CONTRIBUTOR'S ABSTRACTS

3rd day

3A5 Isothermal Gas Chromatography of Chlorides of Zr and Hf as Rf homologs

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Isothermal chromatography is one of the most useful methods which have been applied to the study of transactinide chemistry.

Kadkhodayan *et al.* reported that the volatility of tetrachlorides of rutherfordium and its homologs is following order $ZrCl_4 \approx RfCl_4 > HfCl_4$ [1]. However the attached errors are fairly large. Therefore, in order to obtain more accurate adsorption enthalpy, we have prepared an isothermal chromatography apparatus with a long column (i.d. 3 mm $\phi \times$ 200 cm) to achieve better chromatogram. By the use of this appratus, volatility measurements of Zr and Hf were performed.

The present isothermal chromatograph apparatus is shown schematically in Figure 1. In off-line experiment, ^{95}Zr loaded quartz wool was introduced to a reaction room. He/CCl_4 or He (Cl_2/CCl_4) was added as a reactive gas from the entrance of reaction room. Produced volatile species were transported in the isothermal column and caught at the cold trap. After 30 minutes exposure, the cold trap was measured with HP-Ge detector.

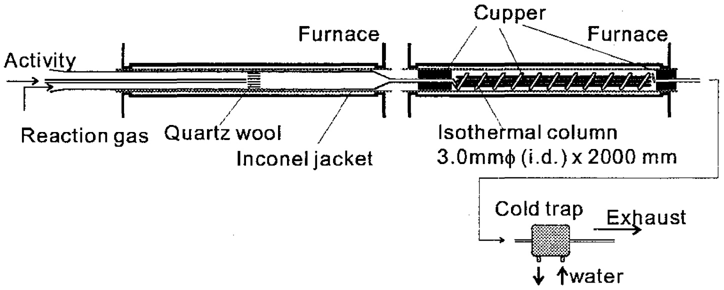

Fig. 1: Schematic diagram of the isothermal gas chromatographic apparatus.

An example of measured yield curve versus isothermal temperature for ^{95}Zr was shown Figure 2. Obtained adsorption enthalpy of Zr compound was approximately 100 kJ/mol.

The detailed discussion will be present.

So far, only halides, oxyhalides and oxide have been applied to separation as volatile compounds. To apply to various kinds of volatile compounds, we have developed a new apparatus which has two reaction rooms to produce different volatile compounds from chlorides form, such as dipivaloylmethane complex.

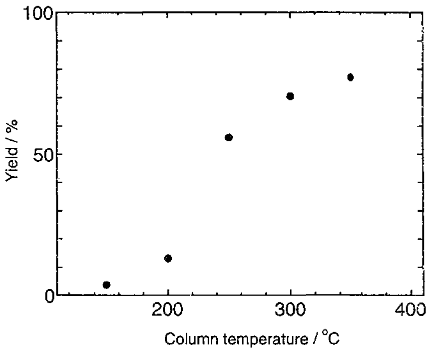

Fig. 2: Yield curves vs. isothermal temperature for ^{95}Zr compounds.

[1] B. Kadkhodayan *et al.*, Radiochim. Acta. **72**, 169 (1996).

3A6 ADSORPTION OF Zr, Hf, AND Th FROM HCl AND HNO_3 SOLUTIONS BY ANION AND CATION EXCHANGES: MODEL EXPERIMENTS FOR THE CHEMICAL CHARACTERIZATION OF RUTHERFORDIUM (ELEMENT 104)

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We have planned to investigate the sorption behavior of element 104 rutherfordium (Rf) on ion exchange resins from simple acid solutions such as HNO_3 and HCl, where it may be easy to deduce complex structures and to perform theoretical molecular orbital calculations. It is important to investigate chemical properties of Rf homologs Zr and Hf and its tetravalent actinide pseudo-homolog Th in order to predict a suitable experimental system for Rf and to verify the influence of the relativistic effects. For this purpose, carrier-free radiotracers ^{88}Zr and ^{175}Hf were produced in the ^{89}Y(p,2n) and ^{175}Lu(p,n) reactions, respectively, at the JAERI tandem accelerator. ^{234}Th was obtained as a daughter of the naturally occurring radioactive ^{238}U. By using these tracers, the distribution coefficients (K_d) on anion (CA08Y) and cation (CK08Y) exchange resins were measured systematically in 1.0–11.5 M HCl and 1.1–13.1 M HNO_3 with the batch method. It was found that the K_d values for Zr, Hf, and Th on CA08Y in 9.5 M HCl are 540, 60, and 0.56 ml/g, respectively, and they are all quite different from each other. On the other hand, the K_d value for Th (510 ml/g) on CA08Y is more than one order of magnitude higher than those for Zr (8.0 ml/g) and Hf (12 ml/g) in 8 M HNO_3, reflecting the difference in complex structures.

We have developed the **A**utomated **I**on exchange separation apparatus coupled with the **D**etection system for **A**lpha spectroscopy (**AIDA**) for atom-at-a-time chemistry of ^{261}Rf. The chromatography unit is almost the same as that of the Automated **R**apid **C**hemistry **A**pparatus (**ARCA**) developed by Schädel *et al.*[1] As a model experiment of ^{261}Rf, the anion exchange separations of ^{85}Zr, ^{169}Hf, and ^{234}Th were performed with AIDA in 4.0–11.5 M HCl and 8 M HNO_3. The isotopes ^{85}Zr and ^{169}Hf were produced simultaneously in the ^{nat}Ge(^{18}O,*x*n) and ^{nat}Gd(^{18}O,*x*n) reactions, respectively, at the JAERI tandem accelerator. The reaction products were transported by the He/KCl gas-jet system through a Teflon capillary on a collection site of AIDA. The tracer solution of ^{234}Th was pipetted on the same collection site and evaporated to dryness. These radiotracers were dissolved with a desired solution and fed onto the micro-column. The flow of eluents was directed through the column by computer control of chromatographic pumps, valves, and mechanical sliders. The effluents were subjected to γ-ray spectrometry by Ge detectors. It was found that the sorption behavior of ^{85}Zr, ^{169}Hf, and ^{234}Th on CA08Y reflected the variation of the K_d values obtained by the batch method. The experimental conditions such as the concentration, volume, and flow rate of the solutions were optimized for the ^{261}Rf experiment.

Quite recently, the on-line anion exchange separation of ^{261}Rf has been successfully performed in 4.0–11.5 M HCl and 8 M HNO_3. In our separate paper[2], the sorption behavior of Rf will be compared to the present results, and the chloride- and nitrate-complexations of Zr, Hf, Th, and Rf will be discussed by referring to the relativistic density functional calculations[3].

1. M. Schädel *et al.*, *Radiochim. Acta*, **48**, 171 (1989).
2. K. Tsukada *et al.*, *a separate paper of this abstract.*
3. M. Hirata *et al.*, *a separate paper of this abstract.*

3A7

ANION-EXCHANGE BEHAVIOR OF RUTHERFORDIUM (ELEMENT 104) IN NITRIC AND HYDROCHLORIC ACID MEDIA

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Most of the experiments on the aqueous chemistry of rutherfordium (Rf, element 104) have concentrated on the competing strength of hydrolysis and complex formation. There still however remain conflicting results [1]. Recently we have successfully produced ^{261}Rf and ^{262}Db at the JAERI tandem accelerator facility [2], and have developed the gas-jet coupled automated liquid chromatography apparatus (AIDA: Automated Ion exchange separation apparatus coupled with the Detection system for Alpha spectroscopy) in order to perform fast and repetitive ion exchange separations of the transactinide elements. Thus we have studied the sorption behavior of Rf on ion exchange resins from simple acid solutions such as HNO_3 and HCl, in which it may be easy to deduce complex structures and to carry out theoretical molecular orbital calculations. In this report, we present the on-line study of the anion-exchange behavior of Rf together with Zr and Hf.

The isotopes ^{85}Zr ($T_{1/2}$=7.9 min), ^{169}Hf ($T_{1/2}$=3.3 min), and ^{261}Rf ($T_{1/2}$=78 s) were produced in the ^{nat}Ge(^{18}O, *x*n), ^{nat}Gd(^{18}O, *x*n), and ^{248}Cm(^{18}O, *x*n) reactions, respectively. The reaction products were transported to AIDA by the He/KCl gas-jet system and deposited onto a collection port. The port was mechanically moved on the top of one of the micro-columns and the deposited products were dissolved, complexed, and eluted. The flow of solutions was directed through a micro-column by computer controlled chromatographic pumps, valves. The effluent collected on a Ta disk was evaporated to dryness using hot He gas stream and a halogen heat lamp, and the disk was mechanically transported to one of the eight vacuum chambers and subjected to α spectrometry by 600 mm^2 PIPS detectors.

In the 8 M HNO_3 system, Rf was not adsorbed on anion exchange resin, indicating Rf behaves like the lighter homologues Hf and Zr and not like the pseudo-homologue Th and the tetravalent Pu ion [3]. In the HCl system, the adsorption behavior of Rf was typical of the group-4 elements and was quite different from that of Th. By detailed comparison of the behavior among the group 4 elements, the distribution coefficients decrease in the order Rf>Zr>Hf at 9 M HCl. In this presentation, we will describe the anion exchange behavior of Rf and discuss the Rf-chloride complexation by comparing with the theoretical calculations [4].

[1] M. Schädel, *Radiochim. Acta* **70/71**, 201 (1995).
[2] Y. Nagame *et al.*, a separate paper of this abstract.
[3] H. Haba *et al.*, a separate paper of this abstract.
[4] M. Hirata *et al.*, a separate paper of this abstract.

3A8

SPECIATION STUDY ON Eu(III) IN ANION EXCHANGE SEPARATION SYSTEM WITH LiCl-H_2O/ALCOHOL MIXED MEDIA BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY

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Introduction. The sorption of a metal ion, M^{n+}, to an ion exchange resin is enhanced by the addition of alcohol. For understanding of the sorption behavior of M^{n+}, it is important to investigate the coordination states of M^{n+} both in the solution and the resin phases. In the present study, the extent of the chloro complexation of Eu(III) in the anion exchange resin (AG 1X8: exchange group, $-CH_2N^+(CH_3)_3$) system with LiCl-H_2O/alcohol mixed media was estimated from the luminescence lifetime and the emission spectrum. The sorption behavior of Eu(III) was discussed on the basis of the coordination states in both phases, and the effects of methanol and ethanol were compared.

Experimental. The inner-sphere hydration number (N_{H_2O}), i.e., the number of water molecules in the first coordination sphere, of Eu(III) was determined from the luminescence lifetime. The correlation between the N_{H_2O} and the reciprocal number of the luminescence lifetime (k_{obs} / ms^{-1}) is expressed as follows: $N_{H_2O} = 1.05 \cdot k_{obs} - 0.44$.[1] The ligand environment both in the inner- and outer-sphere of Eu(III) was estimated from the relative intensity ratio (I_2/I_1) [= $I(^5D_0\text{-}^7F_2)/I(^5D_0\text{-}^7F_1)$] in the emission spectrum. Those were measured as a function of the LiCl concentration (C_{LiCl}) and the alcohol mole fraction ($X_{alcohol}$).

Results and discussion. The K_d and N_{H_2O} of the sorbed species in the ethanol system are shown in Figs. 1(a) and (b), respectively. The increase of K_d due to the increase of C_{LiCl} or $X_{ethanol}$ suggests that the formation of an anionic Eu(III)-chloro complex is enhanced in the system. This is supported by the results of N_{H_2O} and I_2/I_1. As shown in Fig. 1(b), the N_{H_2O} of the sorbed species decreases remarkably with an increase of C_{LiCl} or $X_{ethanol}$, indicating the formation of the anionic inner-sphere chloro complex. The N_{H_2O} of the dissolved species does not indicate the formation of the anionic inner-sphere chloro complex, although the N_{H_2O} decreases with an increase of C_{LiCl} or $X_{ethanol}$. The I_2/I_1 increases with an decrease of the coordination symmetry around Eu(III), which means the increase of the interaction between Eu(III) and Cl^-. The increase of I_2/I_1 in each phase is well correlated with the decrease of N_{H_2O}. Similar tendency was observed in the methanol system.[2] However, the enhancement of the complexation by ethanol is more remarkable than that by methanol.

From the results of N_{H_2O} and I_2/I_1 in both phases, it is found that the chemical environment in the resin phase provides the specific reaction field for the inner-sphere chloro complexation and that the sorption behavior is mainly dominated by the chemical environment in the resin phase.

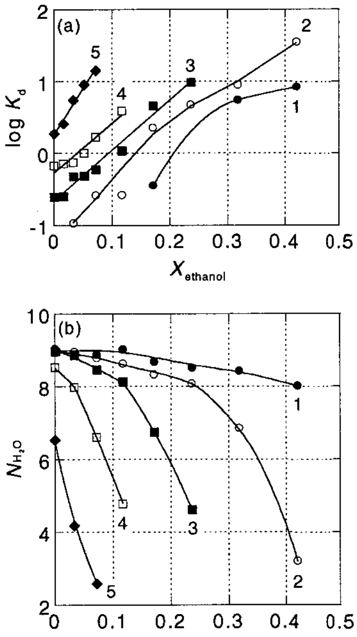

Fig. 1 (a) K_d and (b) N_{H_2O} of sorbed species in ethanol system
C_{LiCl}; 4 M (1), 6 M (2), 8 M (3), 10 M (4), 12 M (5)

1. T. Kimura, Y. Kato, *J. Alloys Comp.*, **275-277**, 806 (1998).
2. M. Arisaka, T. Kimura, H. Suganuma, Z. Yoshida, submitted to *Radiochim. Acta*.

3A9

EXTRACTION AND STRUCTURAL STUDIES OF Sr AND Ba COMPLEXES WITH *N,N'* - DIMETHYL- *N,N'* - DIPHENYL - DIGLYCOLAMIDE AND - 3,6- DIOXAOCTANEDIOIC DIAMIDE

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Multidentate diamide compounds have recently been attractive as selective metal extractants. They showed a high selectivity for trivalent lanthanides.[1] However, studies for divalent ions have been limited. In the present study, the extraction behavior and coordination properties of Sr and Ba with *N,N'* -dimethyl-*N,N'* -diphenyl-diglycolamide (DGA) and -3,6-dioxaoctanedioic diamide (DOODA) (Fig.1) were investigated by solvent extraction and extended X-ray absorption fine structure (EXAFS) spectroscopy.

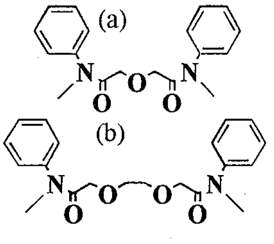

Fig.1. Structure of diamides: (a)DGA;(b)DOODA

Figure 2 shows the distribution ratios (*D*' s) of Sr and Ba as a function of HNO_3 concentration in the DGA and the DOODA systems. The *D*' s of Ba were higher than those of Sr in the both systems. The difference of the *D*' s between Sr and Ba in the DOODA system was larger than that in the DGA system. This suggests that the DOODA forms a ring-like structure in the complex such as macrocyclic ligands and thereby has a good ion recognition property.

In order to clarify this property, EXAFS measurements of the Sr and Ba complexes were performed at the KEK PF BL27B and Spring-8 BL11XU, respectively. Detailed structural information by EXAFS is currently under intensive investigation.

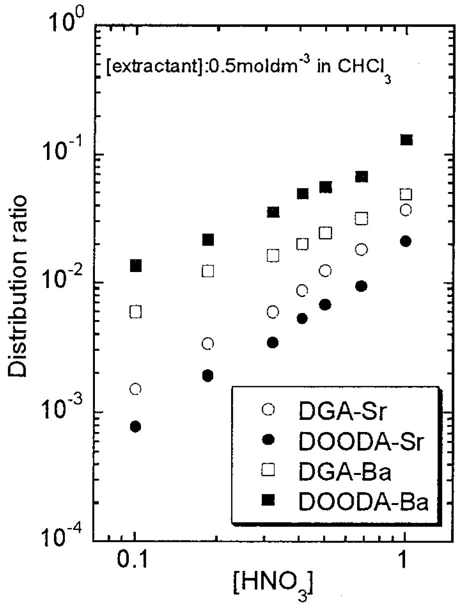

Fig.2. *D*' s of Sr and Ba as a function of [HNO_3] in the DGA and the DOODA systems.

1. H.Narita, T.Yaita, K.Tamura, S. Tachimori, *Radiochim. Acta*, **81**, 223 (1998)

3A 10

PULSE RADIOLYSIS STUDY ON COORDINATION OF EUROPIUM(III) POLYELECTROLYTES IN AQUEOUS SOLUTIONS

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Introduction In order to elucidate the environmental behavior of metal-polyelectrolyte complexes in heterogenious systems, detailed information on the polyelectrolyte itself and complexes is indispensable. In the present study, pulse radiolysis of europium(III)-polyelectrolyte (polyacrylic acid (PAA) and humic acid (HA)) complexes in aqueous solutions was conducted and reactions of hydrated electron (e_{aq}^-) with the complexes studied to reveal the coordination states and reactions.

Experimantal Electron pulses with band width of 20 ps and energy of 38 MeV from L-band LINAC at Radiation Laboratory, ISIR, Osaka University were irradiated into the aqueous samples to observe transient species of e_{aq}^- optically in the wavelength range of 500-950 nm and time range < 5 μs. Rate constants, k_e ($dm^3mol^{-1}s^{-1}$), for the one-electron reduction of the Eu(III) complexes by e_{aq}^- were determined as functions of pH, [-COOH]/[Eu(III)] and ionic strength varied by addition of $NaClO_4$.

Results and Discussion The rates of k_e ranged from 10^8 to 10^9 for Eu(III)-PAA system, while it was the order of 10^{10} for 1:1 complexes of Eu(III)-aminopolycarboxylates [1] considered as diffusion-controlled. The activation free energy change, $\Delta G_e^‡$, for the reactions was found out to be described as the sum of $\Delta G^‡$(Eu(III)L) originating from stability of the complexes and $\Delta G(-CO_2^-)$ from electrostatic potentials formed by dense negative charges of carboxylates in the polyelectrolyte molecule. The $\Delta G^‡$(Eu(III)L) was proportional to ligand coordination numbers, CN_L, estimated for the Eu(III)-aminopolycarboxylates (12-15.5 kJ mol^{-1})[1]. The $\Delta G(-CO_2^-)$ was comparable to the $\Delta G^‡$(Eu(III)L) and dependent on dissociation degree, α (Fig.1, PAA_{5k}), molecular weight of the PAA and cation concentration in solutions. For Eu(III)-HA system, the $\Delta G(-CO_2^-)$ was lowered and residual absorption (Fig.2) observed additionally in the time-profiles of e_{aq}^-. The lowering of $\Delta G(-CO_2^-)$ and absorption ratio of the residual to maximum (OD_{res}/OD_{max}) were discussed in terms of ratio of aromatic to aliphatic content in HA molecules [2].

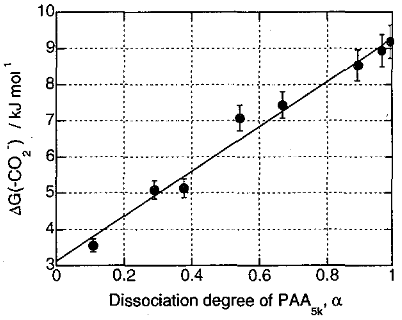

Figure 1 The free enrgy change of $\Delta G^‡(-CO_2^-)$ for the reaction of e_{aq}^- with Eu(III)-PAA_{5k}.

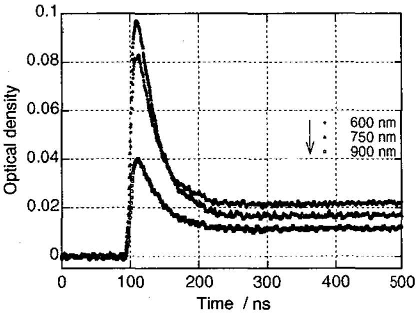

Figure 2 Time-profiles of e_{aq} for Eu(III)-HA in 0.1 mol dm^{-3} $NaClO_4$.

1. R. Nagaishi, T. Kimura, Z. Yoshida, Y. Yoshida, T. Kozawa and S. Tagawa, submitted to *J.Phys.Chem.*.
2. H.-S. Shin, J.M. Monsallier and G.R. Choppin, *Talanta*, **50**, 641(1999).

3A11 FUNDAMENTAL RESEARCH FOR DESIGNING NUCLEAR FUEL RECYCLING PLANTS—EVALUATION OF EVAPORATION BEHAVIOR OF PD, MO, TE, AND SB IN SIMULATED LOW LEVEL LIQUID WASTE

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To develop sophisticated nuclear fuel recycling process, the transfer percentages for palladium, molybdenum, tellurium, and antimony — they contribute largely to fission yields but contribute less to radio activities — should be determined. One liter of simulated liquid wastes for each Pd, Mo, Te, and Sb was fed consistently into the thin film layer evaporator regulated in vac and at 50 ℃.The analyte amounts in the inside of the lid of the evaporator, in the condenser, and in the distillate, were dissolved with hydrochloric acid and were determined by inductively coupled plasma mass spectrometer. The analyte percentage in the inside of the lid, in the condenser, and in the distillate were respectively E-1 %/m^2, E-3 %/m^2, and E-3 %/m^2. The Mo percentages in the condenser and the distillate were lower by a factor of 10 than those for Pd, Te, and Sb. The theorized reason is that the liquid drops of Mo consist of Mo polymers, and the drops are more viscid than those of the Pd, Te, and Sb solutions. The Mo drops could be adhering more readily to the inside of the lid than those for the Pd, Te, and Sb solutions. Thus the transfer rate of Mo drops are less than those of Pd, Te, and Sb drops. The transfer rate of nitric acid ions increased with nitric acid concentrations, however the rates of nitrate ions were nearly constant despite increasing sodium nitrate concentrations.

3A 12 CHEMICAL SEPARATION OF YTTRIUM FROM RARE EARTH ELEMENTS IN XENOTIMA (PITINGA, BRAZIL)

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The increasing request for rare earth elements (REE) all over the world makes essential the accurated REE's determination in minerals. One of the most important sources of REE is xenotima, an yttrium phosphate, found mainly in Amazon, Brazil. The yttrium oxide corresponds to 60% w/w of the xenotima composition, along with 30% w/w of heavy REE's oxides and 8.4% w/w of the light ones [1].

Difficulties arise, however, from the needed separation of Yttrium from the other REE's, since Yttrium, besides being the major constituent of Xenotima, causes interferences in the REE determinations.

In this work, a separation technique is tested, based upon the complexation of all REE in fluoridric medium [2-3] and the ultimate retention of all formed cationic complexes by ion exchange, thus isolating the neutral Yttrium complex in the effluent.

The results demonstrated the analytical level efficiency in the separation of Yttrium from the REE's, allowing a precise determination of their concentration levels.

[1] M.J.B.Macambira et al., Revista Brasileira de Geo-ciencia-dez. -17(4):p.562-570 (1987).
[2] Gmelin Institut fur Anorganische Chemie Der Max-Planck-Geselischaft Zur Forderung der Wissenschaften. "Gmelin Handbook of Inorganic Chemistry". 8d. Berlin, Springer-Verlag, v.39. pt.c3. p.112-127 (1976).
[3] A. D. Paul et al., Journal Phys. Cemistry. V.65. p.441-443 (1961).

3A13 SEPARATION OF RADIONUCLIDES FROM CHEMICAL AND ELECTROCHEMICAL DECONTAMINATION WASTE

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Electrochemical and chemical decontamination belong among the most effective methods of decontamination of the NPP primary circuit internals. In the process, a considerable volume of liquid wastes containing organic complexing agents, such as oxalic (HOx) or citric (HCit) acids, is generated.

Recently, heterogeneously catalysed photodegradation has been demonstrated to be very effective method for the organic species, such as HOx or HCit, decomposition, titanium dioxide was shown to be a very suitable catalyst. Inorganic and/or composite absorbers may be effectively used for the separation of radionuclides from a wide range of solutions. This study was based on attempt to combine these approaches into one multistage process.

The photocatalytic degradation of organic complexants was carried out in a small immersion well photochemical reactor of 80 mL capacity with a 6W low-pressure mercury lamp. Titanium dioxide was used as a photocatalyst. After the degradation of the organic species the solutions were spiked with ^{110}Ag, ^{60}Co, ^{59}Fe, ^{54}Mn and ^{85}Sr.

Two types of sorbents were used in the sorption experiments. In batch experiments, a series of inorganic sorbents was tested. In the dynamic experiments, composite absorbers consisting of the best inorganic ion-exchangers incorporated into a binding matrix of modified polyacrylonitrile, and also a commercial strongly acidic cation exchanger OSTION KS806, were used.

In the first phase of the study, direct separation of radionuclides from both the solutions was attempted. It was found that, from the solutions containing oxalic and citric acids, the radionuclides cannot be effectively separated with any of the sorbents tested.

In the optimisation of the conditions of the photocatalysis, ideal laboratory values of temperature, aeration rate, mass of the catalyst and addition of H_2O_2 were determined. Under the optimum conditions, both the oxalic and citric in the solutions could be quantitatively decomposed within 12 hours of irradiation.

In the batch experiments, distribution coefficients (K_D) of the main radionuclides were determined. For the separation of radionuclides from the solution after chemical decontamination, zirconium phosphate or sodium titanate followed by the crystalline polyantimonic acid were shown to be the most prospective inorganic sorbents. In the case of their separation from the solution after electrochemical decontamination, synthetic zeolite was found as the most effective.

In the dynamic column experiments, the break-through curves of the selected radionuclides were followed. For the group separation of the radionuclides, the standard cation exchanger was shown to be preferable to any of the set of the tested composite absorbers.

The procedure developed was succesfully tested on the real spent chemical decontamination solution from NPP Dukovany, Czech Republic and electrochemical decontamination solution from NPP Jaslovské Bohunice, Slovakia.

In this study, a combined process for the separation of radionuclides from organic complexants containing waste was developed, its efficiency and applicability was demonstrated. A combination of photocatalytic degradation of organic complexants followed by the sorption of the radionuclides onto a strongly acidic ion exchanger offers a promising route for the treatment of the spent chemical or electrochemical decontamination solutions.

3B5

VALENCE STATES OF ^{57}Fe DECAYED FROM ^{57}Mn IMPLANTED INTO $KMnO_4$

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Emission Mössbauer spectroscopy combined with ion implantation has been applied to a wide variety of solid-state materials, and has provided a lot of significant information concerning lattice positions, chemical bonding and structures, and dynamical diffusion of implanted probes. However, the applications of ^{57}Mn as another source nuclide for ^{57}Fe Mössbauer spectroscopy are very rare because its half-life ($T_{1/2}$ = 1.45 min) is rather short. Manganese can take various oxidation states up to 7+ in solids, which is not the case of Fe and Co. Then, exotic chemical species can be expected for ^{57}Fe arising from highly charged ^{57}Mn ions in an appropriate Mn matrix.

We have succeeded in obtaining the well-resolved in-beam Mössbauer spectra of ^{57}Fe arising from short-lived ^{57}Mn implanted into $KMnO_4$ between 11 K and 155 K.[1] ^{57}Mn is produced as a secondary RI beam following the nuclear projectile-fragmentation reaction of ^{59}Co beam (E = 80 *A*MeV) with Be target, and separated by the in-flight isotope separator. Subsequently, the ^{57}Mn beam is directly implanted into a sample of $KMnO_4$ with the implantation energy of 15 *A*MeV and the typical beam current of 5×10^5 /sec.[2]

An in-beam Mössbauer spectrum of ^{57}Fe arising from ^{57}Mn in $KMnO_4$ at 11 K is shown in Fig. 1. Mössbauer spectra obtained below 90 K could be analyzed with two components that consist of a *doublet* and a *singlet*. On the basis of the isomer shift of the *singlet* and the calculations of the molecular orbital wave function, it might be concluded that the *singlet* is assigned to the *substitutional ^{57}Fe atoms* for Mn-sites in tetrahedral $[MnO_4]^-$ with an unusually high valence state of Fe(VIII).

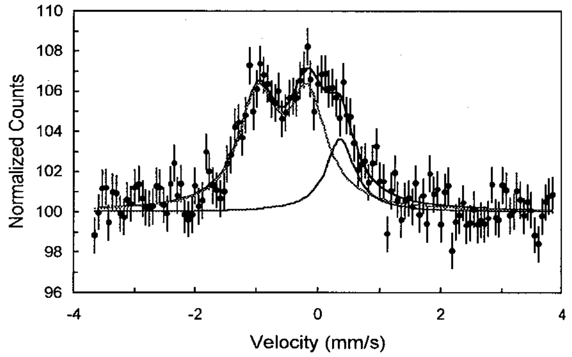

Fig. 1 The in-beam Mössbauer spectra of ^{57}Fe arising from ^{57}Mn in $KMnO_4$ at 11 K.

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3B6

SYNTHESIS AND MÖSSBAUER SPECTROSCOPIC STUDIES OF OXO-CENTERED MIXED-VALENCE TRINUCLEAR IRON-FUMARATE AND IRON-MALONATE COMPLEXES

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After reporting the first oxo-centered trinuclear mixed-valence iron complex, $[Fe_3O(CH_3CO_2)_6(H_2O)_3]\cdot nH_2O$ by Chrétien and Lous[1], this type of complexes have taken into account of special interest for their important role in investigating the intramolecular electron transfer process in mixed-valence system. Mössbauer spectroscopy provides an important information concerning intramolecular electron transfer in mixed-valence iron complexes. A large number of oxo-centered mixed-valence iron monocarboxylates have been studied by various techniques, but similar complexes with dicarboxylic acid ligand have not studied so much. Dziobkowski et al.[2] have reported some Fe(III)-dicarboxylic acid complexes where polymeric structure has suggested for the complexes.

Mixed-valence trinuclear iron-fumarate, $[Fe_3O(C_4O_4H_2)_3(H_2O)_3]\cdot nH_2O$ (n=18~19) and iron-malonate $[Fe_3O(C_3O_4H_2)_3(H_2O)_3]$ have newly synthesized and variable temperature Mössbauer spectroscopy have investigated. Mössbauer spectra of iron-fumarate showed a localized valence state of Fe(II) and Fe(III) at liquid helium temperature with an area ratio of ~ 1:2 and a single absorption peak at room temperature indicating an averaged valence state of Fe(II) and Fe(III) with an isomer shift value 0.65 mm/s (Fig. 1.a). Variable temperature Mössbauer spectra suggest the beginning of thermal electron transfer above 200 K. On the other hand iron-malonate complex showed a localized valence state of Fe(II) and Fe(III) at low temperature also with an area ratio of ~1:2 which remain almost unchanged upto room temperature (Fig. 1.b) with only slight variation in area ratio and spectral line broadening.

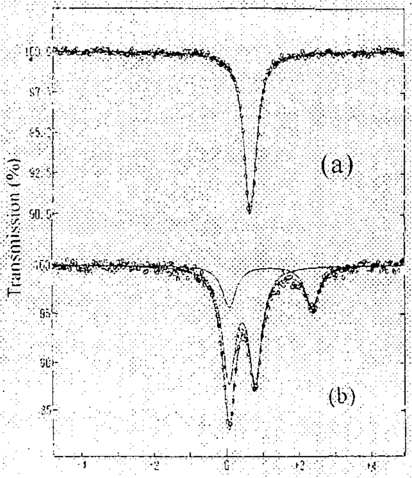

Fig. 1. Mössbauer spectra of (a) iron-fumarate and (b) iron-malonate at room temperature.

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3B7

MECHANISM OF ISOCHEMICAL TRANSFORMATIONS OF IRON(III) OXIDE NANOPARTICLES - MÖSSBAUER STUDY

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Iron(III) oxide is not only a strategic industrial material but also a convenient compound for the general study of the polymorphism, the mutual polymorphous changes and properties of nanoparticles. ^{57}Fe Mössbauer spectroscopy is one of few methods that allows to distinguish and identify individual polymorphs, to analyze their magnetic properties and to study the mechanism of isochemical transformations. The first part of the presented work is aimed at the structural and magnetic characterization of all known Fe_2O_3 polymorphs (corundum structure alpha, spinel structure gamma, bixbyite structure beta and orthorhombic structure epsilon) using Mössbauer spectroscopy.

The differences in the mechanism of the thermal transformation of cubic (β-Fe_2O_3, γ-Fe_2O_3) nanoparticles are discussed in the second part and demonstrated with several experimental examples. Ultrafine particles of β-Fe_2O_3 were prepared by solid-state reaction of NaCl with $Fe_2(SO_4)_3$ in air [1], and by the thermal decomposition of $Fe_2(SO_4)_3$ [2]. γ-Fe_2O_3 nanoparticles were obtained by thermally-induced oxidation of $FeSO_4$ [3] and almandine garnet [4]. Samples of nanocrystalline Fe_2O_3 particles were thermally treated in air at different temperatures and the changes of their structure, size and morphology were investigated using Mössbauer spectroscopy and atomic force microscopy (AFM).

Mössbauer spectra proved the formation of ε-Fe_2O_3 as intermediate during thermally induced transformation of γ-Fe_2O_3 nanoparticles to α-Fe_2O_3 while the direct transformation way was observed in the case of β-Fe_2O_3 (fig.1). All isochemical structural transformations (γ-$Fe_2O_3 \rightarrow \varepsilon$-$Fe_2O_3$, ε-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$, β-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$) were induced by the particle size increase, in accordance with AFM observations.

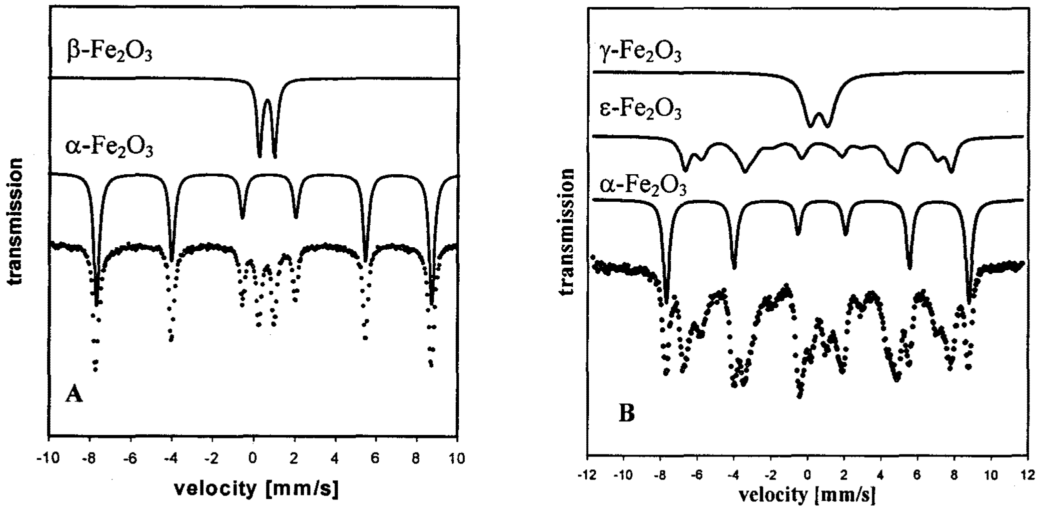

Figure 1. RT Mössbauer spectra of β-Fe_2O_3 (A) and γ-Fe_2O_3 (B) after thermal treatment at 600 °C

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3B8

MÖSSBAUER AND INFRARED INVESITGATION OF THE REACTIONS OF LASER-EVAPORATED IRON ATOMS WITH ETHYLENE

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Laser-evaporated iron atom has translationally and electronically high energy, and reacts with various reactant gases to produce novel compounds. We have studied the reaction of laser-evaporated iron atoms with O_2, N_2, N_2O, SF_6, CH_3I, and CH_4[1]; their reaction products were trapped in low-temperature matrices to observe their Mössbauer and infrared spectra. Mössbauer spectroscopy provides useful information on the electronic properties of iron atom especially valence and spin-state, while infrared spectroscopy provides direct information on the bonding structures of the species trapped in matrices. We applied both Mössbauer and infrared spectroscopy to investigate this system in order to obtain the information of the species produced by the reaction of laser-evaporated iron atoms with ethylene. The assignments of these species were performed in an aid of molecular orbital calculations using Gaussian 98.

Laser light from a KrF-excimer laser or a YAG-laser was focused by a convex lens onto a block of ^{57}Fe in a reaction chamber. The reactant gas (pure C_2H_4 or C_2H_4/Ar mixture) was introduced by a magnetic pulse valve, synchronized with the laser pulses. Iron atoms were laser-evaporated in an atmosphere of the reactant gas, and the reaction took place in the gas phase. The products were condensed on an aluminum plate that had been cooled to 17 K by a closed-cycle helium refrigerator. The pulsed gas introduction and laser-evaporation was repeated 5000 times at 0.2 Hz. Mössbauer spectra were measured at 17 K in transmission geometry with a ^{57}Co/Rh source. Infrared spectra were measured using a CsI plate as a low-temperature substrate instead of an aluminum plate.

Two species **A** and **B** were found as the reaction products of laser-evaporated iron atoms and ethylene molecules. At the low C_2H_4 concentration in Ar matrix, species **A** ($\delta = 0.49$ mm/s, $\Delta E_q = 1.13$ mm/s) as well as Fe atoms and large iron particles were observed. With increasing C_2H_4 concentration, the intensity of species **B** ($\delta = 0.54$ mm/s, $\Delta E_q = 2.46$ mm/s) increases. We performed the molecular orbital calculations for various species with various spin states: the species **A** is assigned to $Fe(C_2H_4)$ (S=1), and the species **B** is suggested to be $Fe_n(C_2H_4)_n$ n>1.

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3B9 Microstructure and CO_2 absorption in $Sr_{0.95}Ca_{0.05}Fe_{05}Co_{05}O_{3-\delta}$ and $Sr_{05}Ca_{05}Fe_{05}Co_{05}O_{3-\delta}$ as studied by emission Mössbauer spectroscopy

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Strontium ferrate analogue perovskites show remarkable physical and chemical properties, e.g. they may find potential application in reduction of industrial CO_2-output. These properties strongly depend on the chemical environment of the B site cations in the ABO_3 structure. $SrFeO_{3-\delta}$ itself shows a rather complicated behavior from this point of view, and the interpretation of the Mössbauer spectra requires careful considerations [1].

We report here on the emission Mössbauer study of $Sr_{0.95}Ca_{0.05}Fe_{05}Co_{05}O_{3-\delta}$ and $Sr_{05}Ca_{05}Fe_{05}Co_{05}O_{3-\delta}$ where the identical occupancy of the B site by Fe and Co offers a good chance for comparison with our previous transmission Mössbauer spectroscopy results on the same compounds [2]. The Ca-substitution at the Sr site is crucial for good CO_2-absorption properties, and results in different crystal and magnetic structure for the two compounds.

It was found that the emission Mössbauer spectrum of $Sr_{0.95}Ca_{0.05}Fe_{05}Co_{05}O_{3-\delta}$ can be decomposed into three doublets which can be assigned to Co sites associated with localized and delocalised electronic states with valence states between III and IV. This decomposition could not be applied to the transmission spectra and at least one of the three components proved to be markedly different.

While the delocalised states make it very difficult to assign the Mössbauer doublets to well defined coordination environments in $Sr_{0.95}Ca_{0.05}Fe_{05}Co_{05}O_{3-\delta}$, the magnetically split emission spectra of the brownmillerite-structured $Sr_{05}Ca_{05}Fe_{05}Co_{05}O_{3-\delta}$ clearly indicated tetrahedral and octahedral sites for Co. The relative intensities of the corresponding sextets were different in the transmission and emission spectra.

These findings verified the difference between the environment of Fe and Co in the lattice, which will be thoroughly discussed with special attention to possible ordered distributions of Co and Fe in the lattice.

Differing CO_2-absorption properties will also be interpreted in terms of various coordination environments of Fe and Co.

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3B10

AN APPLICATION OF COINCIDENCE DOPPLER SPECTROSCOPY TO POLYMER

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Positron annihilation (PA) lifetime spectroscopy is a powerful tool to study characteristics of polymers: the size of intermolecular spaces, relaxation behavior, and thermal properties. A part of positrons injected into polymer samples form positronium (Ps): para-Ps (p-Ps) and ortho-Ps (o-Ps). Due to the intrinsic annihilation of p-Ps or pick-off annihilation of o-Ps, these Ps atoms emit two gamma-rays with an energy of 511keV. The rest of positrons diffuse in polymer structure and annihilate with electrons of the constituent atoms, emitting also two gamma-rays with an energy of 511keV. Commonly three lifetimes are observed in the annihilation spectra in polymers : τ_1(p-Ps) $\approx$0.15ns, τ_2(free positrons) $\approx$0.3ns, and τ_3(pick-off annihilation of o-Ps)$\approx$2ns.

Using two high pure-Ge detectors, the coincidence Doppler spectroscopys[1,2] has been applied to study the interaction of positrons with the specific elements contained in polymers, since the high resolution (peak/BG$\approx 10^6$) of the Doppler spectroscopy makes it possible to identify the PA on core electrons of the elements from the tail of the Doppler broadening. Figure 1 shows the coincidence Doppler broadening spectrum (CDBS) taken with a 2-D MCA, where the coincidence spectrum is shown from the left top to the right bottom. Figure 2 shows the comparison of CDBS in silica aero-gel under vacuum and oxygen atmosphere with that of silicon. The increase in p-Ps annihilation for the oxygen case is clearly observed at lower energy region, while the difference in the annihilation on core electrons of Si and O is seen between 5 and 10 P_L. The increase proves the spin exchange conversion of o-Ps through the reaction with oxygen atoms doped in silica aero-gel.

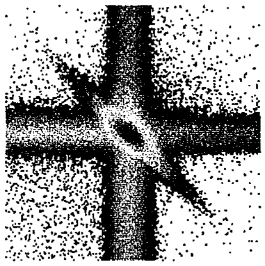

Fig.1 Coincidence Doppler broadening Spectrum (CDBS)

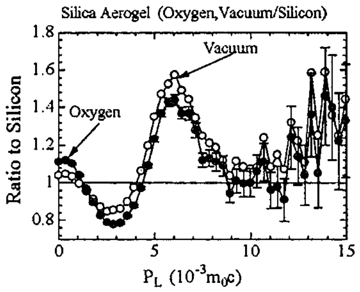

Fig.2 Comparison of CDBS in silica aero-gel under vacuum and oxygen atmosphere.

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3B11

CHARACTERIZATION OF POLYMER SUB-SURFACE USING SLOW POSITRON BEAM

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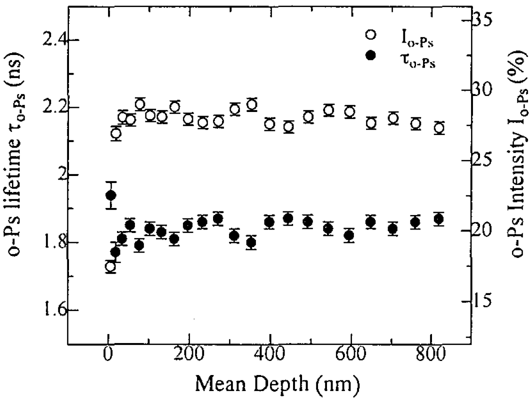
Slow positron beam has been used to study the properties of the near-surface region of polymers.[1, 2] In this paper, a new pulsing mono-energetic slow positron beam as well as the conventional positron annihilation lifetime spectroscopy (PALS) has been applied to study the sub-surface and the bulk of epoxy polymer. The time resolution of the pulsing system is about 500 ps. The spectra were resolved into two or three components: the short lifetimes include the annihilations of para-positronium (p-Ps), free positron and slow positron beam time profile; the long-lived component is an original from ortho-positronium (o-Ps) annihilation in polymer.

In Fig.1., significant changes of o-Ps parameters were found at a short distance from the surface. The lifetime of o-Ps was observed to decrease near the surface as a function of the positron implantation depth, while its intensity increased, which reveals that near the polymer surface the free volume is larger than that in bulk and its number is fewer near the surface or in the sub-surface. Temperature dependence of polymer sub-surface was also investigated. As shown in Fig. 2., the glass transition temperature for the sub-surface of polymer is lower than that for the bulk, which has been studied by other measurement.[3] And the thermal expansion efficiency of the sub-surface was found smaller than that of bulk. All results revealed that the pulsing slow positron beam was a promising and powerful tool to study the sub-surface of polymers.



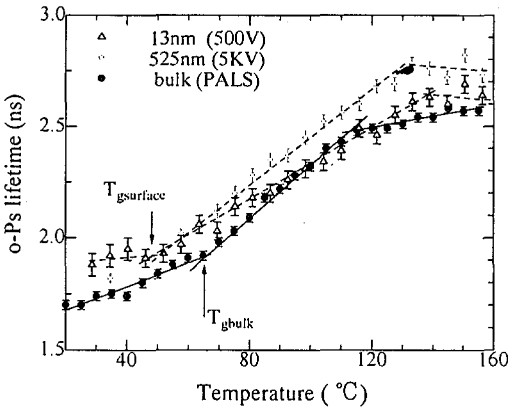


Fig.1. Depth dependence of o-Ps lifetime and intensity obtained by slow positron beam.

Fig.2. Temperature dependence of o-Ps lifetime obtained by PALS and slow positron beam.

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3B12

FREE VOLUME STUDY OF ETHYLENE-VINYL ALCOHOLCOPOLYMER BY POSITRONIUM LIFETIME MEASUREMET

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The nanoscopic structure of semi-crystalline polymers as gas barrier materials was investigated to elucidate a molecular mechanism of the gas permeation process. The positronium annihilation lifetime technique was used to evaluate the free volume property of Ethylene-vinyl alcohol copolymers (EVOHs). EVOHs with various ethylene contents (x_e) of 0 to 74 mol% were studied and the EVOHs (x_e =29mol%) with crystalline degrees of 20 to 60 % were prepared by thermal annealing at the temperature range of 120 to 16°C. The decay curves of positron with total counts of 1 million were measured at 20°C in dry atmosphere using 7.5 $\times 10^5$Bq ^{22}Na positron source. The lifetime of *ortho*-positronium, o-Ps, was analyzed by a non-linear least-square method with the PATFIT-88 computer program. The radius and number concentration of the free volume were estimated from the o-Ps lifetime and the intensity, respectively, using a semi-empirical equation [1,2 ,3]. The samples with an ethylene content of less than 74 mol% were in a glassy state at room temperature. With increasing x_e, the oxygen permeability increased remarkably above x_e =30 mol% and the free volume size increased, but the number concentration did scarcely increase. These indicate that the fractional free volume size is important. The relationship between the oxygen permeability and the fractional free volume size was found to well follow Fujita's free volume theory [4] in the glassy state. On the other hand, the crystallinity influenced only the number concentration of the free volume. However, the oxygen permeability of the samples (x_e=29mol%) with a free volume radius of 0.22 nm was not dependent on the number concentration of the free volume. The relationship between the oxygen permeability and the fractional free volume was not simply described. These suggest that the change of the smaller free volume size may not affect the gas permeation.

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3B13

THERMAL AND OPTICAL SWITCHING OF IRON(II) AND IRON(III) COMPOUND

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A number of spin-crossover iron(II) complexes have been studied. They are important in the development of electronic devices such as molecular switches. Some of them have undergo spin transition from low-spin (LS, S=0) to metastable high-spin (HS, S=2) state by light irradiation at low temperature. This light-induced spin transition effect is termed LIESST (light-induced excited spin-state trapping).[1]

Here, we synthesized the single crystal form of the spin-crossover compounds [Fe(aza)$_2$(NCS)$_2$] (**1**), [Fe(aza)$_2$(NCSe)$_2$] (**2**) (aza = (N-2'-pyridylmethylene)-4-(phenylazo)aniline), [Fe(ipa)(NCS)$_2$] (**3**) and [Fe(ipa)(NCSe)$_2$] (**4**) (ipa = N-2'-pyridylmethylene)-isopropylamine)), and also investigated its crystal structure. Moreover, we determined the structure of the compounds for the LS and HS, and the crystal structures of the compounds exhibiting LIESST effect and not exhibiting LIESST effect were compared in detail. Hence, in order to develop a variety of optically switchable molecular solids, strategies to prevent such a rapid relaxation from a metastable state to a ground state should be developed. We propose the introduction of strong intermolecular interactions in molecular compounds. It is thought that the cooperativity resulting from the intermolecular interaction operates to increase the activation energy for the relaxation processes, enabling the observation of a long-lived metastable state after illumination.

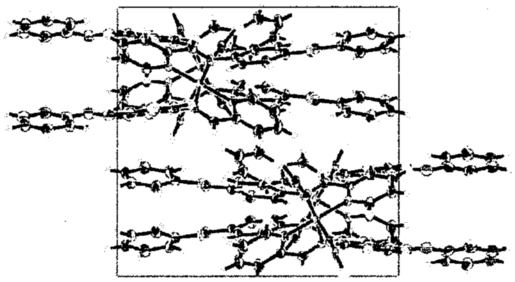

Fig. 1(a) Projection of the crystal structure of 1 along the *ab* plane in the LS at 90 K.

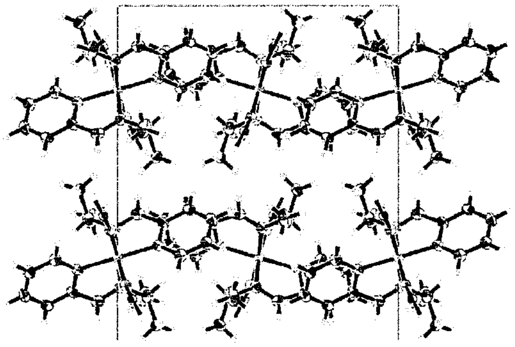

Fig. 1(b) Projection of the crystal structure of 3 along the *ab* plane in the LS at 90 K.

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3C3 TRANSFER OF ^{7}Be, ^{210}Pb and ^{210}Po IN A FOREST CANOPY OF JAPANESE CEDAR

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Particles and gases deposited on the surface of a forest canopy finally fall on the forest floor. How do these depositions pass through the canopy? This way is important for the behavior of chemical species(inorganic species or some insoluble organic compounds) in dry or wet-deposition. Leaf ages(1-6 years old) of Japanese cedar can be easily counted by their ramification because two or more twigs are ramified from a top of the last year twig at spring. Many pieces on leaf ages and locations in a tree of Japanese cedar were used for the study on the transfer of ^{7}Be, ^{210}Pb and ^{210}Po in a forest canopy.

Two whole trees of 17 and 12 years old were totally collected except fine roots, and each was divided into ca. 100 pieces based on the leaf ages, the heights, and the growth ages of the trunk. The concentrations of ^{7}Be, ^{210}Pb and ^{210}Po of these samples, the floor litter and soils were determined by γ - or α -ray spectrometer after appropriate treatments.

The concentrations of ^{7}Be, ^{210}Pb, and ^{210}Po of leaves did not depend on their leaf ages but were lower with their heights, those of barks were higher with their heights of trunk, and those in trunks were not found except small amounts of ^{210}Po. The distribution of these radionuclides in the canopy suggests that these dry- and wet-deposited radionuclides are adsorbed on the top of the canopy, and fall along through water or stem flow water with repeated adsorption-desorption processes. A small part of their nuclides directly falls with powders of leave or withered branches. The average residence times in the canopy are estimated to be 20 days for ^{7}Be and 900 days for ^{210}Pb, based on the balance between these contents of the canopy and the forest floor. The transfer of a substance in a canopy mainly depends on the adsorption property on leaves

3C4 THE ROLE OF MICROORGANISMS IN THE MIGRATION OF RADIONUCLIDE IN SURFACE SOIL

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An interaction with the microorganism can take an important role in migration of the radionuclide in the environment. In this research, it was examined that immobile form of strontium, storontianite ($SrCO_3$), transform into mobile form by microorganisms. The soil samples were collected from the uppermost horizon (0-5 cm) in the cedar woods, and were suspended in the physiology solution of salt. The aliquots were streaked from the solution onto plates of nutrient agar medium containing 3% storontianite to screen for the ability to transform. The culture of the obtained microorganism in soft agar containing pH indicator, 4'-dimethylaminoazobenzene-4-sulfonic acid, Na salt (Methyl Orange; Approx. pH range 3.2-4.4), was indicated that acidic products were secreted from the microbial bodies and controlled the pH condition in the cultured medium. The microorganism was cultured in the nutrient broth with coexistence of the white precipitate of storontianite at 30°C under oxic condition. The large excess storontianite buffered the supernatant solution at a pH slightly over 8. The composition of the supernatant solution was monitored over time. Initially 40 $\mu g\ ml^{-1}$ Sr in the culture solution was confirmed. Although a pH change was suppressed in the supernatant solution, the Sr concentration was gradually increased, and finally 100 $\mu g\ ml^{-1}$ Sr in the solution for about 60days culture was observed in Fig. 1. The increase in Sr concentration in the supernatant solution compared to controls in the experiments is indicated that the dissolution was promoted from the precipitation of storontianite by microorganism. The microorganisms enhanced dissolution of strontium by producing organic and/or inorganic acids as ligand.

Based on the results of these experiments we can determine whether or not microorganisms can affect geochemical reactions, and promote the migration of radionuclide in the surface soil. But it is unclear whether one can extrapolate those results to natural systems and predict the magnitude of any observed effects under field conditions.

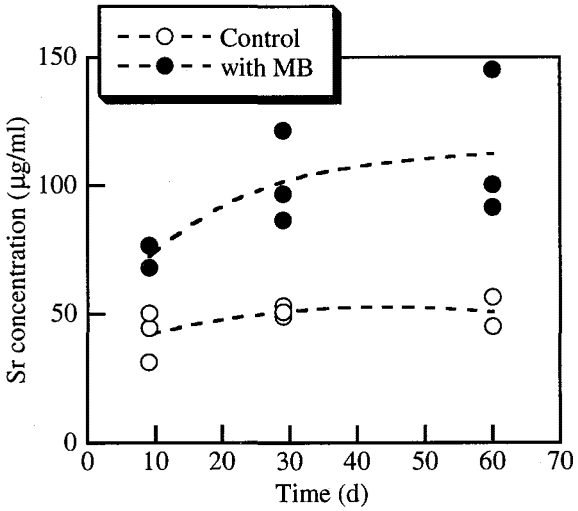

Fig.1 Sr concentration in the culture solution.

3C7

TRANSFER OF ^{137}Cs AND STABLE Cs IN SOIL-GRASS-MILK PATHWAY IN AOMORI, JAPAN

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Radionuclides released into the environment reach the human body through several transfer processes. One important process in estimating internal radiation dose for human is the transfer of radionuclides in the soil-plant-milk pathway. Cesium-137 is an important radionuclide for the assessment of radiation exposure to the public because of its high fission yield, relatively long half-life (30.2 years) and high transferability.

In order to assess more precisely and realistically the internal radiation exposure to the public around nuclear facilities, the soil-to-grass transfer factors (the ratio of the concentration of an element in plant to that in soil) and the grass-to-milk transfer coefficients (the amount of an animal's daily intake of an element as transferred to one kg of milk) of ^{137}Cs and stable Cs were determined for the specific site. Soil, grass and cow's milk samples were collected from Aomori Prefecture in Japan, where the first commercial nuclear fuel reprocessing plant is under construction and related nuclear facilities are already operational. The grass and milk samples for the analysis of stable elements were dried at 70°C and those for ^{137}Cs were ashed lower than 450°C. The soil samples were dried at 60°C and then passed through a 2mm sieve. The concentrations of ^{137}Cs in the samples were measured with a Ge gamma-ray detector connected to a multichannel analyzer system and those of stable elements were determined by neutron activation analysis.

Cesium-137 derived mainly from nuclear weapons testings and the Chernobyl accident has contaminated wide areas in Japan. The concentrations of ^{137}Cs in the soil and grass samples collected from 26 sampling points were 13 ± 12 Bq kg^{-1} and 2.0 ± 2.1 Bq kg^{-1} dry weight, respectively. The geometric mean of soil-to-grass transfer factor of ^{137}Cs was 0.13 and its 95% confidence interval was 0.011-1.6. The transfer factor of ^{137}Cs was higher than that of stable Cs, and they had a positive correlation. The concentration of K in the soil affected both transfer factors. The concentration of ^{137}Cs in milk samples collected from 16 sites was 76 ± 43 mBq kg^{-1} fresh weight and had a positive correlation with that of stable Cs. The geometric mean of grass-to-milk transfer coefficient was 0.0027, assuming that a cow's total daily intake was 20 kg of dry grass. The transfer and distribution of stable Cs in the environment may be regarded as a useful analogue in predicting the long-term fate of ^{137}Cs influenced by site-specific environmental factors.

3C8

ASSOCIATION OF Am WITH HUMIC SUBSTANCES ISOLATED FROM RIVER WATERS WITH DIFFERENT WATER QUALITY

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Macromolecular components of dissolved organic materials such as humic substances (humic and fulvic acids) are widely recognized as important complexing ligands towards trace elements and radionuclides in aquatic environments. This study reports the association properties of Am with humic substances in river waters on the basis of molecular size distribution. Aquatic humic substances were isolated from river waters with different water quality (pH 3.9-8.0 and DOC concentration of 2-40 mg/l), and used for comparing their effects on the association of Am.

The association experiments were carried out in a medium of 0.01M $NaClO_4$ solution at the humus concentration of 10 mg/l and pH6-8. 100 μl of ^{241}Am solution was added to 10 ml of humus solution. The initial concentration of Am was 7.6×10^{-6}M. After 7 days under shaking in an oven at 25°C, the solution was filtered with 450 nm filters and measured for pH. The final pH is 5.8-6.9. Ultra filtration technique was used to size-fractionate Am in the sample solutions.

In the absence of humic substances, 52-94% and 4-33%of Am were found in the molecular size above 450 nm and 450nm-100k Da at pH6-8, respectively because of the polymerization and/or precipitation. Molecular size distribution of Am in the presence of humic substances is shown in Fig. 1. In the presence of humic substances, the amount of Am dissolving in the solutions increases due to the complexation with humic substances. The dominant size fractions of Am are 450nm-100k Da for the Am-Yodo humic acid (HA), and 100k-10k Da for the other HA samples. On the other hand, major part of Am in the presence of fulvic acid (FA) is found in smaller molecular size than the Am-HA systems. These results indicate that differences in characteristics of humic substances may be reflected in the association of Am with humic substances.

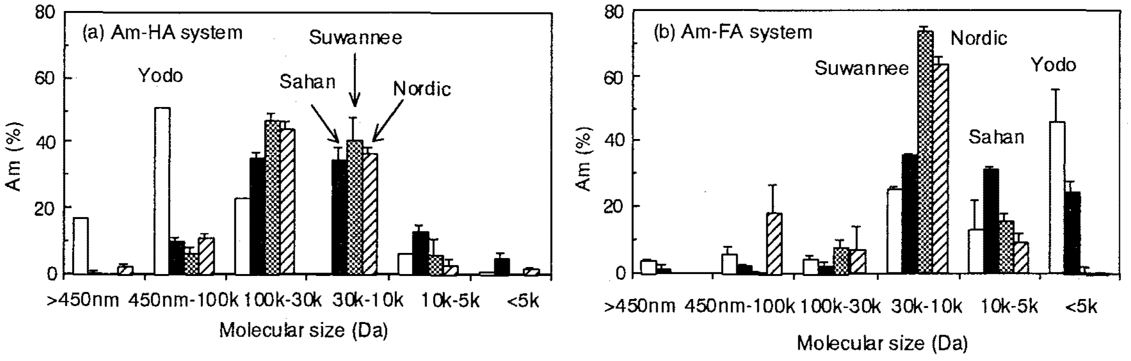

Fig.1 Molecular size distribution of Am in the presence of aquatic HA (a) and FA (b).

3C9

EVALUATION OF RADIOACTIVITY INDUCED IN THE ACCELERATOR BUILDING AND ITS APPLICATION TO DECONTAMINATION WORK

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Evaluation of radioactivity induced in the accelerator components and building is important for the decommissioning of accelerator facility. [1] In 1999, all facilities in Tanashi Branch, KEK were decommissioned. In advance of the decontamination, residual radioactivities in the buildings of 1.3 GeV electron synchrotron and SF-cyclotron have been carefully evaluated with gamma-ray spectrometry of surface and core samples of concrete.

Surface and depth profile of each radioactivity were obtained in accelerator room and experimental room. The major radioisotopes observed in both facilities were ^{152}Eu, ^{60}Co, ^{134}Cs, ^{22}Na and ^{54}Mn, which are generally produced by neutron capture reaction. Nevertheless the concentration of Eu, Co and Cs in concrete are only 1, 10 and 1 μg/g, these activities took greater part of residual radioactivity because of the large neutron capture cross-section. On the other hand, the activities of ^{22}Na and ^{54}Mn were produced by the fast neutron reaction. In case of radioisotopes found in the concrete of wall and floor near the SF-cyclotron, maximum activity was observed at the depth of about 10 cm. The total residual activity is 0.2 Bq/g on its maximum to natural activity of 0.5 Bq/g. It was observed the good linearity between activity of ^{60}Co and surface dose rate. Decontamination area and depth were defined according to the result of surface dose rate and the result of gamma-ray spectrometry, respectively. Tritium induced in concrete was also determined and the linearity between tritium activity and ^{60}Co was observed, therefore tritium observed in both facilities was mostly produced by the neutron reaction as the ^{6}Li(n,α)T reaction.

The results of surface dose rate were good agreement with the result of neutron flux measurement during operation of the SF-cyclotron[2] Therefore, beam control and shielding for beam loss points during operation should be very important not only for reduction of occupational dose for maintenance but also for saving a decontamination cost.

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3C10

SOLVATION STRUCTURE OF LANTHANUM DETERMINED BY ^{139}La NMR, EXAFS, AND NEUTRON DIFFRACTION METHOD

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Mixed solution of water and methanol has been widely utilized for separation of trivalent lanthanides and actinides in ion exchange method, since the separation of these elements in nonaqueous solution like methanol-water mixture is high efficiency. The reason for high efficiency might be attributed to unique solvation structure in comparison with aqueous system. Solvation structure of these elements in the mixed solution, however, has not been understood in detail yet. Therefore, we studied solution and solvation structure of these elements in the mixture of water and methanol: mole fraction (χ_c), $M_{water}/(M_{methanol}+M_{water})=0\sim1$, by the several physico-chemical methods.

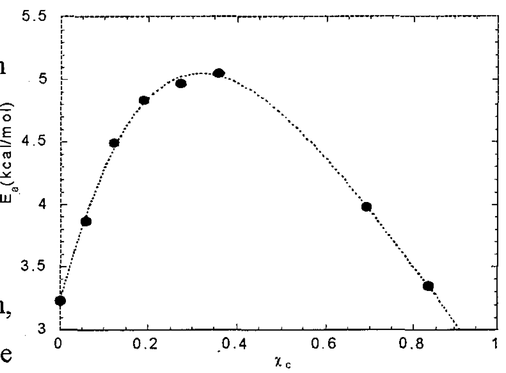

Fig.1 Relationship between activation energy of rotation of $^{139}La^{3+}$ and the mole fraction of the mixed solutions.

* The activation energies were determined by ^{139}La NMR relaxation analysis.

Figure 1 shows the relationship between the activation energy of rotation of La^{3+} and the mole fraction of the mixed solutions. The activation energy curve showed the maximum with χ_c=0.2~0.4, indicating that solvated lanthanum might interact strongly with the surrounding solution-molecules. The real space radial structural functions (RSRDF) of three solutions are shown in Fig.2. The RSRDF below 1Å are mainly consisted of intra-molecule interactions, while the broad peaks around 3.5Å arise from inter-molecule interactions. The solution of χ_c =0.4 is the shape which summed up water and methanol structure in the region around 3.5Å. From this result, each bulk-structure of water and methanol partially coexists in the mole fraction range (χ_c=0.4). In this presentation, EXAFS results are to be given.

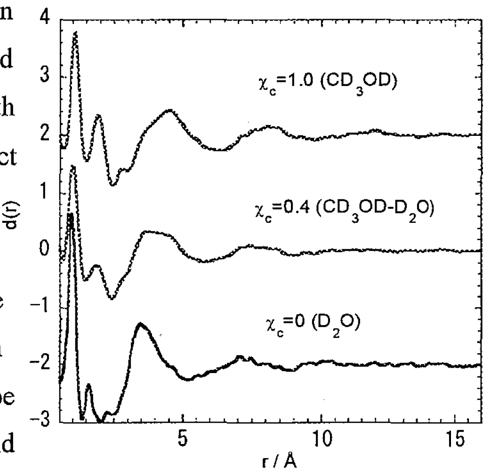

Fig.2 Real space radial distribution functions of pure CD_3OD and D_2O, and the mixed solution by Pulse Neutron Diffraction method.

3C11 Complexation of Actinides with Polyoxometalates

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Polyoxometalates used in the present work ($([P_2W_{17}O_{62}]^{6-}$, $[P_2W_{17}O_{61}]1^{10-}$, $[As_2W_{21}O_{69}]^{6-}$, and $[NaP_5W_{30}O_{110}]^{14-})$ have been shown to fall within the definition of colloids with respect to size, i. e., between 1nm and 1 μm.

Stability constants ($\log\beta_{101}$) of Th^{4+}, $NpO_2{}^{+}$, Am^{3+} with $[NaP_5W_{30}O_{110}]^{14-}$ were determined by solvent extraction (μ= 0.1M NaCl), and found to be 6.18±0.07, 3.80±0.06, 2.98±0.04, and 5.85±0.05, respectively. The order of stability constants; $Th^{4+} > Am^{3+} > UO_2{}^{2+} > NpO_2{}^{+}$ is due electrostatic repulsion between the actinyl oxygens and oxygens on the poloxometalate surface. Stability constants ($\log\beta_{101}$) of Th^{4+}, $UO_2{}^{2+}$, $NpO_2{}^{+}$, Am^{3+} with $[As_2W_{21}O_{69}]^{2-}$ were also measured, and found to be 9.9±0.1, 6.32±0.04, 4.39 ± 0.03 and 10.1 ± 0.1, respectively. The stability constant of the $NpO_2{}^{+}/[P_2W_{17}O_{61}]^{10-}$ complex was found to be 4.81±0.03. Enthalpies of complexation with Th^{4+}, $UO_2{}^{2+}$ and Nd^{3+} were measured calorimetrically with the four polyoxometalates. The stability of complexes that actinides form with $[P_2W_{17}O_{61}]^{10-}$ is based on the charge centered on the metal, i. E., 4 > 3.3 > 3 > 2.2 for Th^{4+}, $UO_2{}^{2+}$, Am^{3+}, $NpO_2{}^{+}$, respectively. The order of stability of actinide/polyoxometalate complexes with $[P_2W_{18}O_{62}]^{6-}$, $[As_2W_{21}O_{69}]^{6-}$ and $[NaP_5W_{30}O_{110}]^{14-}$ is dependent on the geometry of the binding sites. The results indicate that the conformation and charge distribution of the microscopic surface structures are important factors in the formation of pseudocolloids.

3C12

Comparative Study of RNAA and ICP-MS for the Determination of Ultra-trace Th and U in Geological and Cosmochemical Samples

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Thorium and uranium are of considerable interest in cosmochemistry because of their special places in the chart of the nuclides and in the periodic table[1]. They locate at the end of the stable island of elements and uranium is the heaviest element that exists in the nature. It is important to develop a practical method to determine the trace thorium and uranium in geological and cosmochemical rock samples. As these elements are the least abundant elements in our solar system[2], analytical methods with high sensitivity for these elements are to be applied. There are several methods for the determination of thorium and uranium in solid samples, neutron activation analysis (NAA), inductively coupled plasma mass spectrometry (ICP-MS), spark source mass spectrometry (SS-MS), X-ray fluorescence analysis (XRF), etc. Among them NAA and ICP-MS seem to be the most promising analytical methods.

In this study, we developed a radiochemical NAA (RNAA) method (including anion-exchange, coprecipitation and electrodeposition) and an ICP-MS procedure to determine ultra low Th and U in geochemical and cosmochemical samples. In the RNAA procedure, the chemical behaviors of Pa and Np (the neutron capture products of Th and U, respectively) in electrodeposition step were studied, and high chemical yields of Pa and Np in this step were obtained: 85% for Np; 95% for Pa. For the whole procedure the chemical yields were around 50%. Under the experimental conditions applied in this study, the detection limits for Th and U were deduced to be 0.1ppb and 0.2ppb, respectively.

In our preliminary ICP-MS study, an anion-exchange step was introduced after sample digestion to separate many major matrix elements. Thus, the dilution factor was decreased yielding higher sensitivity for Th and U. So far, the detection limits of Th and U were lowered to sub ppb level in cosmochemical or geochemical samples.

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3C 13 Determination of Pu concentration and its isotope ratio in Japanese soils by HR-ICP-MS

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The isotope composition of Pu (^{240}Pu/^{239}Pu ratio) is related to the source of the contamination. However, there is only a limited volume of quality data available on the levels and distributions of ^{239}Pu and ^{240}Pu isotopes in the environment. This is mainly due to the fact that ^{239}Pu and ^{240}Pu have similar alpha-particle energies and cannot be easily resolved by alpha spectrometry. We have recently developed a reliable method for determination of ^{239}Pu and ^{240}Pu by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) using a quadrupole-type mass spectrometer (Yokogawa PMS-2000). We also have demonstrated the utility of the technique by measuring ^{240}Pu/^{239}Pu atom ratios in a series of international reference materials[1] and soil samples from Chernobyl[2]. In this study we have used high resolution-type ICP-MS (HR-ICP-MS) to examine its analytical feasibility (e.g. detection limit) and determined concentrations of both ^{239}Pu and ^{240}Pu in Japanese soils.

Samples (1 - 20 g, depending on the concentration level) were mixed with a known amount of ^{242}Pu and digested with nitric acid. To the filtered leachate $NaNO_2$ was added to convert chemical form of Pu to Pu (IV). Pu was separated with anion exchange resin (Dowex 1X8). Finally, NH_4I (5%) - 10 M HCl solution (40 ml) was added to the column to elute Pu from the resin as Pu(III). Sufficient decontamination factors (10^4 - 10^5) for many matrix elements including U were obtained. The concentrations of ^{239}Pu, ^{240}Pu and ^{242}Pu and their isotope ratios were measured with HR-ICP-MS (Finnigan Element). As a result, the detection limit determined using Pu standard and blank solutions (4% HNO_3) was about 0.001 pg ml^{-1} (ppt) Pu for a counting time of 40 s. This value is about one order of magnitude better than the values obtained by the above-mentioned quadrupole-type ICP-MS. Relative standard deviation during the measurement was less than 1% at the concentration of >2 pg ml^{-1} of Pu. Compared with alpha-spectrometry, the ICP-MS method has significant advantages in terms of prompt measurement time, simple analytical procedures and capability of determining the ^{240}Pu/^{239}Pu ratio.

Concentrations of Pu and its isotopic ratios were determined by this method in several soil samples. from different areas in Japan. Levels of Pu in surface soils collected from forests were significantly higher than those from agricultural fields. Vertical distributions of Pu in soil showed an accumulation of this nuclide in the surface layer. The ^{240}Pu/^{239}Pu atom ratios observed in Japanese soil samples were around 0.17 (range: 0.15-0.19), except for very low ratios found in the Nagasaki area.

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3P01 PRODUCTION CROSS-SECTIONS OF CARBON-14 IN AL BY NUCLEAR SPALLATION REACTIONS

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At high-intense and high-energy accelerator facilities, accelerator components are exposed to primary and/or secondary high-energy particles during the machine operation. As a result, these become radioactive and radioactivities are accumulated in the components along with the operation.

Carbon-14 with a half-life of ~5700y is one of these radio-nuclides. It emits only beta-ray with 156keV, which is possible to contribute to internal exposure. However it is very hard to estimate the radioactivity because there is little information on production cross-sections. In this study, we measured the ^{14}C production cross-sections for the nuclear spallation reaction of Al. The chemical separation method of ^{14}C was also studied.

. The Al targets were made of thin(6.61mg/cm^2) and highly pure foils. The Al foils were bombarded by 12 GeV protons in the external primary beam line of the KEK 12GeV proton synchrotron. The total number of incident proton was calculated to be 1.74×10^{18}, which was evaluated from the ^{22}Na yield in the Al target by using the cross-section of 9.84 mb for the Al(p,spall)^{22}Na reaction.[1]

By combustion method using an electric furnace, all ^{14}C was converted into $^{14}CO_2$, which was then trapped in Carbo-Sorb E. The combustion was carried out at 1100℃ under a stream of air (150ml/min). Carbon-14 radioactivity thus collected was measured using a liquid scintillation counter.

The cross-section of 0.62 mb was obtained for the Al(p,spall) ^{14}C reaction. This value was about five times as small as the one calculated from the semi-empirical systematics. Since the cross section has been obtained only for oxygen, which was 2mb[2] for the $^{16}O(p,3p)^{14}C$ reaction, the semi-empirical systematics seems to be determined using only the oxygen data. Hence the semi-empirical systematics may not be proper to be used for Al case.

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EXCITATION FUNCTIONS FOR ^{248}Cm(^{18}O,5n)^{261}Rf AND ^{248}Cm(^{19}F,5n)^{262}Db REACTIONS

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Recent chemical studies of element 104 use 78-s ^{261}Rf produced in the ^{248}Cm (^{18}O,5n) reaction with a cross section of 5 nb [1], and those of element 105 use 34-s ^{262}Db and partially 27-s ^{263}Db produced in 5n- and 4n-reactions of ^{18}O with ^{249}Bk targets with cross sections of 6 nb and 2 nb [2], respectively. The target material ^{249}Bk is however very rare and highly radioactive, thus the other reaction path ^{248}Cm(^{19}F,5n) producing ^{262}Db has been studied as a possible alternative and the production cross section at a beam energy of 106.5-MeV has been deduced to be 0.26 nb [3]. In the present study, to evaluate the optimum irradiation conditions for the production of ^{261}Rf and ^{262}Db in bombardments of ^{248}Cm with ^{18}O and ^{19}F beams, respectively, we measure excitation functions for each reaction.

The ^{248}Cm target of 590 μg/cm^2 thickness and 5 mm diameter was prepared by electrodeposition onto a 2.2 mg/cm^2 thick beryllium backing foil. Bombardments by ^{18}O and ^{19}F beams were carried out at the JAERI tandem accelerator. The reaction products recoiling out of the target were stopped in He gas ($\sim$1 atm), attached to a KCl aerosol, and were transported through a Teflon capillary to the rotating wheel system. The transported nuclei were deposited on polyethylene terephthalate foils of 120 μg/cm^2 thickness and 20 mm diameter at the periphery of an 80-position stainless steel wheel of 80 cm diameter. The wheel was periodically rotated to position the foils between six pairs of Si PIN photodiodes for α-particle detection. The production cross sections were evaluated from the mother-daughter correlation of α energies between ^{261}Rf and ^{257}No, and ^{262}Db and ^{258}Lr.

The maximum cross sections in each reaction were 13 nb at the ^{18}O beam energy of 94-MeV, and 1.5 nb at the 103-MeV ^{19}F beam energy. In the conference, we describe the experimental details and discuss the analysis of statistical model calculations.

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3P03

Measurement of Excitation Function of ^{63}Cu(n,p)^{63}Ni Reaction for E_n<6.5 MeV

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A purpose of this work is to measure an excitation function of ^{63}Cu(n,p)^{63}Ni reaction. The excitation function is indispensable to estimate radioactivity of ^{63}Ni produced in copper materials at reactor and accelerator facilities, and can also be applied to estimate a neutron flux of the Hiroshima atomic bomb. However, the data in the neutron energy range below 10 MeV is rather scanty. Therefore, there is much request for relevant excitation function measurement in this energy range. The excitation function of this reaction was measured four times by our group. The result of last experiment is shown in Fig.1 with the theoretical estimates of JENDL-3.2[1)] and ENDF/B-VI[2)]. However, there was inconsistency among those results. The inconsistency may be caused by the geometrical error of copper sample setting during the irradiation. Therefore, the new experiment was carried out at the Fast Neutron Laboratory (FNL) of Tohoku University with the samples set carefully in correct position. In this experiment, irradiated neutron energy range was from 1.7 to 6.5 MeV. The ^{63}Ni and ^{60}Co produced in the copper sample are separated chemically, and the ^{63}Ni is measured by a low background liquid scintillation counter and the ^{60}Co by a Ge-detector. In this presentation, the obtained excitation function will be reported and compared with our previous results and theoretical estimates.

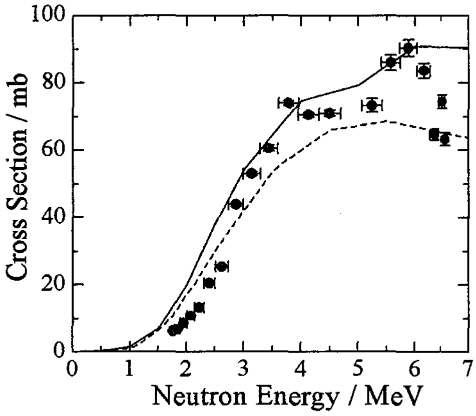

Fig. 1. The results of the previous work and the theoretical estimates (—:JENDLE-3.2, ---:ENDF/B-VI).

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3P04

AN ATTEMPT TO DETECT THE ULTRAVIOLET AND VISIBLE PHOTON EMITTED FROM THE FIRST EXCITED STATE IN ^{229}Th

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The energy of the first excited state of ^{229}Th is reported to be 3.5±1.0 eV[1], which is lower than the first ionization energy of thorium atoms. The expected main decay channels are a direct gamma-ray emission and the transition via an electron bridge mechanism because the internal electron conversion is inhibited. However, no one has observed the decay directly so far[2].

We chemically separated ^{229m}Th from the ^{233}U sample with rapid ion exchange apparatus, and measured the photons from separated sample with a photomultiplier (PM). ^{233}U sample was left during 2-48 hours to grow ^{229m}Th on the assumption that ^{229m}Th has a certain half-life from several minutes to over ten hours. The PM is installed in a PM cooler to cut down the thermal noise. Further, the oval body reflector was employed to focus the light emitted from the sample as many as possible on the photoelectric surface (5 mm × 8 mm) of PM. These apparatuses and procedure are shown in Fig.1. The photon counting was executed in MCS mode to discuss the half-life. Two kinds of samples were measured; one is solution that is hydrochloric acid system, and the other is the dried up sample.

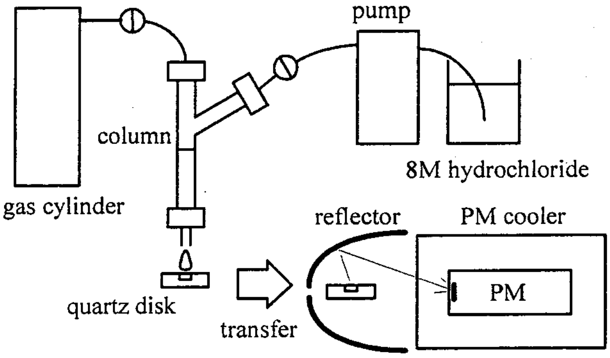

Fig.1. Experimental scheme.

A small amount of photon emitted from the thorium sample was observed. However, there were some problems in reproducibility and stability in the measurement. We are planning to improve the photon measurement system to discuss more details.

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3P05 The k_0 standardization NAA on the low power operation at JRR-4

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Introduction Since Simonits et al. (1975)[1] introduced the concept of single comparator method for neutron acitvation analysis (NAA), the k_0 standardization NAA has been developed to practical use with the improvement of the nuclear data. At Japan Atomic Energy Research Institute (JAERI), it was also incorporated to the NAA support system at JRR-3M[2]. But the neutron flux of JRR-3M is too high to carry out instrumental NAA (INAA) of, for example, rock samples. In terms of neutron flux, low power operation of JRR-4 at 100kW is much more suitable. However, the k_0 standardization NAA at JRR-4 has only been prepared for normal power operation (3.5MW). In this paper, it is aimed to put the k_0 standardization to practical use with low power operation of JRR-4. Some parameters for the k_0 standardization method of JRR-4 (neutron flux, spectrum and so on) were investigated and evaluated. As the first attempt using those parameters, some rock samples were subjected to the k_0 standardization NAA.

Experimental To monitor the stability of flux and spectrum of neutrons, Au, Zr and/or Al were irradiated at the pneumatic irradiation channel of JRR-4 under various operating conditions and then γ-ray measurements were carried out. In the analysis of rock samples, irradiations of three different durations were performed to analyze the nuclides having different half-lives.

Results and Discussions At JRR-3M, the fluctuation of neutron flux was reported to be within 1% over one day[2]. The neutron flux of JRR-4 was also stable at low power operation when the main control rods were not moved. The fluctuation was within a few percent. But change of flux, which exceeds the usual fluctuation, sometimes occurs due to operation of the control rods. At the normal operation of JRR-4, such control rod operations were required a few times during one day operation (6 hours). So irradiation of flux monitor together with samples was required. On the contrary, the stability of neutron flux at low power operation was good and the control rod were merely operated over one week. From the viewpoint of using the k_0 standardization, low power operation of JRR-4 is more suitable than normal operation.

Based on the above discussions, some standard rock samples and meteorites were analyzed using the k_0 standardization method and data reduction is now in progress, these results and their evaluation will be present.

1 A. Simonits;, F. De Corte;, J. Hoste, *J. Radioanal. Chem.*, **24**, 31(1975)

2 F. Sasajima;, H. Sawahata;. K. Onizawa;, S. Ichimura;, A. Ohtomo;, Y. Ito;, M. Takayanagi, *JAERI-Tech 2000-073*

3P06 SPECanal Suite2001

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Personal computer (PC) is usually used for data taking of alpha-, gamma- and X-ray measurement. As modern PC has very high computing power, it is possible to use PC for peak area, decay, and efficiency calculation, and for search for nuclear data. In 1995 and 1997, I reported SPECanal95 and 97 on SORC'95 and APSORC'97, which were DOS and Windows based Suite, respectively. Recently, user friendly operating system, Windows, is loaded on most of PC, and Windows based personal relational database engine makes it easier than ever to build powerful database and to create, access and analyze data. The applications of Suite are blushed up and nuclear database for SPECanalSuite2001 is created to this new engine. In this paper, I introduce new Suite with GUI of Windows. I will also perform demonstration of new Suite by small PC. SPECanalSuite2001 will be able to download from ftp://risite.s.kanazawa-u.ac.jp/SPECanal/win/.

SPECanalSuite2001 delivers a set of 32 bit applications (coded by VC++ and VB6) and nuclear database (mdb file) designed to take advantage of Windows PC. The application in the Suite includes **wPKarea** (peak find and area calculation based on gaussian + exponential tail + arc-tangent bkg function curve fitting enabled to decompose 15(or less) peaks at a peak area), **wPKview** (spectrum viewer and search for nuclear data), **wPKidnt** (automatic nuclide identification derived from peak energy position and branching ratio corrected by detector efficiency), **wPKdecay** (decay analysis based on least square fitting enabled to decompose 5(or less) components), **wPKeff** (gamma-ray detector efficiency estimation by standard source method), **wNuc'Cha** (browser of all nuclear data, its initial screen appears like Chart of the Nuclides) and other utilities designed to help nuclear and radiochemists. Some spreadsheet can be used for the data input to wPKdecay and wPKeff. Installer automatically set up Suite application files.

Nuclear database for SPECanalSuite2001 was compiled from ENSDF (evaluated nuclear structure data file generated at Mar, 2001) of NNDC (National Nuclear Data Center, BNL, USA), and was adapted for PC. This database includes neutron and Hydrogen to 118th element (except for 113th, 115th, 117th) containing over 3,700 entries of stable and radioactive nuclides with over 147,000 alpha-, beta-, gamma-, X-ray and also Auger and conversion electron energy lines. Every data of radioactive nuclide includes half-life, decay mode, energy line and branching ratio with those errors, and classification of lines. Installer automatically set up database file. User easily browses all of nuclear data by wNuc'Cha.

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3P07 Studies on Zinc Deficiency and Recovery : Changes in Trace Elements in Organs and Tissues of Zinc-deficient Mice

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Zinc is one of the most important trace elements in living organisms. Deficiency of Zn leads to skin injury, alopecia, impaired wound healing, growth retardation etc. One method of improving Zn deficiency is Zn therapy, because Zn deficiency is caused by diminution of intake, increased needs, or increased losses.

Previously, we reported that Co content increased significantly in all the organs and tissues of Zn-deficient mice although Zn concentration in the organs of Zn-deficient mice were not distinctly lower than those of control mice except for bone and pancreas.[1] The present study was undertaken to prove the variation in the concentrations of trace elements in the recovery process of Zn-deficiently young mice by administration of Zn.

Male mice of the ICR/jcl strain, 4-week-old, were fed with Zn-deficient diet for beginning 3 weeks (first period), and then, their diet was exchanged to control diet (Zn content was 30μg/g diet), which was made of raw materials for Zn-deficient diet and $5ZnO \cdot 2CO_3 \cdot 4H_2O$, for another 6 weeks (second period). After the second period, 5 organs and tissues, such as liver, kidney, pancreas, testis and bone, were removed and freeze-dried. They were subjected to instrumental neutron activation analysis (INAA). Concentrations of eleven elements, Na, Mg, Cl, K, Ca (only in bone), Mn, Fe, Co, Zn, Se and Rb, were determined. These concentrations were compared with those of mice fed only with Zn-deficient diet (Zn-def. mice) and control diet (control mice) in 4-week-old over a 9-week period, respectively.

Zinc concentrations in all the organs and tissues of Zn-def. mice were lower than those of control mice. On the other hand, Co concentrations of Zn-def. mice were much higher than those of control mice, as it was also recognized in our precious work.[1] At the end of first period, some of the symptoms due to Zn-deficiency were recognized in all the mice fed with Zn-deficient diet. After receiving an additional Zn in second period, symptoms were improved remarkably, especially, for their skin condition and weight gain. However, after the second period, subsequent to Zn deficiency, recoveries of the concentrations of Zn in bone, and Co in bone and testis were incomplete.

It will be concluded that Zn deficiency during growing period may cause more serious damage to metabolism Zn and/or Co in mice.

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3P08 DEVELOPMENT OF RAPID CHMICAL SEPARATION FOR HEAVY ELEMENTS

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Deviations from the regularities of the chemical properties in the periodic table are predicted in the region of the heavy elements[1]. One of our interests is to examine an influence of a relativistic effect on the chemical properties. To study the effects for the heavy elements, we need the rapid chemistry apparatus controlled by a computer system that can repeat automatically a sequence of the chemical separation due to the extremely short half-lives and low production rates.

A gas-jet transfer system and a prototypic ion-exchange separation system[2] were constructed. The ion-exchange separation system, which consists of fluoroplastic tubes, 4-way and 3-way valves, is easily operated by handling the valves and pump. The basic research was carried out with spontaneous fission products of ^{252}Cf to design an on-line experiment system.

We prepared radioactive tracers, ^{88}Zr-^{88}Y, ^{147}Nd and ^{160}Tb, in the ^{89}Y(p,2n), ^{146}Nd(n,γ) and ^{159}Tb(n,γ) reactions, respectively. Mutual separation of Y, Nd and Tb has been performed with the ion-exchange separation system in mixed solution system of mineral acids and alcohol[3] in order to apply the chemical separation for the heavy actinide elements. Furthermore, we were also measured the distribution coefficient over the range from 10^6 to 10^{19} atoms with ^{88}Zr and ^{88}Y nuclides to investigate whether the adsorption behavior on anion and cation exchange resins is dependent on the number of atoms, that is essential problem for single atom chemistry.

We will develop a rapid chemistry apparatus connected a gas-jet system and perform on-line experiments for the heavy actinide elements on the basis of these studies.

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3P09 ANION EXCHANGE BEHAVIOR OF NOBELIUM

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Recently, we have investigated the anion exchange behavior of Rf in HCl and HNO_3 solutions [1]. In the measured ^{261}Rf events, however, the contribution of its daughter ^{257}No needs to be taken into account. Therefore, the present study aims to examine the anion exchange behavior of ^{255}No, produced by the ^{248}Cm(^{12}C,5n) reaction, in HCl and HNO_3 solutions in order to evaluate the contribution of the primordial ^{257}No in the ^{261}Rf experiment.

The excitation function for the production of ^{255}No in the bombardments of ^{248}Cm target with 69-, 73-, 77-, and 81-MeV ^{12}C projectiles delivered from the JAERI tandem accelerator has been measured. The reaction products were transported by the gas-jet system to the rotating wheel apparatus for the measurements of the α decays. Figure 1 shows the excitation functions of ^{254,255,257}No produced by ^{248}Cm(^{12}C,xn) reactions. The circles and triangles are the cross sections in 5n+6n and 3n reactions, respectively. The broken, solid and dotted lines are the calculated (relative) values in 6n, 5n and 4n reactions, respectively, with Alice code. The maximum production cross section of ^{255}No was found to be about 400 nb at 77 MeV, and its half-life value of 3.1±4 min agreed well with the literature value [2].

The anion exchange behavior of ^{255}No has been studied in HCl and HNO_3 solutions using Automated Ion separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA). In the symposium, we will discuss the contribution of the primordial ^{257}No to the alpha events of ^{261}Rf together with our first experimental results on Rf [1].

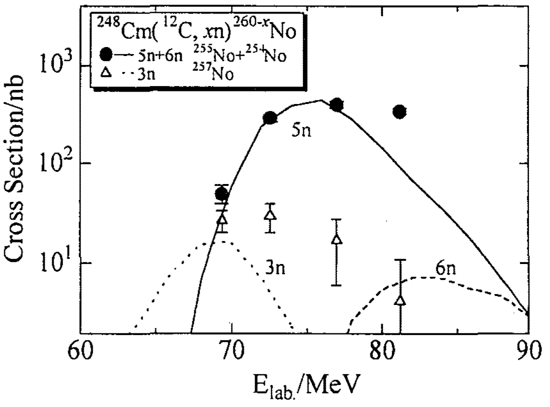

Fig.1. The excitation functions of ^{254,255,257}No produced by ^{248}Cm(^{12}C,xn) reactions.

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[2] T. Sikkeland *et al.*, *Phys. Rev.* **172**, 1232 (1968).

3P 10 STUDY ON THE SOLVATION STRUCTURE OF TRIVALENT LANTHANOID IN A MIXED SYSTEM OF METHANOL AND WATER

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Information on solvation structure of trivalent lanthanoid ions (Ln^{3+}) is very important for separation of f-block elements. We adopted EXAFS method to elucidate quantitatively the structure of Ln^{3+} in a mixed solution of CH_3OH and H_2O.

Sample solutions were prepared by dissolving $EuCl_3$, $SmCl_3$ and $NdCl_3$ into the mixed solvent system. In all the samples, each metal concentration was adjusted to 0.2 $mol \cdot dm^{-3}$. EXAFS measurements were carried out in the transmission mode at the BL27B station of the Photon Factory at KEK. Data analysis[1] was performed using WinXAS 97 and required theoretical values were calculated by FEFF7 code.

Fourier transformed EXAFS oscillations of Sm(III) in the region of $0 \leq$ mole fraction of CH_3OH (X_s) ≤ 0.84 are different from those in $X_s > 0.84$. Therefore, EXAFS spectra in $X_s \leq 0.84$ were analyzed as 1 element model, and spectra as $X_s > 0.84$ by 2 element model. Figure 1 shows the variations in the coordination number (CN) of Sm(III) and the distance (d_{Sm-O}) from Sm(III) to O atom. In $X_s \leq 0.84$, the CN decreases gradually with an increase in X_s. This is caused by a coordination of bulky CH_3OH. In $X_s > 0.84$, the CN decreases rapidly. An increase in the mole fraction of CH_3OH around Eu^{3+} with X_s in $X_s > 0.8$ is steeper than that in $X_s \leq 0.8$.[2] So, it is supposed for the low CN in $X_s > 0.84$ to be caused by a high mole fraction of CH_3OH around Sm(III).

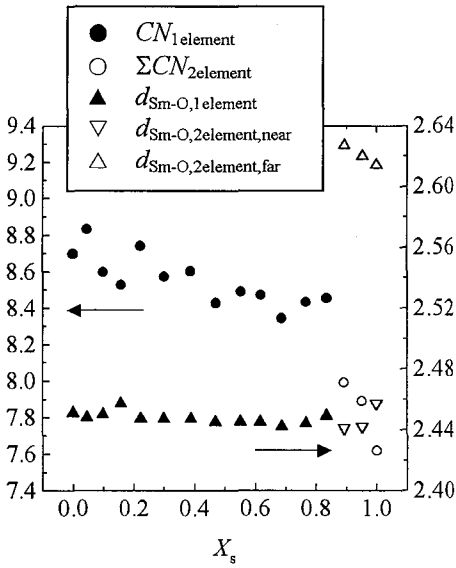

Fig. 1 CN and d_{Sm-O} of Sm(III) in a mixed system of CH_3OH and H_2O

EXAFS spectra of Eu(III) and Nd(III) are also analyzed. Those results are reported together.

1. T. Yaita;, H. Narita;, Sh. Suzuki;, Sh. Tachimori;, H. Motohashi;, H. Shiwaku;, *J. Radioanal. Nucl. Chem.*, **239**, 371(1999)
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3P 11 Behavior of ^{234}Th (^{234}U), ^{230}Th and ^{228}Th recoil atoms in ferriferous inclusions into the natural silicates

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The behavior of ^{238}U, ^{234}U, ^{230}Th, ^{232}Th, and ^{228}Th isotopes at repeated exposure to hydrochloric acid of aegirine, a natural mineral of the pyroxene's group, was studied. It was found out that the ^{230}Th isotope exhibits the highest ability of passing into the liquid phase. In the insoluble residue the ratios of isotopes activity ^{230}Th/^{234}U, ^{230}Th/^{232}Th, and ^{228}Th/^{230}Th are 0.27, 0.33 and 3.3, respectively (taking into account the corrections for ^{238}U and ^{232}Th contents in the mineral). The observed effects cannot be explained by different stabilities of alpha-recoil tracks. It was shown that ^{228}Th and ^{230}Th are leached out of different micromineral phases contained in the aegirine matrix. The former is leached out of Th-Ce-phosphate inclusions and the latter out of Fe-Ti inclusions (iron oxides-hydroxides). It is the author's opinion the stability of ^{228}Th to leaching is the result of low solubility of Th-Ce-phosphate inclusions in hydrochloric acid. Selective isolation of different chemical forms of uranium and thorium make it possible to draw the conclusion that uranium in the Fe-Ti-containing phase forms its own minerals 100 nm in size. The ^{230}Th atoms ejected after the alpha-recoil are retained in the composition of iron oxides-hydroxides in the adsorbed form in contrast to the ^{234}U isotope washed out of the mineral system considered here by natural waters.

3P 12

IN-BEAM MÖSSBAUER SPECTROSCOPIC STUDIES OF CHEMICAL EFFECTS ASSOCIATED WITH THE ^{56}Fe(n, γ)^{57}Fe REACTION

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Chemical effects of the ^{56}Fe(n, γ)^{57}Fe reaction were non-destructively investigated in metallic iron, stainless steel, and potassium tris(oxalato)iron(III) ($K_3[Fe(C_2O_4)_3]\cdot 3H_2O$) by means of in-beam Mössbauer spectroscopy. In our measurements, a target sample was irradiated at room temperature with cold neutrons in the beam-line at JRR-3M of Japan Atomic Energy Research Institute. An in-beam Mössbauer spectrum was measured using a parallel plate avalanche counter by probing the prompt Mössbauer γ -rays of 14.4 keV emitted from the first excited level of ^{57}Fe produced in the neutron capture reaction. As to metallic iron and stainless steel, there was found no difference between the in-beam Mössbauer spectrum and ordinary absorption spectrum, indicating little chemical effect of the (n, γ) reaction. Figure 1 shows the in-beam Mössbauer spectrum of metallic iron observed here. On the contrary, we observed the in-beam Mössbauer spectrum of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ which was substantially different from the absorption spectrum, suggesting that iron states different from the parent high-spin Fe(III) might be produced as a result of the chemical reactions of energetic ^{57}Fe.

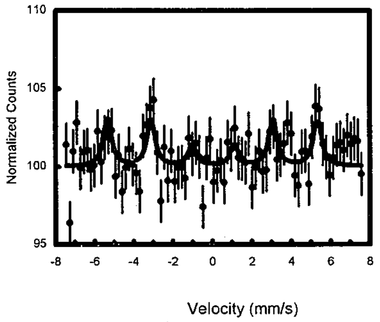

Fig.1, In-beam Mössbauer spectrum of metallic iron

3P13 Affinity of various bio-trace elements to lipid membrane: *In vitro* study using multitracer

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Affinity of several bio-trace elements to various reconstructed lipid membranes (liposomes) was assessed using multitracer analysis technique (MTAT). When multitracer solution was administered to living animal, iron uptake in the liver was higher in microsomal fraction compared with other cell fractions. Not only iron but also other metal ions showed relatively high accumulation in the liver microsomal fraction. To estimate affinity of bio-trace elements to the sub-cellular components such as lipid membranes, MTAT was applied to the simultaneous analysis of several bio-trace elements.

A hydrochloric acid solution containing multitracer was prepared from a silver foil irradiated with a ^{14}N beam of 135 MeV/nucleon at the RIKEN Ring Cyclotron. 7.5 mM chloroform solution of several phospholipids and 1.5 mM chloroform solution of cholesterol were mixed (1 : 1) and evaporated dryness. Lipids were resuspended with 0.01 M Tris-HCl buffer and liposome of the phospholipid was prepared. An aliquot of the multitracer solution was added to liposomal suspension. Liposomes were incubated with multitracer for 1 hr. After incubation, liposomes were collected by centrifugation (3000 rpm, 15 min, 3 times). Affinity of an element was estimated with radioactivity remained on the liposome. The γ-ray radioactivity of the liposome was measured with the high-purity Ge semiconducting detector.

Phosphatidylcholine and sphingomyelin liposomes showed a similar pattern for elemental affinity. Phosphatidylcholine and sphingomyelin have a quanternized amine in its structure. In contrast, phosphatidylserine, phosphatidylglycerol, and phosphatidylinositol liposomes showed another similar pattern for elemental affinity, except that phosphatidylinositol liposome has no affinity with vanadium.

3P 14

PRODUCTION OF ENDOHEDRAL ^{133}Xe-FULLERENE BY ION IMPLANTATION

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Endohedral fullerene, which encapsulates one, two or three atoms within a fullerene cage, has been produced by using arc-discharge, laser-vaporization and nuclear-reaction processes. The products by these methods are mixtures of different species of fullerenes, e.g., C_{82} and C_{84}, with different encapsulated atoms. To obtain a product containing one species of endohedral fullerene in high purity, ion-implantation may be a promising process, in particular for radioisotopes. In the literature, however, light elements such as He and Li have been encapsulated into fullerene by ion-implantation. In the present paper, we describe the production of endohedral ^{133}Xe-fullerene by implantation of ^{133}Xe ions into a fullerene target.

The targets used for ion-implantation were made by vacuum evaporation of 1 mg of C_{60} or C_{70} on Ni foils in an area of 25mmϕ. Implantation of ^{133}Xe ions was carried out with an isotope separator at an acceleration energy of 40 keV. After ion implantation, the targets were dissolved in o-dichlorobenzene. The target solutions were filtered through a millipore filter to remove insoluble materials. The filtrates were injected into a column of 5PBB, 5PYE or Buckyprep supplied by Cosmosil and eluted with o-dichlorobenzene at a flow rate of 1 ml/min. The concentration of fullerene in the effluent was continuously monitored by a UV detector. The effluent from the UV detector was collected for 0.5 min interval and the ^{133}Xe radioactivity in each fraction was measured by γ-ray spectrometry.

Figure 1 shows the elution curves of ^{133}Xe radioactivity and C_{60} concentration obtained by using Buckyprep column. The peak of the UV chromatogram at 4 min corresponds to C_{60}, as determined at the calibration run. The strong correlation observed between the C_{60} and ^{133}Xe peaks corroborates the formation of ^{133}Xe@C_{60}, although the ^{133}Xe peak was followed by a tail. The same strong correlation was observed between C_{60} and ^{127}Xe by Otsuki *et al.*[1)] using a nuclear reaction for production of ^{127}Xe@C_{60}, and also between C_{60} and Ar by DiCamello *et al.*[2)] applying high-pressure and high-temperature for production of Ar@C_{60}, although their column materials were not the same as ours. Similar HPLC data obtained for the ^{133}Xe-implanted C_{70} samples corroborate the formation of ^{133}Xe@C_{70}.

As mentioned above, the ^{133}Xe peak was followed by a tail. Similar tails were observed for the other column materials used. The tailing in the elution of ^{133}Xe suggests a possibility of isolation of endohedral ^{133}Xe fullerene from empty fullerene.

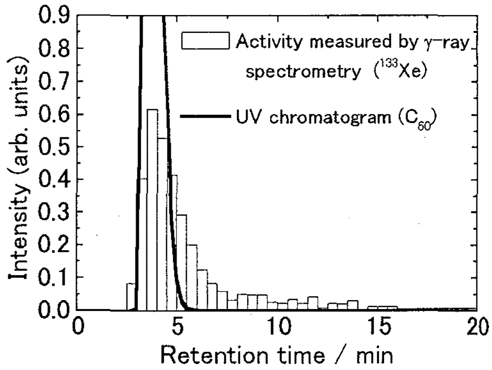

Fig. 1. HPLC elution curves of ^{133}Xe and C_{60} obtained by using Cosmosil Buckyprep column.

1. T. Otsuki *et al.*, *Phys. Rev. Lett.*, 81, 967 (1998).
2. B. A. DiCamello *et al.*, *J. Phys. Chem.*, 100, 9197 (1996).

3P15

The abnormal metabolism of trace elements in mouse induced by Zn deficiency during the growing period

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Zinc deficiency induces various symptoms and abnormal metabolisms of different trace elements. Our previous works have shown the change in the concentrations of Zn and other trace elements, such as Mn, Fe, and Co, in various organs and tissues of Zn-deficient mice.[1a,b,c)] Furthermore, we also found a correlation between Zn and Co concentrations in the liver of the mice fed with Zn-deficient diet during the growing preriod.[1c)] The Zn-deficient symptoms will get worse in younger stage. However, the detail mechanism of the change in metabolism of trace elements during the growing period have not been made clear yet. Therefore, in the present work, we investigated the behavior of Zn and other trace elements in mice fed with Zn-deficient diet in the growing period after weaning using the multitracer technique. We compared the obtained results with those for the adult mice in order to find out more knowledge of functions and interdependencies of Zn and other trace elements in growing organisms.

Three-week old and 8-week old male mice of ICR strain were divided into two groups, respectively; (a) one group was fed with Zn-deficient diet and distilled water, and (b) the other group fed with control diet and distilled water. After 3 weeks of this treatment, a multitracer solution, which was prepared from Ag target, was injected intraperitoneally or orally administered. At 6, 24 and 72 hours after administration, various organs and tissues, such as liver, kidney, pancreas, testis, bone, and intestine, were removed and subjected to gamma-spectrometries. High uptakes of Zn and Co were found in (a) when the multitracer solution was administered orally, whereas no significant differences of Co uptake were found between (a) and (b) when the tracer solution was injected intraperitoneally. The results indicate that this enhancement of Co uptake from intestine in Zn-deficient state will be one reason for a high Co concentration in all the organs and tissues of Zn-deficient mice.

1. a) M. Yanaga, et. al., *J. Radioanal. Nucl. Chem.*, **231**, 187(1998); b) *ibid*, **243**, 661(2000); c) *ibid.*, **245**, 255 (2000).

3P16 ^{57}Fe Mössbauer spectra of (η^6-arene)ruthenium(Ⅲ) complexes having 1,1'-bis(diphenylphosphinomethyl)ferrocene

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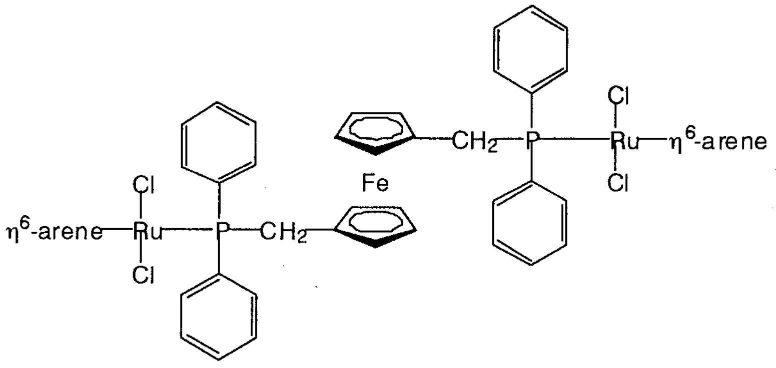
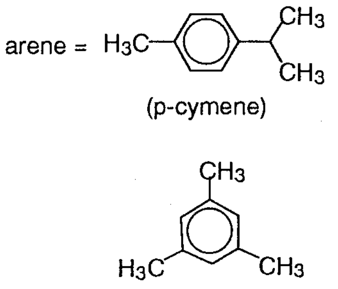
Recently ^{121}Sb Mössbauer spectra of the organometallic compound in which CpFeL (L= (CO)$_2$, (PPh3)$_2$, dppe) coordinate to hypervalent antimony atom were measured, and it was found that the electronic states of antimony atom are affected by the ligand L in the organometallic fragment. However, no significant change in the electronic state of iron atom was suggested by ^{57}Fe Mössbauer spectra. On the other hand, the trinuclear complex [(η^6-arene)RuCl$_2$]$_2$(dpmf) in which 1,1'-bis(diphenylphosphinomethyl)ferrocene (abbreviated as dpmf) coordinates to Ru atom have been reported [1]. A cyclic voltammetric study has shown that a remarkable redox potential change is introduced by changing the arene ligand or bridging ferrocenyl ligand. This study is carried out to examine whether such a change in electronic state of iron atom in the dpmf ligand is observed in ^{57}Fe Mössbauer spectra.





The samples were prepared according to the literature [1]. ^{57}Fe Mössbauer spectra were measured at room temperature and 77 K using a ^{57}Co/Rh source.

Each ^{57}Fe Mössbauer spectrum shows a doublet absorption for the ferrocenyl compounds. The isomer shift (δ:retalive to α-iron foil at room temperature) and ΔE_Q values for [(η^6-*p*-cymene)RuCl$_2$]$_2$(μ-dpmf) at 77 K are 0.51 and 2.40 mms^{-1}, respectively. The δ and ΔE_Q values for [(η^6-1,3,5-Me$_3$C$_6$H$_3$)RuCl$_2$]$_2$(μ-dpmf) are 0.51 and 2.38 mms^{-1}. The value are almost identical between two complexes. These values are also closed those of unsubstituted ferrocene (δ=0.53, ΔE_Q=2.37 mms^{-1}). Our experiment is still in progress to clarify the origin of the negative change in Mössbauer parameters. The Mössbauer spectra for other η^6-arenes such as 1,2,3-Me$_3$C$_6$H$_3$, 1,2,3,5-Me$_4$C$_6$H$_2$, 1,2,3,4-Me$_4$C$_6$H$_2$, C$_6$Me$_6$ will be presented.

[1] Jian-Fang Mai, Yasuhiro Yamamoto, *J. Organomet. Chem.* **560** (1998) 223-232

3P 17 ^{127}I Mössbauer Spectra for Phenyliodonium Ylides

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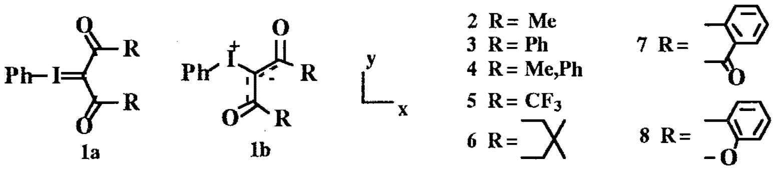
Phenyliodonium ylides are frequently drawn as **1a** in which there is a double bond between iodine and carbon atom is present, but some X-ray diffraction studies have been shown that structure **1b** is actual. Thus we measured ^{127}I Mössbauer spectra for the compounds **2** – **8** to obtain the knowledge of iodine-carbon bond in iodonium ylides.



The compounds were prepared according to the literatures. ^{127}I Mössbauer spectra were measured at 20 K by using a $Mg_3{}^{127m}TeO_6$ source (1.6 GBq) prepared by the neutron irradiation at the reactor core of JRR-3M of JAERI.

The obtained Mössbauer parameters, i.e. isomer shift (δ), quadruplole coupling constant (e^2qQ) and asymmetric parameter (η), estimated valence electron populations (N_I) and electric charge (Z_I) for iodine atom are shown in the Table 1. The populations were estimated by applying the Towns-Dailey and Perlow-Perlow treatments. The axis was adopted as in the above scheme by referring to results of X-ray diffraction, and the population of p_z orbital was assumed to be 2.00 since the orbitals occupied by lone pair electrons. The obtained Mössbauer parameters of 2 – 8 compounds were very close to those of diphenyliodonium salt Ph_2IX, (X=Cl,Br). This means that the electronic structures of the iodonium ylides are almost the same as those of Ph_2IX and the structure **1b** is the preferable expression. To examine the possibilities of some double bond character, the electron populations has been changed to N_z=1.90 from to 2.00. Then the charges on the iodine atom (Z_I) become as large as +1.11 and +1.05 for **3** and **7**, respectively. These values are unreasonably large because iodonium ylides has no electron-attracting group. Such a large values have been observed in iodobenzene dichlorides and iodobenzene diacetates. As a result, ^{127}I Mössbauer parameters suggest the double bond character for iodonium ylides are very small. This agrees with the results of X-ray determinations.

Table 1. ^{127}I Mössbauer parameters and valence electron populations for iodine atom

	δ/mms^{-1}	e^2qQ/ mms^{-1}	η	N_x	N_y	N_z	N_s	N_t	Z_I
2	-0.45	40.4	0.47	1.31	1.05	2.00	1.89	6.25	+0.75
3	-0.48	40.7	0.46	1.30	1.05	2.00	1.89	6.24	+0.75
4	-0.51	40.0	0.46	1.33	1.05	2.00	1.90	6.28	+0.72
5	-0.70	43.2	0.46	1.26	0.99	2.00	1.94	6.19	+0.81
6	-0.45	39.3	0.45	1.32	1.08	2.00	1.89	6.30	+0.70
7	-0.44	38.9	0.45	1.36	1.06	2.00	1.89	6.31	+0.69
8	-0.53	39.4	0.51	1.34	1.07	2.00	1.93	6.32	+0.69
Ph_2ICl	-0.64	42.8	0.40	1.25	1.02	2.00	1.93	6.19	+0.81
$PhICl_2$	-0.87	52.7	0.75	0.64	1.20	2.00	1.93	5.79	+1.20

3P18 X-Ray Diffraction and Mössbauer Studies of First-Row Transition Metal Complexes with Hydroxyquinone Derivatives

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Dianions of 2,5-dihydroxy-1,4-benzoquinone (DHBQ) and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid : CA) are capable of bridging transition metal ions to form coordination polymers. Recently Kawata et al.,[1] have revealed crystal structures of $[M(CA)(H_2O)_2](H_2O)$ ($M=Fe^{2+}$,Co^{2+},and Mn^{2+}), consisting of a one dimensional zigzag polymer chain with two *cis* water ligands. The delocalized π systems of the CA and DHBQ ligands could provide interesting and possibly useful electronic communication between appropriate metal centers. In order to clarify the electronic communication, we have prepared a series of mixed-metal complexes $[MM'(CA)(H_2O)_2](H_2O)$ and $[MM'(DHBQ)(H_2O)_2](H_2O)$ ($M=Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; $M'=Fe^{2+}$; M:M'=2:1), and measured their powder X-ray diffraction (XRD) patterns and Fe-57 Mössbauer spectra.

XRD patterns of the pure metal complexes $[M(CA)(H_2O)_2](H_2O)$ ($M=Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) showed these complexes, except for the Ni- and Cu-complexes, to be isomorphous with the Fe^{2+} analogue. The Ni- and Cu-complexes seem to be a straight chain coordination polymer with two *trans* water ligands in the earlier study.[2] The XRD patterns of the mixed-metal complexes $[MM'(CA)(H_2O)_2](H_2O)$ are similar to those of the corresponding pure metal complexes, except for the Cu-Fe complex, suggesting that the Fe^{2+} ions distribute uniformly. The XRD pattern of the mixed Cu-Fe complex indicates the coexistence of the pure Cu- and Fe-complexes.

An Fe-57 Mössbauer spectrum of the pure $[Fe(CA)(H_2O)_2](H_2O)$ complex suggested that the iron(II) ion is a high spin state with I.S.=1.18 mm/s for relative to α-Fe and Q.S.=2.54 mm/s at room temperature, in good agreement with the previous results.[1,3] The Mössbauer spectra of the mixed-metal complexes $[MM'(CA)(H_2O)_2](H_2O)$ agree with that of the pure Fe-complex, except for the Ni-Fe complex, indicating no electronic communication between the metal centers. The Ni-Fe complex (I.S.=1.15 mm/s and Q.S.=1.80 mm/s) has a different structure from the pure Fe complex.

In the DHBQ complexes of the first-row transition metals the XRD patterns showed these complexes to be isostructural, except for the Cu-complex. The Ni-complex has the same structure with the Fe complex, different from the CA complexes. The XRD patterns of the mixed-metal complexes are similar to those of the corresponding pure metal complexes. The Mössbauer data of $[Fe(DHBQ)(H_2O)_2](H_2O)$ are I.S.=1.16 mm/s and Q.S.=1.46 mm/s at room temperature, in good agreement with the previous data.[3] The Mössbauer spectra of the mixed-metal complexes agree with that of the pure Fe-complex within the error limits. This fact suggests no electronic communication between the metal centers, as well as the mixed-metal CA complexes.

1. S. Kawata;, S. Kitagawa;, H. Kumagai;, T. Ishiyama;, K. Honda;, H. Tobita;, K. Adachi;, M. Katada, *Chem. Mater.*, 10, 3902 (1998).
2. S. Kawata;, S. Kitagawa;, H. Kumagai;, C. Kudo;, H. Kamesaki;,T. Ishiyama;, R. Suzuki;, M. Kondo;, M. Katada, *Inorg. Chem.*, 35, 4449 (1996).
3. J. T. Wrobleski;, D. B. Brown, *Inorg. Chem.*, **18**, 498 (1979).

3P 19

Mössbauer and EPR Spectroscopic Investigations of the [Ethylenediaminetetraacetato]Iron-Hydrogen Peroxide Complex

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It has been known that iron(III)-ethylenediaminetetraacetate (Fe-EDTA) reacts with hydrogen peroxide to form a side-on bound peroxo adduct in an alkaline solution. We have studied the reaction of several iron-polyaminocarboxylate complexes like Fe-EDTA and hydrogen peroxide by using electron paramagnetic resonance (EPR) spectroscopy, UV-Vis absorption spectrometry and cyclic voltammetry. The results obtained were classified into two groups according to the chelate size formed by iron ion and a diamine moiety of the ligands. When hydrogen peroxide was added to the solutions of iron(III) complexes which have a five-membered ring, EPR spectra of the side-on bound peroxo complex were observed around pH 10. Intensity of EPR signal of the side-on bound peroxo complex decreased with increasing pH.[1] In addition, small EPR signal of Fe(II)-superoxo complex was also observed. These EPR spectral changes indicate that iron(III) ion is reduced by peroxo anion to form an iron(II)-superoxo complex. On the other hand, when hydrogen peroxide was added to the solutions of iron(III) complexes having a six-membered ring, EPR spectra of only iron(II)-superoxo complex were observed.

In this study, to characterize the electronic states of these complexes in detail and to obtain the direct evidence of the existence of Fe(II)-EDTA, we applied Mössbauer spectroscopy to the Fe(III)-EDTA and hydrogen peroxide system. NMR studies showed that Fe-EDTA in aqueous solution is in an equilibrium of various ionic forms such as $[\text{Fe-EDTA-H}_2\text{O}]^-$, $[\text{Fe-EDTA-OH}]^{2-}$ and $[\text{Fe-EDTA-(OH)}_2]^{3-}$ according to the pH of the solution.[2] From Fe-57 Mössbauer spectra of frozen solution of Fe-EDTA (77 K), $[\text{Fe-EDTA-H}_2\text{O}]^-$ (IS=0.45mm/s) $[\text{Fe-EDTA-OH}]^{2-}$ (IS=0.46mm/s, QS=1.7mm/s) and $[\text{Fe-EDTA-(OH)}_2]^{3-}$ (IS=0.46mm/s, QS=0.68mm/s) were assigned. We are now measuring Mössbauer spectra of the reaction mixture of Fe-EDTA and hydrogen peroxide. The reaction mechanisms based on the results obtained will be discussed.

1)S. Fujii. H. Ohya-Nishiguchi, N. Hirota; *Inorg. Chim. Acta,* 175 (1990) 27-30

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3P 20

X-RAY CRYSTALLOGRAPHIC AND MÖSSBAUER STUDIES OF TETRAALKYLAMMONIUM HEXACYANOFERRATES(III)

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Potassium hexacyanoferate(III), $K_3[Fe(CN)_6]$ has been investigated by ^{57}Fe Mössbauer spectroscopy from the early days of the spectroscopy. Some extent of line-broadening, indicating the slow paramagnetic relaxation of electronic spins, was observed in the Mössbauer spectra at low temperatures.[1] In the present study, we have studied two kinds of $[Fe(CN)_6]^{3-}$ complexes with bulky cations, $[NEt_4]_3[Fe(CN)_6]$ (**1**)[2] and $[NBu_4]_3[Fe(CN)_6]$ (**2**), to compare their Mössbauer behaviors with that of $K_3[Fe(CN)_6]$.

Compound **1** crystallized in the monoclinic $P2_1$ space group ($Z = 2$) with Fe-Fe distances of 8.9 and 9.2 Å; similar monoclinic lattices were often reported for $M_3[Fe(CN)_6]$ and $M_2M'[Fe(CN)_6]$ complexes. The longer Fe-Fe distances than those of alkali metal salts of $[Fe(CN)_6]^{3-}$ (5.4 Å for $M = K^+$), exert a distinct effect on the ^{57}Fe Mössbauer spectral shape. As shown in Fig. 1, compound **1** began to clearly show a magnetically-relaxed spectrum below ca. 40 K, and its line width at 4.2 K was much greater than that of $K_3Fe(CN)_6$, suggesting a decreased spin-spin relaxation rate in **1**. The sign of the principal component of the electric field gradient (V_{zz}) was determined to be negative from the asymmetry of the line-shape. Compound **2** showed further broadened spectra, which would reflect the difference in bulkiness between NEt_4^+ and NBu_4^+.

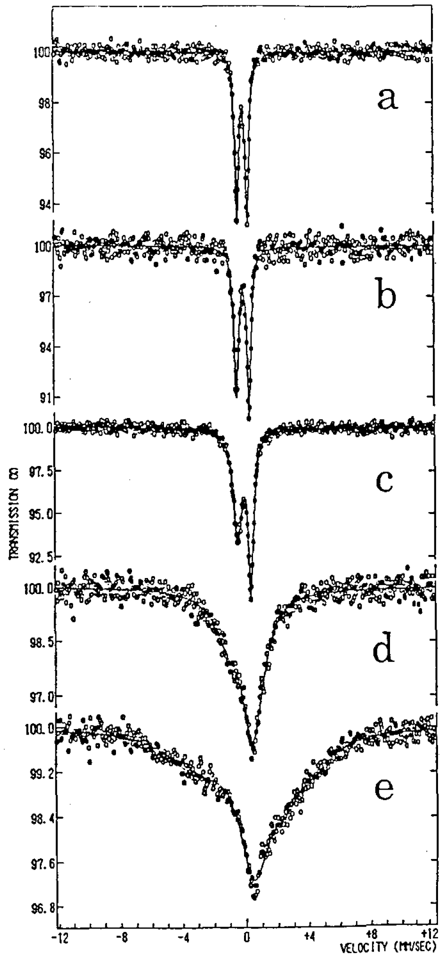

Fig. 1 Mössbauer specra of **1** at (a) 200 K, (b) 120 K, (c) 78 K, (d) 40 K and 4.2 K.

1. W. T. Oosterhuis; G. Lang; S. Debenedetti, *Phys. Lett.*, **24A**, 346 (1967).
2. P. K. Mascharak, *Inorg. Chem.* **25**, 245 (1986).

3P 21

^{121}Sb and ^{57}Fe Mössbauer spectra of iron carbonyls having Sb–Fe bonds

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Organometallic compounds having main group element–transition metal bond have been extensively studied from the many aspects in these two decades. We have been interested in the bonding in such a compound and undertaken Mössbauer spectroscopic studies using ^{121}Sb and ^{57}Fe nuclides. Quite recently we have reported the Mössbauer spectra for $[\mathrm{RSb}\{\mathrm{Fe(CO)_4}\}_3]^{n-}$ {R = H (**1**), $\mathrm{Fe(CO)_4}$ (**2**)} in which $\mathrm{Fe(CO)_4}$ fragments are coordinate to antimony atom. This study is carried out with the intention of extending to other iron carbonyl clusters having Sb–Fe bonds. In this paper ^{121}Sb and ^{57}Fe Mössbauer spectra for 11 iron carbonyl clusters are reported.

The clusters were prepared in a glove box filled with highly pure nitrogen according to the literatures. ^{121}Sb Mössbauer spectra were measured at 20 K using a $\mathrm{Ca^{121m}SnO_3}$ source. An Austin S-600 spectrometer and LC-9 laser interferometer were used for the measurement. The spectra were analyzed using a transmission integral method and the isomer shift (δ_{Sb}) values are given relative to InSb at 20 K. ^{57}Fe Mössbauer spectra were measured at 80 K using a ^{57}Co(Rh) source on a Wissel Mössbauer driving system.

Most of ^{121}Sb Mössbauer spectra other than $[\mathrm{XSb}\{\mathrm{Fe(CO)_4}\}_3]^{2-}$ {X=Cl (**3**), Br (**4**), I (**5**)} are symmetric and suggest rather small quadrupole coupling constants (e^2qQ) and/or large asymmetry parameters (η). The spectra for $[\mathrm{HSbFe_4(CO)_{13}}\}]^{2-}$ (**6**) shows truly small e^2qQ and those of $[\mathrm{SbCrFe_3(CO)_{17}}]^-$ (**7**) and $[\mathrm{SbFe_4(CO)_{14}}]^-$ (**8**) indicate moderately large e^2qQ and large η, indicating large imbalance in electron populations. $[\mathrm{SbFe_4(CO)_{16}}]^{2-}$ (**9**), $[\mathrm{Sb_2Fe_5(CO)_{17}}]^{2-}$ (**10**) and $[\mathrm{Sb_2Fe_6(CO)_{20}}]^{2-}$ (**11**) have rather small e^2qQ and large η values, and for this reason there is some difficulty in determining the sign of e^2qQ correctly. The compounds **3**– **5**, having an electron-withdrawing atom, have large negative e^2qQ values. There is an approximately linear correlation between δ and $|e^2qQ|$ values as shown in Fig. 1. Interestingly the e^2qQ values decrease with increase in the negative charge of the cluster. This suggests that the electrons provided from the iron fragments, negative charge in other word, are accommodated in the antimony's p orbitals and not in iron's orbital. In the ^{57}Fe Mössbauer spectra, the different iron sites are distinguished into the terminal $\mathrm{Fe(CO)_4}$ fragments and the bridging $\mathrm{Fe(CO)}_n$ (n = 3,4) fragments.

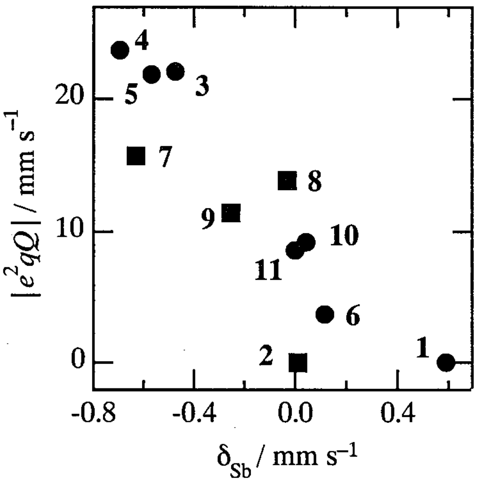

Fig. 1 Plot of $|e^2qQ|$ against δ of ^{121}Sb Mössbauer spectra

3P 22 Erbium-166 Mössbauer Spectra of Er(III)-EDTA Complexes

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In the rare earth (Ln) complexes it is well recognized that the gradual decrease of ionic radii Ln^{3+} causes a change in coordination number. In the case of EDTA complexes, the coordination number is varied from 9 to 8 and this occurs at erbium. Recently we have found that Er^{3+} complex of EDTA adopts both coordination number. In this paper we report the X-ray crystal structures for $M[Er(edta)(H_2O)_n]\cdot m(H_2O)$ ($M = Na, K, NH_4$) and their ^{166}Er Mössbauer spectra. The difference in the coordination number is found to induce the difference in paramagnetic relaxation time.

The EDTA complexes were prepared by the reaction of Er^{3+} and H_4edta followed by the pH adjustment with MOH (M = Na, K) or ammoniac water. The single crystals were obtained by slow evaporation of water from their aqueous solution. ^{166}Er Mössbauer spectra were measured at 12 K using a $^{166}Ho/Y_{0.6}Ho_{0.4}H_2$ source prepared by a neutron irradiation of $Y_{0.6}Ho_{0.4}H_2$ in JRR-4 of JAERI.

The Na salt, $Na[Er(edta)(H_2O)_3]\cdot 2H_2O$ has a nine-coordinate monocapped square antiprismatic structure while the K salt $\{K[Er(edta)(H_2O)]\cdot H_2O\}$ and NH_4 salt $\{NH_4[Er(edta)(H_2O)_2]\cdot 4H_2O\}$ adopt eight-coordinate square anti prismatic structures. In the K salt, interestingly a carboxylic oxygen atom coordinates the neighbouring complex, completing the coordination. The mean bond lengths for the Na salt are Er–O(edta) = 236 pm, Er–O(H_2O) =244 pm and Er–N = 266 pm. Those for the K salt are 230, 238 and 255 pm, and for the NH_4 salt 230, 234.2 and 254.3 pm, respectively. These data indicate that the bond length for the 9 coordination is longer than those for the 8 coordination as expected. The shortest Er–Er distances are 608.1 (Na salt), 578.20 (K salt) and 588.6 pm (NH_4 salt).

The ^{166}Er Mössbauer spectra for these complexes are shown in the figure. Each spectrum shows a paramagnetic relaxation. The Nowick-Wickman model analyses give the relaxation times (τ) of 1.7 ns (Na salt), 0.3 (K salt) and 0.2 ns (NH_4 salt). The difference in τ cannot be simply interpreted by the Er–Er distances in the crystal, but the difference in coordination number , thus the electronic structure, would play important role in the relaxation.

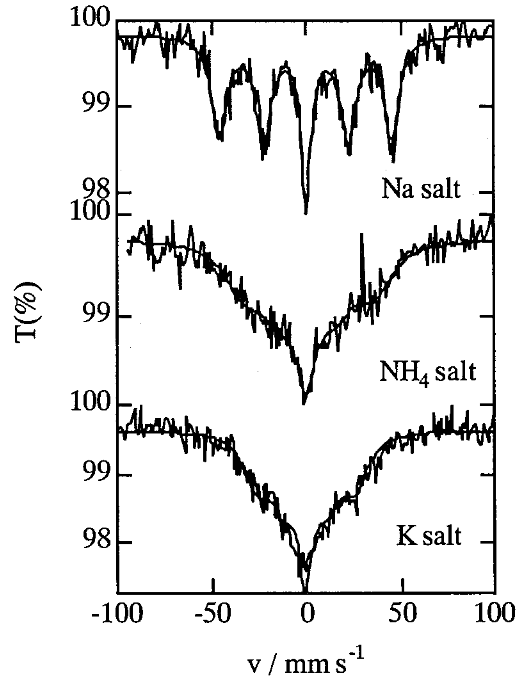

Fig. ^{166}Er Mössbauer spectra for Er-EDTA salt at 12 K

3P23 ^{57}Fe MÖSSBAUER SPECTROSCOPIC STUDY FOR SPIN CROSSOVER COMPOUND $Fe(pyridine)_2Ni(CN)_4$

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Recently, active controls of spin properties by chemical and physical techniques have been attracting much attention in assembled metal coordination polymer system. Spin-crossover behavior in coordination polymer complexes have been associated with the active controls of spin properties. Cooperative effects between the spin-changing molecules are different between the discrete molecular systems and coordination polymer system, thus causing potential differences in spin transition mechanisms. So we have been interested in the two dimensional coordination polymer compounds based on iron(II) tetracyanonickelate (II), whose sheet has pyridine derivatives protruding up and down at each octahedral iron(II) atom. The Hofmann pyridine complex $Fe(py)_2Ni(CN)_4$ **1** shows iron(II) spin-crossover behavior[1]. The spin-transition of octahedral iron(II) site in **1** occurs between 210 K and 170 K with hysteresis. Emission Mössbauer spectroscopic studies for ^{57}Co-labelled analogous complexes are in progress to study the nuclear-decay-induced exited spin state trapping (NIESST)[2].

The spin crossover is influenced by several factors. Some of them belong to the sample itself such as preparation, handling and composition. We report here ^{57}Fe Mössbauer spectroscopic studies on $Fe(py)_2Ni(CN)_4$ **1** samples treated by gaseous xenon at high pressure. The sample was exposed for 15 days to gaseous Xe compressed to 10 kbar (1.0 GPa) at temperature 298 K in a piston-cylinder high pressure apparatus. After reduction of pressure the sample was taken out from the apparatus and used for ^{57}Fe Mössbauer measurements. IR data and TG data did not indicate that Xe atoms were accommodated with the framework of **1**. ^{57}Fe Mössbauer spectra suggest that the spin crossover behavior of the sample is the same as that without the high pressure treatment.

[1] T. Kitazawa, Y. Gomi, M. Takahashi, M. Takeda, M. Enomoto, A. Miyazaki and T. Enoki, *J. Mater. Chem.*, 1996, **6**, 119-121.

[2] T. Sato, F. Ambe, T. Kitazawa, H. Sano and M. Takeda, *Chem. Lett.*, 1997, 1287-1288.

Microstructure Analysis of (BaCa)(FeMg)$O_{3-\delta}$ for CO_2 Rapid Absorption by Mössbauer Spectroscopy

3P24

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(Ba,Ca)(Fe,Co)$O_{3-\delta}$ and (Sr,Ca) (Fe,Co)$O_{3-\delta}$ for CO_2 rapid absorption at high temperatures have been studied by Mössbauer spectrometry[1,2]. Mg ion is one of alkaline earth ions to form carbonate ~~ion~~ so easily that the carbonates can decompose at lower temperatures than the other alkaline earth metal carbonates. Mg ion is expected to occupy in the B site of perovskite oxides because of the small ionic radius. (Ba,Ca)(Mg,Fe) oxides or (Sr,Ca)(Mg,Fe) oxides are interesting for the CO_2 absorption properties and Fe ion behavior in these oxides. These mixed oxides were prepared by mixing the metal compounds by ball milling for 30 min and heated in air at 850°C for 12 hours and 950°C for 24 hours.

$(Ba_{0.5}Ca_{0.5})(Fe_{0.5}Mg_{0.5})O_{3-\delta}$ was cubic structure and the lattice constant increased at higher temperatures than around 400 °C although many oxygen defects were produced, whereas $(Ca_{0.95}Ba_{0.5})(Fe_{0.5}Mg_{0.5})O_{3-\delta}$ was orthorhombic structure, and the lattice constant in C axis increased remarkably with the temperatures. The CO_2 absorption properties of these mixed oxides were examined by thermal gravimetric analysis at heating rate of 20°C/min in CO_2 atmosphere. The maximum amount of $(Ba_{0.5}Ca_{0.5})(Fe_{0.5}Mg_{0.5})O_{3-\delta}$ and $(Ca_{0.95}Ba_{0.5})(Fe_{0.5}Mg_{0.5})O_{3-\delta}$ were 0.5 mole CO_2 and 0.45 mole CO_2 at 890°C, respectively. At 1000°C, the absorbed oxides were decomposed, but the remaining amounts of CO_2 were 0.27 mole for the former and 0.03 mole for the latter, respectively. In XRD, the Ba and Ca carbonate compounds were identical, but the other peaks were very weak, and so Mössbauer spectroscopy is good tool for microanalysis of these oxides structures. Paramagnetic doublets with IS=0.31mm/s and QS=0.11mm/s, and IS=-0.1mm/s and QS=0.8mm/s were observed in Mössbauer spectra of $(Ba_{0.5}Ca_{0.5})(Fe_{0.5}Mg_{0.5})O_{3-\delta}$, and after CO_2 absorption, three magnetic components of a pair of tetrahedral Fe(III) (Bin = 43.4T) and octahedral Fe(III) (Bin=51.0T) and spinel Fe(III) (Bin=47T) were produced. In the Ca rich mixed oxides, a pair sextet of tetrahedral and octahedral Fe(III) were observed with a small amount of paramagnetic peaks, and the pair sextet remained with the reducton of paramagnetic peaks without the formation of spinel compound after absorption and desorption of CO_2. CO_2 is considered to be trapped in the layer structures of brownmillerite. The relationship of Mössbauer parameters and amount of CO_2 absorbed will present in this paper.

3P25

DEVELOPMENT AND APPLICATION OF PARALLEL-PLATE AVALANCHE COUNTER FOR IN-BEAM MÖSSBAUER SPECTROSCOPY

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A parallel-plate avalanche counter (PPAC), a gas-filled resonance detector where conversion electrons from resonantly absorbed 14.4 keV of a Mössbauer γ-ray are detected, has been employed for in-beam Mössbauer experiments. The detector has high detection efficiency and a large signal-to-noise ratio with high counting rate. Since the performance of the PPAC is strongly dependent on several factors (the kinds of counter gases and their pressures, applied voltage, and so on), we have evaluated the influence of them against the counting efficiency of the PPAC.

In this study, the PPAC was modified to a gas-flow type in order to maintain a constant counting rate for over a few days. Isobutane was used as a counter gas, and γ-ray of a ^{57}Co/Rh Mössbauer source was detected. Figure 1 shows the pressure dependence of the counting rate and the area intensity under the condition of the gas flow-rate of 5.0 cc/min and an applied voltage of -735 V. A small cusp of the area intensity was observed around 26 mbar of the counter-gas pressure, though the counting rate decreased with the increase of the pressure.

Optimum condition to operate the PPAC, especially in coexistence with energetic β- and γ-quanta that could cause in high background level in in-beam experiments, will be discussed.

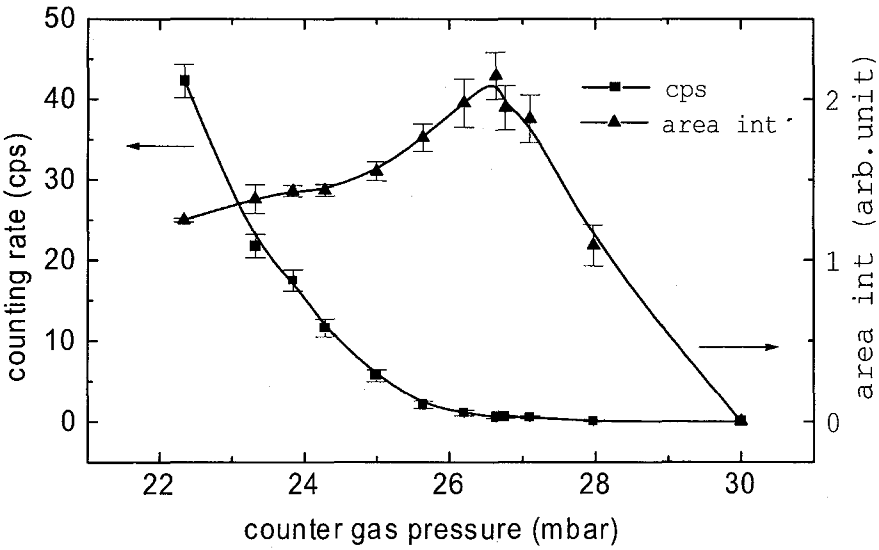

Fig. 1. Pressure dependence of counting rate and area intensity under a gas flow of 5.0 cc/min and an applied voltage of −735 V.

3P 26

SYNTHESES AND MAGNETIC PROPERTIES OF IRON(III) COMPLEXES WITH IMIZAZOLE GROUPS

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Iron(III) complexes with the general formula of [Fe(R-Himap)$_2$]X and [Fe(R-Himat)$_2$]X (R= H, Me, Ph; X= ClO_4, NO_3, BPh_4) have been synthesized. The complexes have a N_4O_2 donor set or a N_4S_2 donor set The complexes have 5 and 5 member rings around an iron(III) atom per one chelate ring, that is, “5-5 member rings”. The crystal structure, Mössbauer spectra, magnetic properties and absorption spectra of the complexes were examined. In addition, [Fe(Himsa)$_2$]ClO_4 having “5-6 member rings” of a N_4O_2 donor set has been synthesized. [Fe(Ph-Himap)(Ph-imap)] obtained by the deprotonation from [Fe(Ph-Himap)$_2$]ClO_4 with a N_4O_2 donor set has been also synthesized. Mössbauer spectra and magnetic properties of those complexes were examined. The X-ray structure of single crystals of [Fe(Himap)$_2$]BPh_4 was determined: $C_{44}H_{36}N_6BO_2Fe$, triclinic, space group P__ (# 2), a = 12.452(2) Å, b = 12.748(2) Å, c = 11.996(2) Å, _ = 103.97(1)°, _ = 90.78(1)°, _ = 84.70(1)° and Z = 2. The moiety of an iron atom of [Fe(Himap)$_2$]BPh_4 was a pseudo octahedral with a FeN_4O_2 geometry. In solid state, [Fe(R-Himap)$_2$]X was in the high-spin state (about 5.9 B.M. at 80 K), and [Fe(R-Himat)$_2$]X was in the low-spin state (about 2.0 B.M. at 293 K). The complex [Fe(Himsa)$_2$]ClO_4 with “5-6 member rings” and the deprotonated complex [Fe(Ph-Himap)(Ph-imap)] with a N_4O_2 donor set were also in the high-spin state (6.0 B.M. at 80 K).

It was concluded that ligand field strength of [Fe(R-Himat)$_2$]X with a N_4S_2 donor set is stronger than that of [Fe(R-Himap)$_2$]X with a N_4O_2 donor set in solid state, the ligand field strength of a N_4S_2 donor set being stronger than that of a N_4O_2 donor set.

3P 27

MECHANISM OF Fe^{2+} OXIDATION IN OLIVINE STRUCTURE - MÖSSBAUER STUDY

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The mechanism of the thermally induced oxidation of Fe^{2+} in olivine, $(Mg,Fe)_2SiO_4$, was studied using ^{57}Fe Mössbauer spectroscopy. Three iron(III) oxides were identified as products of the thermal conversion of olivine in air. The air-oxidation of Fe^{2+} in the range of 600-800 °C results in the formation of superparamagnetic γ-Fe_2O_3 nanoparticles, which are represented in room temperature (RT) Mössbauer spectra by a broad doublet with hyperfine parameters $IS_{Fe}=(0.36\div0.39)$ mm/s and $QS=(0.55\div0.67)$ mm/s. Low temperature Mössbauer measurement (15 K) showed two magnetic hyperfine field distributions with unequal isomer shifts corresponding to A- and B-sites of ferric ions in the spinel structure of γ-Fe_2O_3 $(Fe_A(Fe_{5/3}\square_{1/3})_B$, A-tetrahedral site, B-octahedral site, $\square$-vacancies). These thermally unstable nanoparticles undergo the isochemical structural change to α-Fe_2O_3 at temperature higher than 700 °C. The large widths of spectral lines reflect the wide distribution of internal magnetic fields in α-Fe_2O_3 phase. The relative ratio of Fe_2O_3 polymorphs depends on the heating time and temperature. At temperatures above 900°C, the transformation mechanism changes and ferrimagnetic $MgFe_2O_4$ appears as the product of Fe^{2+} oxidation. Two non-equivalent sites of iron in the spinel structure of $MgFe_2O_4$ correspond to two sextets with parameters of the hyperfine structure: $IS^1_{Fe}=0.33$ mm/s, $QS^1=-0.05$ mm/s, $B^1=46.2$ T and $IS^2_{Fe}=0.35$ mm/s, $QS^2=-0.10$ mm/s, $B^2=48.9$ T. The increase of values of quadrupole splitting and the significant narrowing of spectral lines observed at higher temperatures could be explained by the gradual crystallisation of $MgFe_2O_4$ particles. RT Mössbauer spectra in figure 1 demonstrate two different mechanisms of iron transformation during the thermal decomposition of olivine in air.

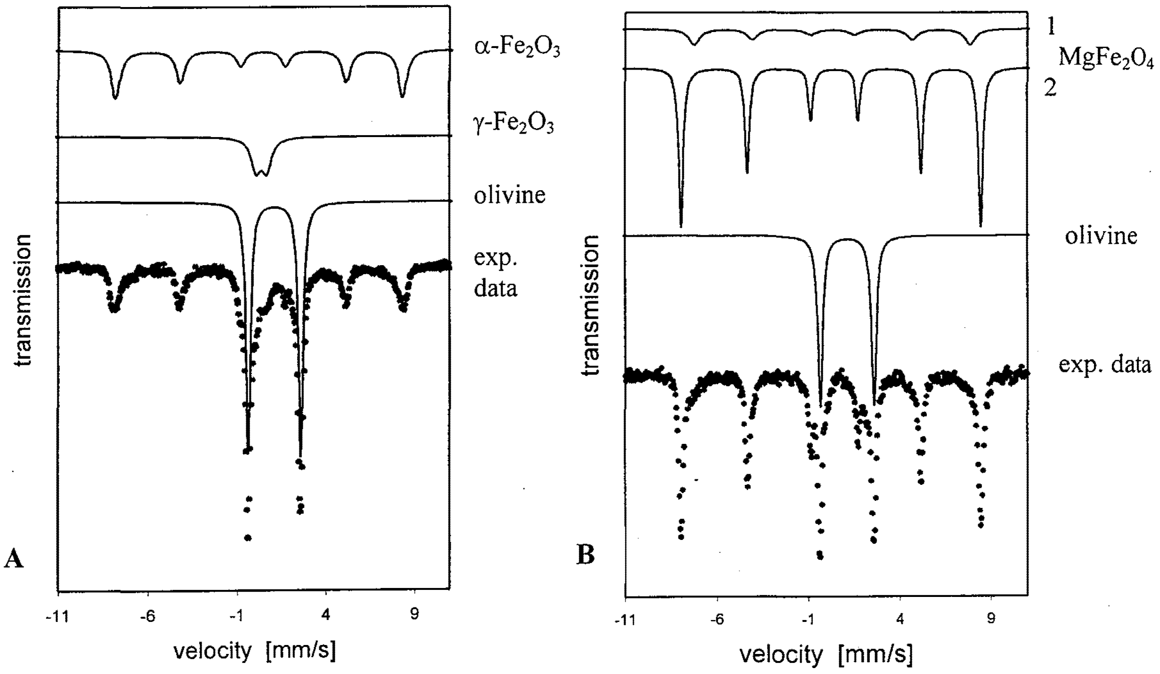

Figure 1. RT Mössbauer spectra of olivine thermally treated at 800 °C (A) and 1200 °C (B) for 1 hour

3P 28

A new analytical method for ^{226}Ra and ^{228}Ra in environmental waters
-Application to the field works-

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New analytical methods were discussed for ^{226}Ra and ^{228}Ra concentrations in environmental waters. These methods were aimed to be applicable to the field works.

Radium is adsorbed on the cation ion exchange resin by a succesive adsorption procedures : the second adsorption procedure is applied to the same sampled water, and Ra concentration can be estimated from the amount of Ra recovered in the two operations by the following calculation.

$$C_1 = C_0 \bullet \alpha \quad \ldots\ldots\ldots \ (1) \qquad C_2 = (C_0 - C_1) \bullet \alpha \quad \ldots\ldots\ldots \ (2)$$

$$\therefore \alpha = 1 - (C_2 / C_1) \qquad C_0 = C_1 / [1 - (C_2 / C_1)]$$

where, C_0 : total amount of Ra in the initial sample water, C_1 : recoverd amount from the initial sample water by the 1st operation, C_2 : recoverd amount by the 2nd operation on the remaining sample water after removal of the 1st operation resin and α : adsorption coefficient.

The recoverd resins were packed into a tin container and activity of ^{226}Ra and ^{228}Ra were measured by a γ-ray spectrometry for the 609keV and 911keV γ-rays from ^{214}Bi and ^{228}Ac in equilibrium respectivily.

Eight hot-spring waters (10 l) and one well water (50 l) were employed for the testing sample. Result are given in Table 1. This method is applicable to 10 l of sample water, having ^{226}Ra conentration of larger than 10 mBq/l and is also applicable to the ordinary ground waters of less than 1 mBq/l by use of 50 - 100 l of sample water.

When the concentration of radium is futher small, and futher large amount of sample water is needed (eg. river water and sea water) , adsorption on the manganese-impregnated aclyic fiber is effictive. Mn-impregnated fiber can concentrate Ra from sevaral handreds liters of sample waters, and the ^{228}Ra/^{226}Ra activity ratios can be obtained by a γ-ray spectrometry.

Table 1 Concentation and activity ratios of radium isotopes in sevaral environmental waters

Sample	^{214}Bi (mBq/*l*)	^{228}Ac (mBq/*l*)	^{228}Ra/^{226}Ra
Hot-spring waters			
Tamagawa	46 ± 8	1120 ± 110	24 ± 5
Masutomi - 1	11 ± 3	-	-
Masutomi - 2	39 ± 4	56 ± 10	1.4 ± 0.3
Masutomi - 3	1020 ± 120	2410 ± 130	2.4 ± 0.3
Sarugajo	40 ± 4	-	-
Arima - 1	157 ± 11	64 ±26	0.41 ± 0.17
Arima - 2	65 ±10	46 ±13	0.71 ± 0.23
Onogawa	281 ± 35	495 ± 60	1.8 ± 0.3
Well water*)	0.64 ± 0.15	-	-

*) Well water from Meiji Univ., Kawasaki

3P 29 Variation of ^{7}Be concentration in surface air at Kagoshima

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1. Introduction

^{7}Be is one of the radioactive products from the cosmic ray spallation reaction with nitrogen and oxygen. Radioactivity of the atmospheric airborne dust is observed around Sendai nuclear power station in Kagoshima Prefecture, Japan and ^{7}Be is always detected. ^{7}Be concentration shows daily, seasonal and annual variations.

2. Experimental

The atmospheric airborne dust for investigation of daily variation of ^{7}Be concentration was collected on the filter by high-volume air sampler. The sample collection was done from April 1999 to March 2000. The atmospheric airborne dust for investigation of seasonal variation of ^{7}Be concentration was collected on the filters by a radioactive dust monitor (low-volume air sampler). The collection period is three months, i.e., January-march, April-June, July-September and October-December. The sample collection was done from 1982 to 2000. ^{7}Be radioactivity of filter was measured by γ -ray spectrometry using high pure Ge-detectors. Annual mean concentration of ^{7}Be was calculated from the data of seasonal variation of ^{7}Be concentration.

3. Results and discussion

Daily variation of ^{7}Be concentration from fall to spring is several times as large as in summer and ^{7}Be concentration is the lowest in summer and high from fall to spring. Annual variation has a cycle of about 10 years .It is suggested that daily and seasonal variations are caused mainly by meteorological conditions and annual variation is caused mainly by solar activities.

Daily and annual variations of ^{7}Be concentration are shown in Fig.1 and Fig.2 .

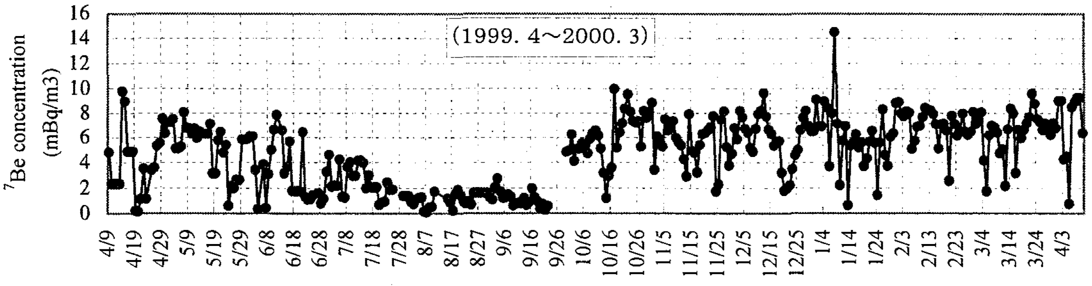

Fig.1 Daily variation

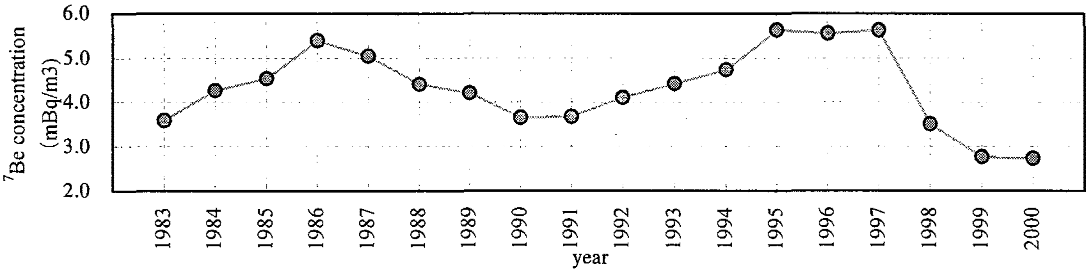

Fig.2 Annual variation

3P30 TRITIUM SEPARATION FROM HEAVY WATER BY ELECTROLYSIS WITH SOLID POLYMER ELECTRODE

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A tritium separation from heavy water by electrolysis using a solid polymer electrode layer was specified on investigation.

Equipments and Methods: Tritium spiked heavy water (~10 Bq g^{-1}) and light water (~80 Bq g^{-1}) were electrolyzed using an electrolysis device with the solid polymer electrode layer. The cathode was porous electrode made of stainless steel or nickel. The temperature around the electrolysis cell was kept at 5 °C, 10 °C, 20 °C and 30 °C. Each experiment was carried out for an hour at the electrolysis current 20A (at 10, 20 and 30 °C) or 15A (at 5 °C). Generated hydrogen and oxygen gases were recombined under a palladium catalyst at ~ 300 °C with nitrogen gas as a carrier. The recombined water was collected with a cold trap. Specific activities of pre-electrolysis and post-electrolysis water in the cell ($\overline{S}_{Cell}$), and that of the recombined water (S_{Rec}) were measured by a liquid scintillation counter. The apparent separation factor (*SF*) was calculated as

$$SF = \frac{\overline{S}_{Cell}}{S_{Rec}} \tag{1}$$

Results: Charge voltage to keep the current 20A was 2-3V. The most appropriate flow rate of the nitrogen gas was 4 L min^{-1}. Yields of the recombined water were more than 90 %. The apparent tritium separation factors of the light and heavy water were ~ 10 and ~ 2, respectively. The temperature dependence of the separation factor of the heavy water was relatively small.

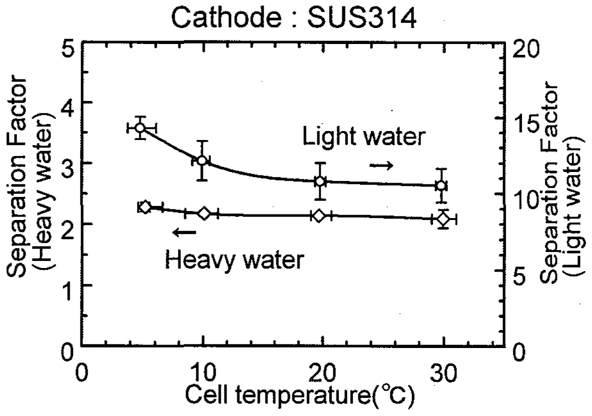
Cathode : SUS314

Figure Separation factor of heavy and light water with SUS cathode.

1.H. K. Rae (Editor), *American Chemical Symposium Series 68* (1978)
2. Kalyanam, K. M. and Sood, S. K. *Fusion Technology* **14**, 524(1988)
3. Saito, M., and Takata, S. *Radioisotopes* **45**, 483(1996)
4. Kakiuchi,, M. *Radioisotopes* **48**, 79(1999)

3P31 ENRICHMENT OF ATMOSPHERIC HYDROGEN BY CRYOPUMP FOR TRITIUM ANALYSIS

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In the atmosphere, artificial and natural tritium exists in several chemical forms such as water (HTO), hydrogen (HT), and methane (CH_3T). The concentration of atmospheric tritium increased considerably by the nuclear tests carried out in 1950s and 1960s. The HT concentration had decreased at slower rate after the Partial Test Ban Treaty (PTBT) in 1963 than the residence time of HT in the atmosphere, which was estimated to be about 4.8 years. The specific activity of HT is about 10^4 times higher than that of HTO. So it is supposed that HT is released from nuclear facilities, probably as T_2. To obtain the information of source for HT in the atmosphere, an analysis of hydrogen isotopes (HT, DT, T_2) would be useful. To analyze hydrogen isotopes in the atmosphere, an atmospheric hydrogen enrichment apparatus and a cryogenic gas chromatographic column were made and their performance were examined.

The atmospheric hydrogen enrichment apparatus provides three cryopumps (ALVAC CRYO-U8H, 6H) which isolates atmospheric hydrogen by condensation of atmospheric component gases that have higher boiling point than hydrogen. The first cryopump removes nitrogen, oxygen, and other high boiling point gases and the second one removes neon in the off gases. Finally the hydrogen and helium is adsorbed on active charcoal. The amount of treatable air strongly depends on the ability of the first pump. To examine the performance of the first pump, introduction rates of air to the first pump was changed from 0.2 to 0.5 L/min and changes in temperature and pressure in the first pump were measured during the experiment. The apparatus was possible to process about 350 L of air by one sequence of the continuous introduction of air. About 1000 L of air was possible to be processed when the introduction of air was controlled by monitoring temperature and pressure of the pump. When the pressure and temperature of the pump began to increase, the introduction was stopped and waited until the pressure and temperature decreased.

The separation column packed 80/100 mesh activated alumina coated with ferric oxide in a 6 m×3 mm stainless steel column was prepared. The column was activated for 3 hours at 145℃ purging helium gas before use and connected with a gas chromatograph (SHIMAZU GC-8A). The column was cooled at 77 K by liquid nitrogen, and helium was used as the carrier gas (70 ml/min.). Mixtures containing stable isotopes (H_2, D_2, HD) were separated at sufficient resolution. The separation factor was similar to the report by Smith et al.[1)], which done the separation of hydrogen isotopes containing tritium.

By the combination of the atmospheric hydrogen enrichment apparatus and the separation column will enable us to analyze tritium isotopes in the atmospheric hydrogen.

1. H.A.Smith et al., *JPhs.Chem.*, **67**,1512,(1963).

3P 32 RARE EARTH ELEMENTS VERTICAL PROFILES IN Pb-210 AGE-DATED SEDIMENT CORES FROM SOUTHWESTERN GULF OF CALIFORNIA

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Vertical profiles of rare earth elements (REEs) were examined in four ^{210}Pb age-dated sediment cores collected from the shelf and slope of the southern Baja California peninsula (areas in front of Santa Rosalia, Loreto, El Coyote and San Juan de La Costa) using instrumental neutron activation analysis technique. No significant anthropogenic impact on the content of REEs in sediments was found. Some variations of REEs concentrations seen down cores probably have natural origins, and are attributed to temporal changes of the ratio of terrigenic and marine biogenic supplies of REEs from the water column to the deposits of the sea floor.

Shale-normalized REEs data for sediment cores from Santa Rosalia area and from the Loreto Bay manifest a positive Eu anomaly in comparison with other REEs which probably reflects some influence of hydrothermal activity from the bottom of the adjacent part of the Gulf of California in the past or at the present time. In contrast, in laminated sediment cores taken in front of the El Coyote fan-delta and San Juan de La Costa phosphorite mine, and of the La Paz Bay, strong minima of the shale-normalized ratios for Eu were registered reflecting the periodic existence of depositional conditions with elevated contributions of Eu-depleted material in the coastal suspended particulate matter.

3P33 MIGRATION OF RADIONUCLIDES INDUCED IN SOIL BELOW THE 12 GeV PROTON ACCELERATOR FACILITY AT KEK

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The 12 GeV proton synchrotron of the High Energy Accelerator Research Organization (KEK) has been utilized for twenty years since the first experiment started. In the past twenty years, various radionuclides have been produced by spallation reactions with high energy hadrons (mostly neutrons) or thermal neutron capture reactions and accumulated in the shield and floor concrete[1] and the soil below the slow extracted proton beam line (EP2 beam line). The radioactive concentrations of various radionuclides induced in the soil below EP2 beam line were observed.

The measurements samples were cored out the soil (depth: 3m) below EP2 beam line during summer shutdown(about 3 months after the end of accelerator operation) . The concentrations of radioactivities induced in the soil were measured by the P. Ge detector system for gamma-emitters and liquied scintillation counter for H-3. From the results of radioactive measurements, the depth profiles of various radionuclides in soil were obtained.

H-3, Be-7, Na-22, Sc-46, Mn-54, Co-60, Cs-134, Eu-152 and Eu-154 were observed in samples. In these radionuclides, H-3 concentration was highest to be about 10 Bq/g in the soil. On the other hand, H-3, Na-22 and Mn-54, which were leached from the soil were slightly found in the groundwater. From the comparison with radioactive concentrations in soil and groundwater, the order of leaching percentage were H-3 > Na-22 > Mn-54.

The migration experiments were performed in RI laboratory using the soil and groundwater below EP2 beam line. From these experiments, the ion velocity of Na-22 was faster than one of Mn-54 in the groundwater, but both were slower than the velosity of groundwater.

1. T. Miura, S. Takahara, S. Ishihama, N. Ohtsuka and T. Kunifuda, *J. Nucl. Sci. Tech.*, Supplement 1, 183(2000).

3P 34

THE DISTRIBUTION OF ^{239,240}Pu AND ^{241}Am IN THE WATER COLUMNS OF THE JAPAN AND BONIN TRENCHES

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Plutonium-239,240 (half-lives: 24,131 y and 6,570 y) were released to the worldwide environment by atmospheric nuclear explosions during the years from 1945 to 1980, and production of Pu in nuclear facilities has increased these ~30 years the total amount of the nuclides on the Earth. Since marine sediment is expected to be the ultimate depositional sink of environmental Pu, particular attention has been paid to biogeochemical behavior of Pu in oceanic environment. Although many studies on Pu in oceanic environment have been carried out, further studies are required to fully understand the biogeochemical nature and behavior of Pu in the open ocean water column.

In the present work, with the above points as background, depth distribution of ^{239,240}Pu in deep water column was measured to discuss sinking behaviour of Pu.

Seawater samples were collected from various depths using large-volume sampler during 1984 and 1994 cruises of R.V. Hakuho-Maru (Ocean Research Institute, The University of Tokyo) in the sea area of Japan and Bonin Trenches. About 250 L aliquot of unfiltered water was subjected to radiochemical analysis of ^{239,240}Pu. For the 1994 sample, ^{241}Am was analyzed together with ^{239,240}Pu.

Plutonium-239,240 and ^{241}Am were detectable throughout the water columns studied in this work, and it was found that considerable change took place during 1984 and 1994 in the vertical profile of Pu (Fig. 1). This may be explained by repetition of reversible processes of vertical transport of Pu by settling particles and release of Pu from the particulate matters to water. This mechanism may also involve a reversible process of 'breakdown of large (settling) particles associated with Pu into small (suspending) particles' and 'aggregation of small particles to form large particles'.

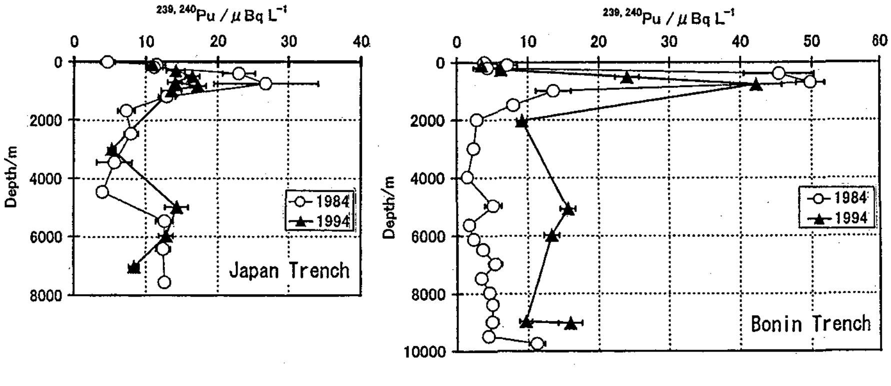

Fig.1 The depth distribution of ^{239,240}Pu in the water columns of the Japan and Bonin Trenches: comparison of 1984 profile (O) and 1994 profile (▲).

3P 35

PRETREATMENT OF PLANT SAMPLES FOR THE DETERMINATION OF RHENIUM BY ICP-MS

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Rhenium transfer factors from soil to plant can be used as a surrogate for technetium in the natural environment because of their chemical similarities. Although the amount of Re in the environment is higher than that of global-fallout ^{99}Tc, no data are available for terrestrial plant samples until now because Re is one of the rarest elements in the earth's crust. In this study, we carried out a radiotracer experiment for the determination of trace levels of Re in plant samples.

Ten radish samples (*Raphanus sativus* L.) were grown in solution culture using Hyponex® for 30 days. Each sample was then transplanted separately into a new vessel containing 50 mL of nutrient solution contaminated with ^{184}ReO$_4^-$. After 24 h, the samples were then separated into leaves, turnips and roots and subsequently oven dried at 60°C for 72 h. For each part, 5 samples (each containing 2 sub-samples) were prepared and the activity of ^{184}Re in each sample was determined by NaI (Tl) autowell scintillation counter (Aloka, ARC-300). Next, the sample was incinerated in an electric furnace at 450°C for 3 h. Then, the ^{184}Re was extracted from the incinerated samples using 10 mL of acid mixture (HCl+HNO$_3$ [1+1]) heating at 90°C for 3 h and the solution was filtered (<0.45μm). Rhenium-184 was measured after incineration and after filtration. The Re loss ratio for each step was calculated based on the oven dried sample.

After the incineration at 450°C for 3 h, no loss of Re was found for any plant sample parts. This behavior of Re was highly similar to that of Tc.[1] Results of Re recovery in the acid leaching step are shown in Fig. 1. Koide *et al.*[2] reported that when Re in strong acid solution was heated at higher than 90°C to near dryness, it can be partially volatilized. However, under the acid leaching condition used in this study, Re was extracted from the samples to acid solution without any loss. Probably because of insubstantial volume loss during heating, Re could remain in solution as ReO$_4^-$. Throughout the procedure, almost all Re was recovered from the samples. There was no difference in recoveries among the sample parts. The samples pretreated by this method can be subjected to separation using a TEVA resin for Re determination by ICP-MS.[3]

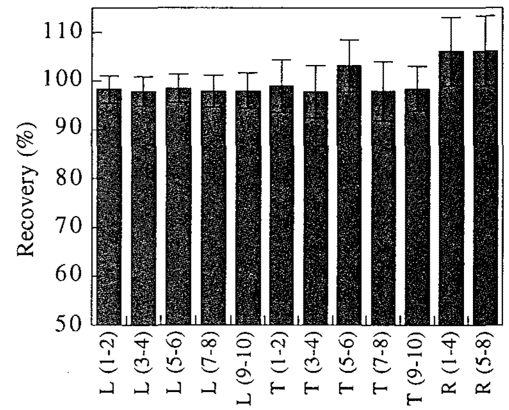

Fig. 1. Recoveries of Re after acid leaching step from incinerated plant samples (L: Leaves, T: Turnips, R: Roots). Error bars are ±1SD.

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3P36 Determination on Elemental Composition of Airborne Dust from View Point of Environmental Monitoring

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Introduction : For the assessment of environmental impact of nuclear materials, radionuclides and air-pollutants, monitoring of these amounts and composition are important. As airborne dust is direct carrier of these materials, it is often used as an indicator for these monitoring. The dust comes from different origins such as sea, minerals and soot. The elemental and isotopic composition of airborne dust gives a useful information on the origin. However, the amount and elemental composition of the dust in the atmosphere may vary with season and weather.

To investigate the effect of weather on the composition and the possible origin of the dust, the elemental composition of airborne dust was determined.

Experimental : The dust samples ('air-dust') were intermittently collected with a high-volume air sampler (flow rate : 120 m^3/h) at the JAERI-Tokai since May of this year. Each sampling time was 2-6 days, and the total sampling volume was 5700-18000m^3. The dust ('rain-dust') was also collected from rainfalls of 100-500 ml by filtration. The elemental composition of the dust samples was determined by instrumental neutron activation analysis (INAA). Aliquots of these samples (0.5-8 mg) on the filter were used for INAA.

Results and Discussion : Figure 1 shows the concentration of typical elements in both types of the dust samples. The concentration in the air-dust samples collected during the sunny days (light gray histogram) and the rainy days (dark gray histogram) were also shown in Fig.1.

The analyzed elements could be classified into 3 groups by the variation of concentration in the samples : Na and Cl (Group-1), V and Cr (Group-2), Al, Fe, Sc and Th (Group-3). For both Group-1 and Group-3, the concentrations in the air-dust collected during rainy days were lower than those collected during the sunny days. For Group-1, the concentrations in the rain-dust were lower than those of the air-dust. For Group-3, however, those of the rain-dust were same as those in the air-dust collected during the sunny days. The concentration of Group-2 elements did not vary with the type of samples.

The difference in concentration pattern may reflect the effect of rainfalls. The elements of Group-1 were easily dissolved in rainfalls, those of Group-3 were washed out but were not dissolved, and those of Group-2 were neither washed out nor dissolved.

For further discussion on the weather effects and the possible origin of these types of dust in details, the elemental analysis of rainfall samples and data accumulation from intermittent collection of dust samples in long period will be carried out.

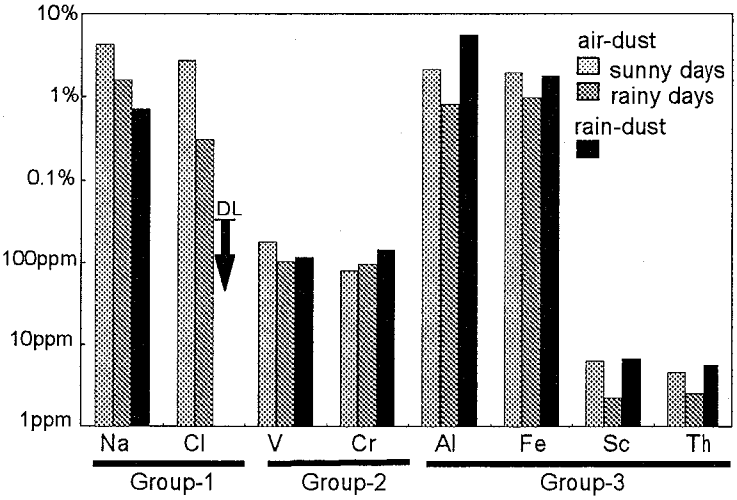

Fig.1 Concentration of typical elements in air-dust (gray histograms) and rain-dust (black histogram). The Cl data of rain-dust is less than the detection limit, 'DL', (2 standard deviation).

3P 37 ANALYTICAL PROCEDURE FOR ^{99}Tc IN SOIL AND WATER SAMPLES BY ICP-MS

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^{99}Tc is produced from the fission of ^{235}U or ^{239}Pu in high yield of ca. 6 % and has been released into the environment as a result of nuclear explosion tests and nuclear waste reprocessing. Due to its long radiological half-life ($2.11\text{x}10^5$ year) and its large amounts of products, the study of the behavior of ^{99}Tc in the environment is very important.

As its concentration is very low in the environment and the nuclide emits only β-ray (Emax = 292 keV), the analysis of ^{99}Tc is difficult. Recently the development of analysis by ICP-MS made possible a high sensitivity determination of low-level ^{99}Tc[1]. However, careful chemical separation of Tc species is necessary before measurements, especially the removal of interfering elements such as Ru traces is essential.

Tc is purified by small volume of extraction chromatographic resin (EIChroM Industrials Inc., TEVA Resin)[2], but recovery of Tc is not enough high when the sample volume is very large such as 100 g soil samples or 50 l water samples for example. And the volume of reagents using final purified step must be reduced as the reagent contains a slight amount of Ru.

So we examined the characteristics of Tc and TEVA Resin to Tc and Ru in various conditions, and developed an analytical procedure for ^{99}Tc in soil and water samples by ICP-MS. This procedure consists of incineration, digestion, coprecipitation, reduction and oxidation. This is easier than previous methods[1,3], and matrix materials were sufficiently removed. The recovery of Tc was 70-80 % for 100 g soil samples and 60-70 % for 250 l water samples. In this study, we used ^{95m}Tc[4] as a tracer.

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3P 38 RECENT LEVEL OF ATMOSPHERIC HTO, HT and CH_3T CONCENTRATIONS IN JAPAN

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National Institute for Fusion Science (NIFS) is now constructing a new fusion device and related facilities at Toki city in Gifu prefecture, Japan. In the future a fusion reactor which uses tritium as a fuel would become a significant source of atmospheric tritium, that is, tritiated water vapor (HTO), tritiated hydrogen (HT) and tritiated hydrocarbons (primarily tritiated methane, CH_3T). Thus tritium concentrations of atmospheric HTO, HT and CH_3T have been successively investigated in Fukuoka prefecture from 1984 to the present and a few times a year in the Toki city from 1990 to establish the general database on behavior of atmospheric tritium.

Average monthly HTO concentrations expressed in Bq/L-H_2O vary within ranges of 0.99 to 2.45 and the minima of the HTO concentrations in each year are all observed in July or August. This is understandable because the Fukuoka area in July and August is covered by an oceanic air mass that has a low tritium level of water vapor. Atmospheric HTO concentrations expressed in mBq/m^3-air vary within ranges of 7.8 to 46.1 and have a strong correlation with the atmospheric humidity, being high in summer and low in winter. On the contrary, in the case of HT and CH_3T, no seasonal variations were observed with average monthly values of 20.3 to 61.0 mBq/m^3-air and 8.2 to 23.9 mBq/m^3-air, respectively. The present HTO concentration has been already close to the tritium level before nuclear era, but the present concentrations of HT and CH_3T are still higher by a factor of about 120 and 30, respectively, than those before the tests.

Tritium concentrations in Fukuoka were almost comparable with those in Toki. Consequently, we could say that our results obtained were the representation of the atmospheric tritium concentrations in Japan. We discuss recent level of atmospheric HTO, HT and CH_3T concentrations in Japan.

3P 39 Distributions of ^{7}Be and ^{10}Be in the atmosphere and surface water : An investigation in the Western North Pacific

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The cosmogenic nuclides, ^{7}Be ($T_{1/2}$=53.3d) and ^{10}Be ($T_{1/2}=1.5\times10^{6}$y), are produced at the atmosphere by nuclear reaction between the atmosphere and the cosmic ray. After it was produced in the atmosphere, these nuclides deposit from the atmosphere to surface of the sea, and deposit from seawater to the deep-sea sediments. Therefore, these nuclides were useful as environmental tracer of the global range. It will be mentioned about the behavior during the environment of these nuclides in this study.

Be isotopes in the atmosphere and surface water were collected during the KH00-03 cruise of R/V Hakuho-Maru (during the summer season in 2000 at the Western North Pacific Ocean.). Aerosols were collected on filter papers using high volume air sampler (sampling average, 800m^{3}), and Seawater were collected using large volume water sampler in the depth from 0m to 500m (sampling average, 250L). After Be isotopes in each sample were recovered, ^{7}Be concentration was measured by HP-Ge detectors, and ^{10}Be concentration was measured by AMS on the MALT 5UD Pelletron at the University of Tokyo.

The concentrations of these nuclides in the atmosphere showed latitudinal distribution. This characteristic profile showed good agreement with ^{7}Be in the rainwater.[1] The reason for these profiles can be explained by the global air circulation. On the other hand, the depth profile of these nuclides in the surface water was also characteristic. The concentration of ^{7}Be decreases together with the depth and ^{10}Be increases. The atomic ratio of these nuclides, ^{7}Be/^{10}Be, almost became a constant in the depth 0-40m, and showed surface mixed layer. These results were the useful key to estimate Be flax across the Ocean surface.

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3P 40 Fate and transport of radionuclides from uranium mill tailings and related waste materials

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Specific extraction studies in our laboratory have shown that iron and manganese oxide- and alkaline earth sulfate minerals are important hosts of radium in uranium mill tailings. Iron- and sulfate-reducing bacteria may enhance the release of radium (and its analog barium) from uranium mill tailings, jarosite (a common mineral in sulfuric acid processed-tailings), and oil field pipe scale [a major technologically enhanced naturally occurring radioactive material (TENORM) waste]. The concept of anaerobic microsites in soils and a brief review of the occurrence of iron and sulfate reduction in mine tailings will be presented. These research findings will be discussed in the context of nuclear waste forms (such as barium sulfate matrices), radioactive waste management practices, and geochemical environments in the Earth's shallow subsurface region.

3P 41 Determination of Technetium -99 in Soil Samples by 3M Empore^{TM} Technetium Rad Disk

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Technetium had been recognized as one of important radionuclides in medium and high-level waste for the calculation of long-term collective dose. Therefore, the analysis of technetium-99 in environmental samples is necessary to the assessment of its environment impact. The objective of the 3M Empore^{TM} Technetium Rad Disk is to allow rapid and economical analysis for technetium-99 in surface and subsurface waters. It contains high-density GD-1 absorbent grains to separate TcO_4^- ion from sample solution. It has very good absorption ability of TcO_4^- ion when the pH value of the solution is between 2 to 12 with a flow rate below 50 ml/min. Its recovery is 100% nearly for the assay of water samples. A new pretreatment method to couple with using Technetium Rad Disk is developed for the determination of technetium-99 in soil samples in this study. Using rhenium as a technetium recovery tracer is satisfactory to the method and that can avoid producing radioactive waste because all of technetium isotopes are radioactive.

Keywords: Technetium, soil, Rhenium, 3M Empore^{TM}, disk

3P42

Cumulative Dose Measurements using Radiophotoluminescence Glass Dosimeter in Cold Area

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Since October 1983, the Niigata Prefectural Government has carried out the measurements of cumulative dose using thermoluminescence dosimeters (TLDs) around the Kashiwazaki Kariwa nuclear power station. In recent years, it is well known that radiophotoluminescence glass dosimeter (RPLD) has good characteristics as repeated readout capabilities, excellent batch uniformity in sensitivity and long-term stability for fading.

In order to introduce RPLD to routine environmental monitoring in the future, cumulative dose was measured using RPLD simultaneously with TLD from the first quarter of 1999 to the 4th quarter of 2000 at the same monitoring points.

There was the almost good correlation between the measurement results from RPLD and those from TLD. However, the results from RPLD showed about 5% lower values in comparison with those from TLD in the 4th quarter (January to March) in winter season, when mean temperature became down to 4°C or less. On the other hand, in the other quarters, when mean temperature became up to 13 – 26°C, the results from RPLD and TLD coincided practically within ±5% after correcting each fading effect (Fig.).

To elucidate these phenomena of sensitivity decrease, the gamma-ray irradiation experiments were carried out under the different room temperatures and exposure times. The lowering results of 3 – 4% from RPLD were detected at less than 6.3 °C, in comparison with negligible contributions at beyond 8°C.

As a result of this research, RPLD seems to have the sufficient availability as a dosimeter for environmental monitoring. Nevertheless, it is necessary to mind in the sensitivity change of RPLD lowering at about 5%, when it is used in the cold area in the winter.

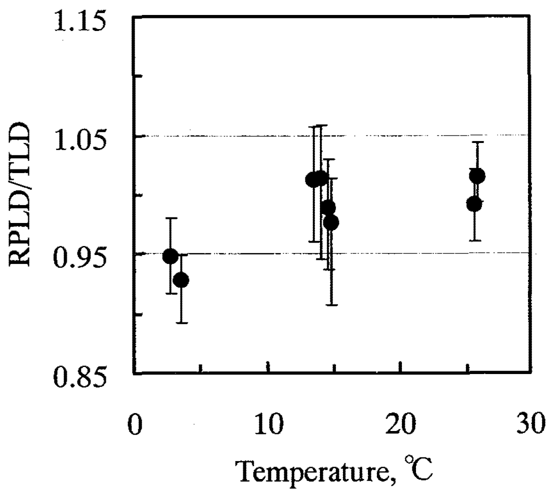

Fig. Temperature dependence of RPLD/TLD ratios after correcting each fading effect.
The average values of 24 monitoring points are plotted together with respective minimum and maximum values.

3P 43 Thermochromatographic behavior of fission products combined with dipivaloylmethane

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In recent years, the chemical properties of transactinoid elements have been investigated. Since most of these elements have short half-lives and low production cross sections, they are available only in an atom-at-a-time scale. Therefore, rapid and selective chemical procedures are required for the research of their chemical properties. One of the useful methods is a gas phase chemical separation method. The adsorption enthalpy and entropy are estimated from the chromatographic behavior.

It is well known that many β-diketonates have a high vapor pressure and a reasonable thermal stability. So for, dipivaloylmethane, dpm, has been examined as a complexing agent in a gas phase separation in our laboratory. In this work, the basic characteristics of the gas phase reaction between fission products from ^{252}Cf and dpm was investigated in order to apply the metal chelate formation to a rapid chemical separation at an on-line isothermal chromatography.

First of all, fission products from ^{252}Cf were transported by a He/KCl gas-jet system to a reaction chamber in which dpm was introduced. Produced volatile dpm complexes were carried to an isothermal quartz column, and then deposited at the cooling position. The identification and determination of the activity was made by a γ-ray spectrometry using a HPGe detector.

Up to now, Ru, Rh, Te and I isotopes were detected at the cooling position when the temperatures of the reaction chamber and the isothermal column were elevated. The activities of Ru and Rh isotopes at the cooling position were maximum when the reaction temperature was 350°C, and decreased over 350°C. This is probably because dpm molecule itself or dpm complexes might be unstable over 350°C. Certain amounts of Te and I isotopes were detected even in the case of no dpm. Oxides and oxychlorides of Tc and Ru are known to have a high vapor pressure. Accordingly the observed Ru and Rh activities might come from the decay of short-lived precursor Tc. However, if no dpm was introduced, no activities of Ru and Rh were observed. All other elements were remained on the quartz wool in the reaction chamber. It is concluded that volatile dpm complexes of Ru and Rh were formed selectively.

3P44 α-SOURCE PREPARATION METHOD FOR ON-LINE AQUEOUS CHEMISTRY

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Many heavy- and trans-actinoid elements have short half-lives, and the identification and determination of them are primarily made by on α-ray spectrometry. To measure precise α-ray energies, it is necessary to prepare thin and uniform sources, and measurements should be carried out under vacuum. A source preparation in an aqueous chemistry is usually make by evaporating to dryness in atmospheric pressure, and then the source is moved to a vacuum chamber for measurement. In this work, we have tried to prepare on α-source for on-line chemical separation by spraying a liquid samples in vacuum.

Experimental setup is shown in Fig. 1. A chamber was kept at low pressure, and liquid sample was introduced into the chamber with air at atmospheric pressure.

Sample was sprayed on a heated tantalum plate and evaporated on it. Copper pipe was inserted between a heater and the tantalum plate in order to make thermal gradient on the surface of tantalum plate, when liquid sample is evaporated on a heated plate. It is known that the higher temperature at periphery of the plate prevents an escape of droplet from the plate.

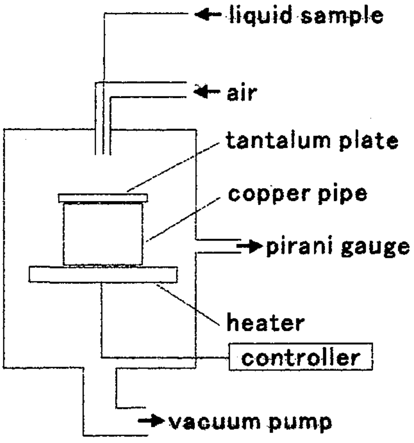

Fig. 1 Experimental setup

The temperature of the tantalum plate was monitored with a thermocouple. In this work, an aqueous solution of lanthanum was used as a sample solution. Measurement of the efficiency of solute attachment to the tantalum plate was carried out by an absorption spectroscopy.

Efficiencies at several temperatures were measured. For example, at 200℃, temperature of the center of the tantalum plate was 50℃ lower than that of the periphery. Temperature of tantalum plate has fallen when spraying sample, because of the heat of vaporization of the solvent. At high temperature, sample solution has evaporated and dried instantly when it was sprayed on a plate.

3P 45

PRODUCTION OF NO-CARRIER-ADDED ^{177}Lu VIA THE ^{176}Yb(n, γ)^{177}Yb → ^{177}Lu PROCESS

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The β^- emitter ^{177}Lu ($T_{1/2}$ = 6.73 d) is a promising therapeutic radioisotope for the treatment of cancer because of its energetic beta particle ($E_{\beta,\mathrm{max}}$ = 498 keV) and gamma rays (E_γ = 208 keV (11.0%) and 113 keV (6.4%)) suitable for imaging. Lutetium-177 can be usually produced at nuclear reactors with high yield and high specific radioactivity by the ^{176}Lu(n, γ)^{177}Lu reaction with the very high cross section of 2100 barns. However, radioisotopes with higher specific radioactivity are required in the field of radioimmunotherapy using labeled monoclonal antibodies or peptides. Thus, an alternative production route, namely the ^{176}Yb(n, γ)^{177}Yb→^{177}Lu process was studied to produce no-carrier-added (nca) ^{177}Lu in this work. The important process in this work is the separation of nca ^{177}Lu from macroscopic amounts of the ytterbium target. A liquid-liquid extraction method[1] using 1% HDEHP in cyclohexane and a Na(Hg) cementation method[2] followed by final cation exchange purification has been developed for the separation of nca Lu from macroscopic ytterbium target. In the present work, a separation method by reversed-phase ion-pair chromatography was investigated.

The enriched ^{176}Yb$_2$O$_3$ target (97.6% enrichment, Nippon Sanso Co.) was irradiated for 3 h in JAERI JRR-3M (thermal neutron flux of 1 × 10^{14} n cm^{-1} s^{-1}). The yield of ^{177}Lu was 8.1 MBq/mg Yb at 90 h after EOB. Ytterbium-175 ($T_{1/2}$ = 4.2 d) was also produced due to containing 1.93% of ^{174}Yb in the target, and was used a tracer of ytterbium. The irradiated Yb$_2$O$_3$ was dissolved in 6 M HCl-30% H$_2$O$_2$. The ^{177}Lu solution containing 5 mg of Yb$_2$O$_3$ was loaded on the column (Waters Resolve C$_{18}$ Radial-Pak Column, 8 mm × 300 mm) and was separated with 0.2 M 2-hydroxyisobutric acid (2-HIB) /10 mM octanesulfonic acid at a flow rate of 2 mℓ/min. Effects of concentration of 2-HIB in the eluent, the type of C$_{18}$ column and length of the column on separation efficiency were examined. Under the optimum conditions, the nca ^{177}Lu was obtained in radiochemical pure form with a separation yield of approximately 60% within 8-9 hours, as shown in Fig. 1. The pure ^{177}Lu fraction was finally purified by a small cation-exchange column (DIAION SK-1, H$^+$ type, 10 mm × 100 mm) to eliminate 2-HIB and octanesulfonic acid and was recovered in approximately 90% yield with 6 M HCl.

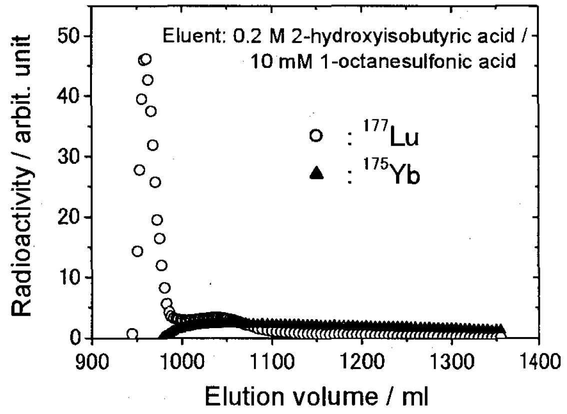

Fig. 1. Typical elution curve

In conclusion, radiochemically pure nca ^{177}Lu was obtained by reversed-phase ion-pair chromatography followed by cation-exchange purification with an overall separation yield of 55%.

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3P46

Preparation and properties of ^{213}Bi-labeled biotin derivatives for pretargeting radiotherapeutic study

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Alpha-particle emitting nuclide is of considerable interest for radioimmunotherapy (RIT) in medicine due to its characteristic physical properties compare to β^- particle emitter. The higher LETs (100keV/μm) of α-particles are more cytotoxic and their shorter ranges (40-80μm) are able to kill neighboring cancer cells without further irradiation damage of normal tissues. Bismuth-213 ($t_{1/2}$= 45.6min), which can be generated from ^{225}Ac, is a promising α-emitting radionuclide for applying to RIT studies. In addition, ^{225}Ac(4n+1) series has no Rn isotopes and few high-energy gamma emissions in the decay chain, so that it is possible to handle these nuclides safely in clinical field. We have developed the generator system of ^{225}Ac/^{213}Bi and evaluated the optimum condition of labeling yield of immunoglobulin G (IgG) with ^{213}Bi. The labeling yields of ^{213}Bi conjugate to IgG were found to be approximately 60%.[1]

In this study, we applied ^{213}Bi to a promising pretargeting RIT. Pretargeting has several potential advantages over using conventional RIT. We selected (strept)avidin-biotin system for ^{213}Bi RIT from the following reasons: 1) *In vivo* stability of ^{213}Bi conjugate are expected due to strong binding affinity and specificity of (strept)avidin and biotin. 2) Rapid delivery and targeting to tumor in short time are expected to efficient therapy for particularly short half-life nuclide such as ^{213}Bi. As a biotin derivative, biotin-putrescine-isothiocyanato-benzyl-EDTA (Biotin-P-SCN-Bz-EDTA, see Fig) was prepared and labeled with ^{213}Bi. We evaluated the optimum condition of labeling efficiency, immunoreactivity and *in vitro* biochemical stability of ^{213}Bi-Biotin- P-SCN-Bz- EDTA.

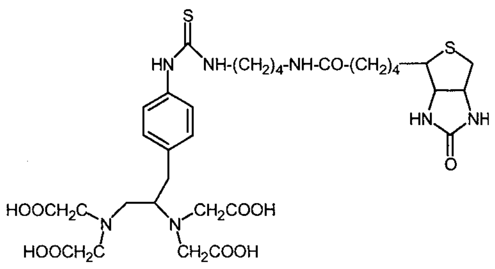

Fig. Structure of Biotin-P-SCN-Bz-EDTA

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3P47 Study on the Ion Recognition Mechanism for Alkali and Alkaline-Earth Metals by Calixcrown Ethers

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Removal of Cs from a high-level liquid waste (HLW) produced by nuclear fuel reprocessing is recommended for the rational geological disposal of the HLW, since Cs is the main heat-source in the initial several hundreds years of the disposal. Thus the development of extractant having high ion selectivity and complexation ability toward Cs is needed for the partitioning of the HLW. In this work, we studied the ion recognition mechanism on complexation of Cs with the noble extractant: calix[4]-bis-crown-6 (CC) and calix[4]-bis-2,3-naphthocrown-6 (CNC).

The dependencies of the distribution ratios of Cs^+ and Rb^+ on calixcrown concentration indicated that the ratios of metal to calixcrown were all unity. The calixcrowns, therefore, coordinated to one Cs^+, although the calixcrowns have two crown ether sites and one calixarene site in a molecule. NMR spectroscopy supported the stoichiometry and the result, furthermore, indicated that the calixcrown coordinates to Cs^+ on the crown ether site.

The distribution ratios of alkali and alkaline-earth metals with the calixcrown decreased in the order: $Cs^+ > Rb^+ > Ba^{2+} > Sr^{2+}$. This order agrees with that of the ionic radius, suggesting that the selectivity of calixcrown in complexation might depend on the ring size of crown ether group.

The structure of the Cs-calixcrown complex was also studied by the measurement of the extended X-ray absorption fine structure (EXAFS). Bond distances between Cs and the nearest neighbor atoms were 3.07 Å and 3.15 Å for CNC and CC, respectively. The coordination numbers are 6. Figure shows the structure of the complexes minimized by molecular mechanics by adapting to the bond distance obtained from EXAFS. This suggests that naphthyl group bends to the horizontal direction. Distribution ratio of Cs^+ with CNC is slightly higher than that with CC[1]. It is considered that this bending contributed to the stability of the complex and increase in distribution ratio.

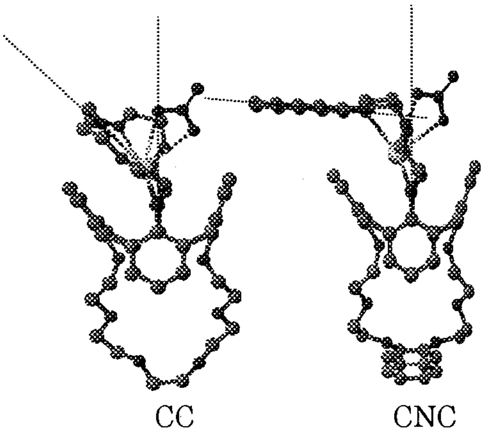

Figure Results of EXAFS and MM2 calculation

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3P48

GROUP SEPARATION OF TRIVALENT ACTINIDES AND LANTHANIDES BY TERTIARY PYRIDINE-TYPE ANION-EXCHANGE RESIN EMBEDDED IN SILICA

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The group separation of actinides and lanthanides is one of the important problems for the nuclear reprocessing. The mutual separation of miner actinides and the partitioning of actinides and lanthanides are, especially, critical issue to create the nuclear fuel cycle in consideration of the actinide burning and transmutation. In the present work, the separation of trivalent actinides and lanthanides was studied by using newly developed high porous tertiary pyridine-type anion-exchange resin embedded in silica beads. The average diameter of this resin is 60 μm. This resin has the high radiation resistance.

The mixture of trivalent actinides and lanthanides that contained ^{141}Am, ^{142}Cm, ^{144}Ce, ^{155}Eu and ^{160}Tb was prepared from a neutron irradiated ^{241}Am. The mixture was dissolved in a 30vol% methanol-hydrochloric acid mixed medium. The solution was fed into a column with 10 cm resin height. The elution experiments were carried out by using the same methanol-hydrochloric acid medium at room temperature. The chromatogram of this experiment is shown in a figure. Actinides are detected by an α-spectrometer, lanthanides are detected by a γ-ray detector. This figure shows that a well symmetric elution curve was observed for each element. We confirmed that actinides and lanthanides were eluted according to the reverse order of their atomic number and that the ^{242}Cm and ^{241}Am were eluted out from the column after the elution of ^{144}Ce.

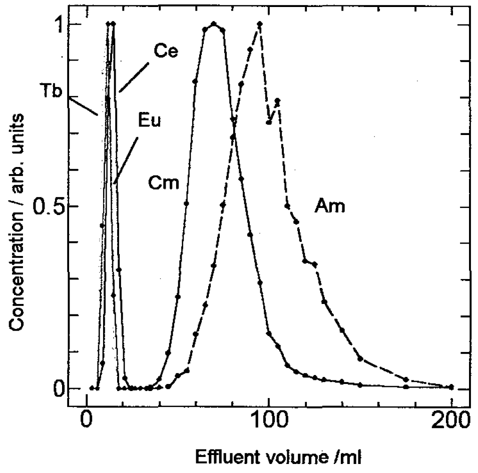

Fig. Chromatogram of actinides and lanthanides by using tertiary pyridine type ion exchange resin in methanol-hydrochloric acid mixed medium.

In conclusion, this finding implies that the tertiary pyridine-type anion-exchange resin embedded in silica beads is quite useful for the group separation of trivalent lanthanide and actinides. And it is suggested that the mutual separation of these elements is also possible at room temperature by applying a longer column to the separation.

3P 49 EFFICIENT REMOVAL OF Cs-134 FROM AQUEOUS SOLUTIONS BY ZIRCONIUM PHOSPHATE

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The wide spread applicability of zirconium phosphate (ZP) in removal of several radiotoxic ions has long been studied by various authors in the past but the results obtained are not well consistent, actually it depends on the way zirconium phosphate has been Ssynthesized and of course the degree of crytallinity, chemical composition and water content of the sample. Here, we synthesized the amorphous type of zirconium phosphate by adopting the known method as described elsewhere[1], dried the solid at room temperature, crushed, grined and sieved for 120-170 BS mesh size and kept over saturated ammonium chloride solution. Caesium is one of the important fission fragments in radioactive wastes, hence the synthesized zirconium phosphate has been employed for the removal of Cs-134 by adopting the radiotracer technique and the study has been widely carried out as a function of sorptive concentration , temperature, pH and the presence of several anions. Irradiation effect on ZP is also included in the study.

The adsorption of Cs-134 on zirconium phosphate has been carried out as a function of sorptive concentration at very low pH~2.40 and at constant temperature 303 K. It has been observed that with increasing sorptive concentration from 1.0×10^{-5} to 1.0×10^{-2} mol dm^{-3} the amount adsorbed/removed increases respectively from 0.984×10^{-6} to 0.915×10^{-3} mol dm^{-3}; however, for the same increase in sorptive concentration the percent adsorption decreases respectively from 98.4 to 91.5. This decrease in percent adsorption at higher Cs concentration is to be explained on the basis that relatively lesser number of surface active sites are available for higher number of adsorbing species. Moreover, beyond the sorptive concentration 1.0×10^{-5} mol dm^{-3} (i.e., upto 1.0×10^{-8} mol dm^{-3}), practically a constant value of adsorption is obtained. Further, the sorption data obtained for different sorptive concentration is found to be fitted well for Freundlich adsorption isotherm as a good linearity is obtained between Log q_e (amount adsorbed at equilibrium) vs Log C_e (equilibrium concentration). The Freundlich constants i.e., 1/n (adsorption intensity) and K (adsorption capacity) values are found to be 0.981±0.002 and $9.54 \pm 0.03 \times 10^{-2}$ mol g^{-1} respectively. A higher value of K further suggests the higher affinity of Cs towards zirconium phosphate and the fractional value of 1/n indicates the hetrogeneous surface nature of the solid. Temperature dependence study reveals that no significant change in sorption is found for increasing the solution temperature from 303 to 333 K, which clearly suggests about the chemical type of sorption take place at the surface of ZP and it appears to be irreversible in nature as no significant desorption takes place in the bulk concentration (1.0×10^{-5} mol dm^{-3}) at even elevated temperatures (303 K to 333 K).

The change in solution pH (*ca* 2.4 to 10.2) does not affect the sorption of Cs onto the surface of zirconium phosphate, hence the solid should found a potential application in the removal of Cs from radioactive waste solution, throughout the entire pH range (2.4 to 10.2). Similarly, the presence of several complexing agents (six fold) i.e., EDTA, glycine, phosphate, sulphate etc. does not appreciably affect the removal efficiency of Cs by this solid.

Irradiation stability of zirconium phosphate is an important property as this can provide the information about the suitability of the soild in radioactive waste management. In view of this, we obtained the sorption data for Cs onto zirconium phospahte by prior irradiation of the solid using a 11.1 Gbq neutron source (Ra-Be) having neutron flux of *ca.* 3.2×10^6 n cm^{-2} s^{-1} associated with nominal γ-dose (*ca* 1.72 Gy/h) and the results show that no significant change in sorption of Cs took place on the surface of zirconium phosphate, hence the solid is to be stable at least towards the employed exposure for the removal of Cs.

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3P50 EVALUATION OF SELF-ABSORPTION OF β-RAY IN GEL - SUSPENSION SAMPLES BY MONTE CARLO SIMULATION

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Environmental carbon-14 is of great interest because of the biological importance of carbon and the long half-life (5730 y). For the monitoring of C-14 concentrations in environmental materials, liquid scintillation counting technique is widely used. In our previous work, we have developed simplified sample preparation method for the liquid scintillation counting of C-14 concentration in environmental samples[1]. In this method, C-14 is measured as calcium carbonate ($CaCO_3$) in the gelated scintillator. This method, Gel-Suspension Method, does not require complicated chemical procedure, expensive equipment or considerable technical skills. The gel-suspension method was successfully applied for the determination of C-14 concentrations in tree rings[2].

Because C-14 is measured as $CaCO_3$ particle in the gelated scintillator, however, a part of or all of the energy of β-ray is lost in the $CaCO_3$ particle before coming out into the scintillator. As a result of this, the shape of the β-ray spectrum is changed and the counting efficiency is reduced. Therefore, the effect of the self-absorption of β-rays by the sample itself has to be considered.

To understand the process of the energy loss of the β-ray in gel-suspension samples, Monte Carlo simulation was carried out. In the simulation, the effect on the counting efficiency and the shape of the β-ray spectrum was evaluated considering the multiple scattering and energy loss of β-rays in $CaCO_3$ particles and the quenching of scintillation light. Fig.1 shows the β-ray spectrum obtained by the simulation.

In this presentation, the result of the simulation will be reported and compared with the experimental measurement.

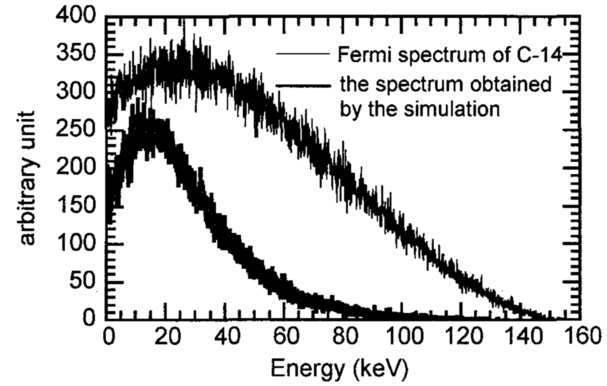

Fig. 1 The result of the Monte Carlo simulation

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3P 51 SEASONAL VARIATIONS ON THE ATMOSPHERIC DEPOSITIONAL FLUXES OF ^{7}Be AND ^{210}Pb AT FUKUOKA

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Beryllium-7 (half-life 53.29 d) is one of the radionuclide produced by spallation reactions of cosmic rays with light atmospheric nuclei, such as carbon, nitrogen and oxygen. ^{7}Be rapidly associates primary with submicron-sized aerosol particles. Lead-210 (half-life 22.3 y), which is one of the natural radionuclide of the ^{238}U decay series, is widely used as a tracer. ^{222}Rn (half-life 3.8 d), noble gas of the ^{238}U decay series, easily diffuses out mainly from land surface to the atmosphere via a series of short-lives secondary nuclides and becomes irreversibly attached to submicron-sized aerosols.

These two radionuclides with their different sources are therefore useful to understand the mechanisms of aerosol removal. The activity ratio in the precipitation is expected to vary with location and time. These radionuclides have measured routinely in many places of the world in order to study the description of environmental processes such as aerosol transit and residence times in the troposphere, aerosol deposition velocities and aerosol trapping by ground vegetation. Seasonal variations in the concentration of ^{7}Be in surface air have often been attributed to the influence of variations in the rate of exchange of air between the stratosphere and the troposphere. Other factors influenced to seasonal variation are the rate of vertical mixing within the troposphere, the rate of pole ward transport of air masses from middle latitudes to high latitudes and the rainfall rate indicating the importance of washout of the atmospheric aerosol.

Samples have been collected at Fukuoka in Japan. Deposition samples including rain and atmospheric deposition (wet deposition and dry deposition) were collected routinely throughout every month with a collector that has a surface area of 0.5 m^{2} from 1995 to 2000. The collected deposition samples were evaporated to dryness. Activity of ^{7}Be and ^{210}Pb in each sample was measured by non-destructive gamma-ray spectrometry using gamma rays of 478 keV and 46.5 keV, respectively. Aerosol samples have been collected using high volume air sampler with pumping rate of 1000 l/min to estimate wet and dry deposition rate.

The depositions of ^{7}Be and ^{210}Pb during these periods vary by more than a factor of 10 and 6, between 1.11 and 11.54, and 0.19 and 1.31 Bq/m^{2}/d. There are seasonal variations of ^{7}Be and ^{210}Pb activity on the deposition samples in Fukuoka: high in winter (^{7}Be and ^{210}Pb) and spring (^{7}Be). The higher values of ^{7}Be and ^{210}Pb during winter (November to February) are attributed to the increased horizontal transport rate from the continental region of higher latitudes. There is an increased transfer of ^{7}Be from the stratosphere to the troposphere in spring. The good correlation was observed between ^{7}Be and ^{210}Pb activities and the amount of precipitation. But this correlation depends on the season. The fallout composition divided into two fractions: wet deposition and dry deposition. The wet deposition was major process to remove the ^{7}Be aerosol from atmosphere. The scavenging by the washout and dry deposition also contribute the fallout process. The relationship of ^{7}Be and ^{210}Pb deposition pattern is almost similar, indicating utility as a useful tool of atmospheric tracer. We applied the prediction model. The calculated data are in good agreement with the observed data.