



INSTITUTE OF ISOTOPES
HUNGARIAN ACADEMY OF SCIENCES

1121 Budapest, Konkoly Thege Miklós út 29-33., Mail: 1525-HU Budapest, P.O.B. 77.

phone: +36 1 392-2531
e-mail: wojn@iki.kfki.hu

telefax: +36 1 392-2533
homepage: www.iki.kfki.hu

dr. László Wojnárovits director

Report on the scientific activity - 2011

I. Main duties of the research unit in 2011

The expected activities of the institute's expertise have been focussed on four directions:

Regarding ***nuclear analytical methods***

the emphasis was expected to be laid on application with respect to

- the determination of nuclear constants and other basic input data, which are necessary for the design of the operation parameters of transmutation and GEN-IV reactors,
- pursue the fruitful studies commenced on the objects of cultural heritage,
- provision of the cold-neutron facility in the framework of the EU FP7 NMI3-II project,
- continuation of the participation in MANREAD (Minor Actinide Neutron Reaction Data, IAEA CRP).

In the field of the development and improvement of methods in the framework of *national projects* with respect to the work carried out in the cold neutron beam were considered

- improvement of methods of data acquisition and digital data processing in the PGAA technique,
- adaptation of the neutronoptical and radiography equipment to provide possibility for measurements for materials science studies.

In the field of studies related to ***nuclear materials and radioisotopes***

- development of methods used for nuclear security studies (laser induced plasma spectroscopy, adaptation of methods for analysis of single separated particles),
- development of methods for analysis of long lifetime radioisotopes in biological samples,
- application of highly sensitive coincidence method to detect uranium by interrogation with cold neutrons,
- preparation for environmental screening measurements to contribute to the selection of an appropriate location for the new power plant site,
- analysis of the possible diversions of nuclear materials and technologies,
- study of redox processes in minerals of geological formations considered as perspective media for future nuclear waste sites.

In the field of ***radiation chemistry and dosimetry***

- identification of contaminants and determination of their amounts in pharmaceutical waste waters in the process of their radiation treatment. Detection of intermediates in the process of decomposition by pulse radiolysis and determination of the products by HPLC-MS,
- continuing development of the methods for retrospective dosimetry,
- preparation of novel thermoluminescent substances with increased sensitivity, study and comparison of their TL properties and the LET dependences in mixed radiation (gamma and neutron) fields.

In the field of *catalysis research*

In *gold catalysis* the effect of composition and structure in gold based multicomponent catalysts with complex active centers is to be studied. Au-CuO-CeO₂-M_xO_y (M-Ti, Mn, Zr) catalyst systems in PROX reaction, SiO₂, TiO₂, CeO₂, MnO_x, CoO_x supported bimetallic AgAu catalysts in CO oxidation, in selective oxidation of glucose and NO_x reduction are to be investigated.

Regarding the *methane dry reforming* the study of various mixed oxide supported Ni and bimetallic AuNi catalysts prepared by colloid chemical and conventional methods is to be continued in cooperation in an international consortium. The structural characterization, kinetic and stability investigations of the catalysts are to be carried out. The study of mechanism of deactivating carbon formation is to be commenced using ¹³CO₂.

Environmental catalysis research comprises

- the treatment of wastewaters with oxidation, the investigation of reactions with high energy irradiation in order to determine the necessary radiation dose and optimal parameters. They study the reactions taking place during common application of catalysis and irradiation.
- the study of hydrodesulphurization by measurement of the conversion of S-35 radioisotope labelled thiophene and thiophene-tetrahydrofuran, thiophene-butadiene mixtures is to be continued involving C-14 labelling. The HDS mechanism is to be studied on further catalysts applied or planned to be applied in industrial processes.
- the nitrous oxide decomposition and methane-nitrous oxide total conversion on Ir/H-ZSM-5 és Ir/Ga/H-ZSM-5 catalysts is to be optimised complemented with Mössbauer spectroscopy measurements.

Within *green chemistry research* the investigation of kinetic resolution of cyclohexanones with proline and the asymmetric hydrogenation of the chiral dimethyl cyclohexenone are to be carried out (on own initiation).

The investigations of *hydrocarbon reactions* on PtIr and PtRh catalysts is to be widened by investigation of these catalysts containing a third metal component (as Sn or Ge). In international cooperation CeO₂ supported Pt catalysts will be investigated in model hydrocarbon reactions.

A significant part of the institute's activity is devoted to supply technical supporting expertise (primarily as one of the Technical Support Organisations of HAEA) in the fields of nuclear security, radiation protection, transport and registry of radioisotopes, as well as at identification of seized radioactive materials of unknown origin.

II Outstanding research and other results in 2011

II/a Outstanding research and other results

On the field of ***improvement and development nuclear analytical methods***

- a method based on the GEANT4 simulation code has been developed for the determination of the yield and response function of HPGe detectors. By this means the accuracy was increased, yield estimations within a few per cent in the 50 keV – 10 MeV region were attained,
- they improved the accuracy of (n, γ) spectra of certain isotopes by using enriched rare earth and W samples in cooperation with the Lawrence Berkeley Laboratory,
- a method has been developed for the determination of composition of samples containing enriched isotopes and contaminants,
- new sample chamber and holder as well as network data acquisition module has been accessed for the NIPS equipment,

- Monte Carlo method has been developed to determine the internal elemental composition of objects measured by PGAI. The procedure has been developed in the framework of ANCIENT CHARM project and published in two chapters of relevant books,
- they have designed, constructed and installed a neutron radiograph, and –tomograph instrument (called NORMA),
- a method has been developed to determine the amount and distribution of boron in alloys. The bulk amount of boron can be determined by PGAA method, the distribution can be determined by particle trace detectors using the $^{10}\text{B}(n,\alpha\gamma)$ reaction,
- it has been proved that the EGAF (Evaluated Gamma-ray Activation File) complemented with Monte Carlo simulation can be used for the completion of the nuclear level schemes and for the determination of capture cross sections,
- they improved the sensitivity of the detection of uranium in cold neutron beam, a detection limit less than 1 microgram ^{235}U has been reached.

In the field of the ***application of nuclear analytical methods***
in *archeometry*

- provenance study of chipped and polished archeological objects from the paleolithic and neolithic collected in the Carpathian-basin have been performed with PGAA technique in collaboration with experts of the Hungarian National Museum and with other European institutes,
- compositions of the late neolithic ceramics originated from the North-Hungarian region (so called „Bükk culture”) were compared with compositions of ceramics from other coexistent cultures (Zselic, Bükk and Vinca). It was found that the classification based on their chemical composition does not coincide with the former typological characterisation.

in *chemical and materials science* studies

- by means of *in situ* PGAA
= distribution of chlorine among the reactants has been studied in the Deacon reaction catalysed by RuO_2 . These studies may promote the exact description of the reaction mechanism, and the development of a closed, environmentally safe production cycle.
= the hydrogen contents were determined in Pd and Ti based substances prepared freshly and having stored for some years. The long-term hydrogen storage capacity can be estimated based on these measurements,
- *in situ* Mössbauer spectroscopy was applied to study mesoporous ferrisilicates. Ti doped (Fe,Ti)-MCM-41 and novel FeKIL-2 structures were investigated. Changes in the coordination states of iron ions have been monitored. It was found that $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ reversible transformation may proceed more easily than in zeolite analogue microporous systems.

In the field of ***analysis of nuclear materials***

- novel method has been developed to determine the cross sections of neutron capture by ^{235}U and ^{238}U . The method is based on the mass spectrometric detection of ^{236}U and ^{239}Pu nuclei formed during the capture,
- the laser ablation ICP-MS method developed earlier for the determination of the uranium content in separated single particles has been adapted to analysis of scrap-collected samples. The method provides a mean for the exact determination of the extent of the enrichment in micrometer size particles, thereby enabling analytical measurements for nuclear safeguards and forensics applications.
- a chemical separation method has been developed for the rapid determination of total amount of long life-time actinides (primarily uranium) in *biological samples*. The amount of actinides can be analysed by ICP-MS. The method allows the estimation of the incorporated

dose as well as the internal contamination from samples (blood, urine) collected from victims of nuclear accidents or terrorist actions within 1-2 days.

- enrichment of fuel rods in novel type profiled fresh fuel assemblies has been verified by HPGe and CdZnTe gamma spectroscopies. The method has been used in routine for the control, ~10 per cent of the assemblies incoming in the power plant are checked recently.

- burnup in spent fuel assemblies at various sides and vertical positions have been determined by gamma spectrometry. A specific evaluation software has been developed. The direction dependence of burnup in the assemblies has been observed in correlation with the calculations. The $^{134}\text{Cs}/^{137}\text{Cs}$ ratio well characterizes the burnup within a few per cent precision. It is foreseen that the experimental results can be used to further improve the accuracy of the burnup calculation code, thus enabling more efficient use of the nuclear fuel and decreasing the costs of energy production..

- the possibilities for the deviation of nuclear materials and techniques have been analysed. The suitability of the directed graph model has been demonstrated for the analysis of the nuclear infrastructure of the IAEA member states,

- they analysed whether coupled redox processes ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$) taking place in clay minerals may play a role in the migration of long life-time isotopes (UO_2^{2+}) in geological media, considered as perspective host for high level nuclear waste in Hungary. They found that uranium strongly sorbs on the mineral particles of Boda Claystone samples without any coupled redox process.

In the fields of *radiation chemistry and dosimetry*

- The ionizing radiation induced degradation of pharmaceuticals, analgetics and antibiotics was investigated in dilute aqueous solutions. It was found that during the degradation of the aromatic ring cyclohexadienyl type radicals are formed. In the presence of oxygen they transform to peroxy type products. The OH radicals preferentially react with the aromatic ring and OH derivatives form.

In the degradation of ketoprofen in dilute aqueous solutions OH radical was found to be much more effective than hydrated electron. In paracetamol solutions the degradation was 2-3 times more effective in the presence of oxygen. At low doses an increased toxicity of the solution was found due to the formation of highly toxic degradation products (acetamide, hydroquinone).

- Hydrogels of high swelling ability (5000%) were synthesised from N-vinyl pyrrolidone monomer by high-energy irradiation initiated polymerization. Pastilles were pressed from the hydrogel mixed with CEPA (2-Cl-ethyl phosphonic acid). Using these pastilles a gas releasing system was developed able to keep a constant concentration of ethylene gas in a ventilated container during 72 hours. The system will be used to develop fruit ripening box produced by the cooperating partners.

- in the course of development of retrospective dosimetric methods they compared properties of surface mounted different electronic components (SMD resistances). They found that in the case of samples from same brand (producer) the nominal value of resistance has only minor influence on the thermoluminescence (TL) properties. Furthermore the decrease of the signal is anomalously fast at room temperature in the first 24-36 hour following the irradiation. The development of dose reconstruction process based on comparison with the empirical decay dependence has commenced.

The study of the SMD resistances with optically stimulated luminescence (OSL) has also been started. The dose – OSL signal correlation is unambiguous in the 0.1-50 kGy region as the first results attest.

- they performed the evaluation of the newly developed *dosimeter materials*, based on doped lithium tetraborate. The copper doped one is the most suitable for practical applications.

Catalysis

- In methane dry reforming, $CH_4 + CO_2 = 2CO + 2H_2$, (for utilization of biogas or methane wells of high CO_2 content) investigation of the novel AuNi catalysts was in progress in the frame of an ERAChemistry project (with French and Irish partners). $MgAl_2O_4$ supported Ni and AuNi samples were prepared with various Au/Ni ratio by (i) impregnation+deposition precipitation with urea and (ii) novel sol method. In case of impregnated samples increasing the metal loading the decrease of dispersion and activity was observed. The final dispersion and activity of the monometallic Ni catalysts of the same metal loading was similar regardless the preparation method. During the methane dry reforming in the 10% Ni-containing catalyst prepared by impregnation around the 30-100 nm large Ni and AuNi particles carbon shell evolves, on the smaller particles carbon nanotubes form, while on the smallest ones, below 6-8 nm in diameter none of these carbon deposition could be detected. The impregnated samples can be efficiently regenerated, not as the bimetallic sol derived ones with higher Au loading.

- In $CH_4 + N_2O$ reaction (for removal of N_2O having strong greenhouse and ozone depleting effect, for biogas pretreatment before methane dry reforming) on calcined H-ZSM-5 supported extra activity, multifunctional Ga and M (Fe, Co, Ni, Mo, Ir, Ag, Au) containing catalysts clear synergism was observed, which could be originated in the presence of bifunctional active sites, where Ga favoured the reducibility of M. On the effect of reduction in hydrogen the synergism disappeared, since the forming instable, mobile Ga^+ moved from the vicinity of M, the decreasing acidity weakened the stabilizing effect resulting in the decomposition of the bifunctional active sites.

- In PROX process (Preferential oxidation of Pd electrode catalyst poison CO from hydrogen for fuel cell application) the interaction of Au and CuO was investigated on SiO_2 , CeO_2 and 23% CeO_2/ZrO_2 supported catalysts. Gold was deposited from two different Au sols, CuO was formed from $Cu(NO_3)_2$ by calcination on the different oxide supports. CuO_x and nanodispersed Au nanoparticles interfacing and cooperating with CeO_2 were found to be the most active components. No synergism was observed between CuO_x and Au. The maximum CO conversion varied depending the support material in order of $SiO_2 < CeO_2/ZrO_2 < CeO_2$. On SiO_2 both in reduced and calcined form the 2%Au was more active and more selective than the 4% CuO, the activity and selectivity of bimetallic 2%Au4%CuO/ SiO_2 was between that of the monometallic analogous. On CeO_2 and 23% CeO_2/ZrO_2 supports 4% and 12.5% CuO provided higher conversion accompanied with higher selectivity, than 2 and 1% Au, respectively. Maximum CO conversion of 2%Au/ CeO_2 and 4%CuO/ CeO_2 was 90 and 100%, respectively.

PtSn alloy was prepared by reduction of Pt and Sn salt solutions with hydrazine. The product contained about 70% Pt and 30% Sn. This PtSn catalyst was more active in PROX reaction, than Pt.

Environmental catalysis

Wet oxidation of wastewaters

The effect of parameters on oxidation rate has been investigated with three model and one real wastewater using design of experiments. The leading parameter was temperature besides reaction time, the partial pressure of oxygen and intensity of mixing have smaller influence on reaction conversion. The obtained equations are important tools of scale-up.

The oxidation with high energy irradiation has been investigated with gamma and electron beam radiation. The oxidation of model compound phenol took place already at room temperature. The laboratory autoclave has been adapted for working with irradiation and at

higher temperature at the same time. Ti mesh monolith catalysts were compared in the oxidation of two wastewaters. Most effective were the catalysts containing Ru and Ir oxides together, in uniform distribution on the surface.

- CO oxidation, hydrodesulfurisation

SiO₂ supported Au catalysts promoted by CeO₂ and CuO „active” oxides were prepared using Au colloids: on the surface of about 6 nm in diameter Au particles 1-3 nm size oxid patches were formed. Au particles covered partially by CeO₂ and CuO are more stable against sintering and provided superior activity in CO oxidation as compared to gold dispersed on bulk type active oxides. The synergetic effect of active oxide – Au interface stabilised on SiO₂ support can be explained by the increased oxygen-activation on the thin oxide layers interfacing with gold. The bulk type active oxides far from the gold did not contribute to the catalytic process.

The study of activity-structure relationship on FeO_x/Ag or Au, and FeO_x/AuAg inverse model systems developed on SiO₂/Si(100) surface was continued. The monometallic Au, Ag or bimetallic AuAg of different composition, then Fe overlayer was deposited by molecular beam epitaxy (MBE) in collaboration with Institute for Solid State Physics and Optics. The CO oxidation activity changed linearly with the Ag/Au ratio, the Ag-rich samples were more active than the Ag-lean ones. No synergism was found between gold and silver in CO oxidation.

During the study of the mechanism of desulfurization it was confirmed that in HDS of thiophene the recyclization is significant decreasing the efficiency of desulfurization. In more detailed investigation butadiene + H₂S and butadiene + S_{cat} reactions were studied revealing, that butadiene can react with sulfur bound irreversibly on the surface forming thiophene. The inhibiting effect of H₂S in HDS process is not originated in the hampering of active sites, but in the reverse process of desulfurization, the recyclization.

- Green chemistry - Asymmetric hydrogenations

The kinetic resolution of 2-Me and 3-Me cyclohexanone was investigated with proline additive in reductive alkylation. The enantioselectivity was higher in the case of ortho derivative than with para compound, both of these values were much lower than that of isophorone, which could be explained with steric effects. The hydrogenation of prochiral and at the same time chiral 3,5-dimethyl-cyclohex-2-enon was investigated, as well. The stereochemistry of this reaction was unambiguous, only the meso compound was formed, with chiral modifiers and additives the process could not be diverted.

II/b Dialogue between science and society

It is a continuous intention that the activity and work carried out in the Institute of Isotopes should be made open for the public, for interested persons and organisations, too. One of the possibilities to comply this effort is to present an appropriate home page. The home page provides informations not only for the experts, topics which may merit more broad interest have also been reported in the „News” section. One among the reported events was the session of the „Academy of Nuclear Journalists” held in 5th May. In a series of lectures the experts of the institute gave accounts on their recent work. Further, on 5th December a small workshop was organised in the topic of treatment of water and waste waters, which might attracted broad public interest. In the same topic in a TV broadcast series (ENCOMPASS – ENCycloPedic knowledge Made a Popular ASset) in the episode entitled „Hungary on a dividing ridge: surface and groundwater in the country”

(<http://mindentudas.hu/riportfilm/item/2810-madlne-magazinmusor.html>) the procedure developed and applied for treatment of waste waters in the institute was demonstrated.

III. A presentation of national and international relations

Regarding the *national relations* it should be mentioned in the first place that the Institute of Isotopes is one of the Technical Support Organisations of the Hungarian Atomic Energy Agency. The institute thereby may directly contribute to the development and improvement of processes used to strengthen the nuclear security by providing a firm background of expertise.

Events with international participation

The „12th Tihany Symposium on Radiation Chemistry” was organised by the institute. The event was held in Zalakaros, between Aug. 27th and 1st Sept. (see the home page of the conference at <http://www.tihany.kfki.hu>). The participation was broad, 140 attendants arrived from 30 countries. More than 50 lectures were held, and over sixty posters were presented.

International relations

The institute is participant in several bi- and multilateral cooperations. The number of cooperating partners is the largest in the EU FP-7 and COST projects. (FP-7 : NMI3 – Neutron, Muon Integrated Infrastructure Initiative, MANREAD – Minor Actinide Neutron Reaction Data, CHARISMA – Cultural Heritage Advanced Research Infrastructure, RECOZY – Redox Controlled Systems, and COST : Interfacial functionalisation of (bi-metallic nanoparticles to prepare highly active catalysts).

Numerous other formal and informal cooperations help the work carried out in the institute, 60 % of communications published in 2011 were accomplished by utilizing the advantages of the international cooperations.

Provision of measuring infrastructure for international partners

The Department of Nuclear Research has also the duty to maintain the PGAA measuring facility in the cold neutron beam at the Budapest Research Reactor, and provide this measuring infrastructure to applicants from abroad. Significant part of the measuring capacity is utilized in this arrangement, 10 visitors used the facility for different projects in 2011.

Mobility of researchers

Several visitors were hosted in the institute within the framework of various cooperations in ca.25 instances. The visits were one week long in most of cases – the visitors held seminars in some cases, too. In reverse, the extent of visits of the researchers from the institute to abroad reached a similar measure.

Participation in the education

An Agreement of Cooperation has been signed with University of Óbuda. In the framework of this cooperation the institute provides its facilities and infrastructure as well as consultancy for MSc, BSc and PhD students of the University.

In the framework of earlier cooperations with certain universities the researchers of the institute

- delivered regular university courses,
- provided consultancy for PhD theses (6 cases), and master's reports (for 11 students)
- were responsible for practical laboratory exercise courses (6 instances)

IV. Brief summary of national and international research proposals winning in 2011

A Coordinated Research Project (CRP) grant of the International Atomic Energy Agency was obtained (Research Contract No. 16485) in the topic "Radiation Treatment of Wastewater Containing Pharmaceutical Compounds". Participants from 21 countries cooperate in this project.

OTKA #NNF2 85631 (Gold and silver catalysts for abatement of environmentally harmful materials). The interaction of Ag and Au and the support effect is studied in high surface area MnO_x and CoO_x supported Au-Ag bimetallic catalysts in CO oxidation and reduction of NO_x (NO or N₂O) by CO, which reactions have important role in vehicle emission control and the removal of greenhouse effect gases.

V. List of important publications in 2011

1. Wojnárovits L.,
Radiation Chemistry,
in: Handbook of Nuclear Chemistry, Eds: A. Vértes, S. Nagy, Z. Klencsár, R.G. Lovas, F. Rösch, Springer, pp. 1267-1331. (2011)
2. Révay Z., Lindstrom, R.M., Mackey, E.A., and Belgya T.,
Neutron-induced prompt gamma activation analysis (PGAA),
in: Handbook of Nuclear Chemistry, Eds: A. Vértes, S. Nagy, Z. Klencsár, R.G. Lovas, F. Rösch, Springer, pp. 1619-1672. (2011)
3. Horváth A., Beck A., Stefler G., Benkó T., Sáfrán G, Varga Z., Gubicza J., Guczi L.,
Silica-supported Au nanoparticles decorated by CeO₂: Formation, morphology, and CO oxidation activity,
J. Phys. Chem. C., 115: pp. 20388-20398. (2011)
4. Paál Z., Wootsch, A., Teschner D., Lázár K., Sajó I.E, Győrffy N., Weinberg G., Knop-Gericke A., Schlögl R.,
Structural properties of an unsupported model Pt-Sn catalyst and its catalytic properties in cyclohexane transformation,
Applied Catalysis A: General, 391: pp. 377-385. (2011)
5. Homlok R., Takács E., Wojnárovits L.,
Elimination of diclofenac from wastewater using irradiation technology,
Chemosphere 85: pp. 603-608. (2011)
6. Cámara, A.L., Kubaczka A., Schay Z., Koppány Zs., Martinez-Arias A.,
Influence of calcination temperature and atmosphere preparation parameters on CO-PROX activity of catalysts based on CeO₂/CuO inverse configurations,
Journal of Power Sources, 196: pp. 4364-4369. (2011)
7. Horváth A., Stefler G., Kiennemann, A., Pietraszek, A., Guczi L.,
Methane dry reforming with CO₂ on CeZr-oxide supported Ni, NiRh and NiCo catalysts prepared by sol-gel technique: relationship between activity and coke formation,
Catalysis Today, 169: pp. 102-111. (2011).

8. Beck A., Magesh, G., Kuppan B., Schay Z., Geszti O., Benkó T., Viswanath, R.P., Selvam, P., Viswanathan B., Guczi L.,
Specific role of polymorphs of supporting titania in catalytic CO oxidation on gold,
Catalysis Today, 164: pp. 325-331. (2011)

9. Györffy N., Tungler A.,
Effect of basic and acidic additives on the (S)-proline and Pd mediated kinetic resolution of
3,5,5-trimethyl cyclohexanone and asymmetric hydrogenation of isophorone,
Journal of Molecular Catalysis A: Chemical, 336: pp. 72-77. (2011)