acid, monomethylarsinic acid, arsenobetaine, and organically bound arsenic (OBAs) species in water and in foods of marine origin. We are presently extending these methods to include simultaneous speciation of As, Sb and Se. We have also developed SNAA methods employing biochemical techniques for the simultaneous separation, preconcentration and characterization of metalloproteins and protein-bound trace element species in bovine kidneys. Much of our work focuses on Se along with As, Br, Cd, Cu, Mn and Zn. Lately, we have concentrated our efforts to develop SNAA methods in conjunction with NMR and MS for the simultaneous separation and characterization of extractable organochlorine, organobromine and organoiodine species in fisheries samples. We have also developed SNAA methods for studying speciation of trace-element analogues of radionuclides (*e.g.* trivalent lanthanides for trivalent actinides) in simulated vitrified groundwater leachates of high-level wastes under oxic and anoxic conditions and estimated their migration potentials through geochemical barriers.

JAWL Emission Mössbauer Spectroscopic Studies in Hot-Atom Chemistry

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Typical examples of emission Mössbauer spectroscopy applied to the studies of the chemical consequences associated with nuclear transformations in solid were demonstrated in a variety of systems in order to elucidate the processes after the nuclear events.

Emission Mössbauer spectroscopic studies of ^{57}Co -labeled Co(III)oxalate coordination compounds indicated that oxalate anions located close to the decaying ^{57}Co atoms have a greater effect in producing ^{57}Fe atoms in a divalent state than those located in the second coordination sphere. It was confirmed that the chemical consequences associated with nuclear transformations can be explained in terms of local radiation-chemical processes, as was previously suggested based on the conventional hot-atom chemical studies in $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$ reactions in a series of the Co(III)oxalate coordination compounds.¹⁾

Radical formation accompanied in the nuclear transformation was verified based on the absence of magnetic hyperfine structure in the emission Mössbauer spectrum of ^{57}Co -labeled diamagnetic Co(III)acetylacetonate. The absence of magnetic hfs in the spectrum was ascribed to the enhanced spin-spin interaction between $^{57}\text{Fe}(\text{II,III})$ atoms and some paramagnetic species, such as organic radicals, produced in the vicinity of the nuclear events.²⁾

It was found that one of the structural isomers of ^{57}Co -labeled $\text{Co}(\text{py})_2\text{Cl}_2$, the polymer (violet) $\alpha\text{-Co}(\text{py})_2\text{Cl}_2$, shows a higher recoil-free fraction than the monomer (blue) $\beta\text{-Co}(\text{py})_2\text{Cl}_2$. The results suggested that the produced ^{57}Fe atoms could remain in the host lattice,³⁾ although there was no direct proof for their retaining chemical bonds with their nearest atoms in the host lattice. The ambiguity had remained not clarified until the absorption and emission Mössbauer spectroscopic studies were carried out on a series of oxo-centered triangular $\text{Fe}(\text{II,III,III})$ acetate complexes. A good similarity found in the temperature dependences of intramolecular valence-delocalization in each isomorphous pair of the triangular $\text{Fe}(\text{II,III,III})$ and ^{57}Co -labeled $\text{Co}(\text{II})\text{Fe}(\text{III,III})$ acetate complexes indicated that most ^{57}Fe atoms produced after EC-decay are involved in valence-delocalization retaining intramolecular bonds at the original site. It was also suggested that some valence-delocalization takes place during the Mössbauer nuclear lifetime through the excited states of the ^{57}Fe atoms caused in EC-decay.⁴⁾

1) H. Sano, M. Harada, K. Endo, Bull. Chem. Soc. Jpn., 51, 2583 (1978).

2) H. Sano, J. Radioanal. Chem., 36, 105 (1977).

3) H. Sano, M. Aratani, H. A. Stöckler, Phys. Lett., 26A, 559 (1968).

4) T. Sato, M. Katada, K. Endo, M. Nakada, H. Sano, J. Radioanal. Nucl. Chem., Articles, 173, 107 (1993).

**RADIOCHEMICAL STUDIES OF PHOTONUCLEAR
REACTIONS AT INTERMEDIATE ENERGIES
–RECOIL STUDIES OF PHOTOSPALLATION
AND PHOTOFISSION–***

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Photons of low and intermediate energies are expected to be unique probes to look inside atomic nuclei through giant resonance, quasi-deuteron mechanism, and Δ resonance. These initial interactions of photons with nuclei are purely electromagnetic and are quite different from that of hadron-induced reactions initiated by the strong nucleon-nucleon interaction. It is of interest to investigate whether there exist similarities or not in the final steps in these two types of nuclear reaction. In the author's group, yields and recoil properties of radionuclides formed in bremsstrahlung-induced reactions such as photopion reaction, photospallation, photofission, and photofragmentation on various targets have been measured by radiochemical techniques in order to extract information on reaction mechanisms and nuclear structures. These systematic studies are also of importance for practical applications such as medicine, accelerator technology, and nuclear waste transmutation. Presented here is a brief review on the recent kinematic studies on the photospallation¹⁻³ and the photofission^{4,5} by a nuclear recoil technique.

Recoils of 137 radionuclides formed in the photospallation reactions on ^{27}Al , $^{\text{nat}}\text{V}$, $^{\text{nat}}\text{Cu}$, ^{93}Nb , $^{\text{nat}}\text{Ag}$, $^{\text{nat}}\text{Ta}$, and ^{197}Au , induced by bremsstrahlung of end-point energies (E_0) from 60 to 1100 MeV, have been investigated using the thick-target thick-catcher method. Reflecting the resonance character in the photonuclear reaction, the mean ranges FW and BW in the forward and backward directions, respectively, are E_0 -independent at $E_0 \geq 600$ MeV and classified into two groups accounting for the (γ, xn) ($x \geq 1$) and $(\gamma, xnyp)$ ($x, y \geq 1$) processes. The forward-to-backward ratios (F/B) are independent of the mass difference (ΔA) between a product (A_p) and a target (A_t) and also of A_t . The kinematic properties of the product nuclei were analyzed by the two-step vector velocity model⁶. The forward velocity v after the first step of photon-reaction at $E_0 \geq 600$ MeV is quite different from that of proton-reaction at proton energies of $E_p \leq 3$ GeV, though the difference disappears at higher energies. On the other hand, the mean kinetic energy T of the residual nucleus in the second step is almost equal to that of proton-reaction irrespective of E_p . An average kinetic energy carried off by the emitted particles $\varepsilon_s = T/(\Delta A/A_t)$ of both photon- and proton-reactions seems to increase with an increase of A_t up to around $A_t = 100$, and become almost constant at larger A_t , implying some change in the nuclear structure effect in this heavy target region. The recoil properties and yields of the photofission products from ^{197}Au and ^{209}Bi were also measured at $E_0 = 300\text{--}1100$ MeV using the catcher foil technique with the aid of intensive chemical separations. The fission characters such as charge and mass yield distributions were successfully deduced. In the symposium, these results will be discussed together with those of the competitive processes such as spallation and fragmentation, by referring to the proton results as well as the theoretical calculations by the photon-induced intranuclear cascade and evaporation analysis code⁷.

1. H. Haba *et al.*, *J. Radioanal. Nucl. Chem.* **239**, 133 (1999).; 2. H. Haba *et al.*, *Radiochim. Acta* **85**, 1 (1999).; 3. H. Haba *et al.*, *ibid.* **88**, 375 (2000).; 4. H. Haba *et al.*, *J. Nucl. Radiochem. Sci.* **1**, 53 (2000).; 5. H. Haba *et al.*, *ibid.* **1**, 69 (2000).; 6. L. Winsberg, *Nucl. Instr. Meth.* **150**, 465 (1978).; 7. T. Sato, private communication.

*This work was performed at the Radiochemistry Laboratory of Kanazawa University.

