



INSTITUTE of ISOTOPES HUNGARIAN ACADEMY of SCIENCES

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Report on the scientific activity in 2009

I. Main tasks of the research institute in 2009

The Institute of Isotopes carried on different types of activities in 2009. The activity devoted to scientific research was distributed among four fields: i/ nuclear science, ii/ studies on the effects of radiation, dosimetry, iii/ studies on catalysts and catalytic processes, iv/ applications of irradiations with high energy and catalysts in processes of environmental importance. The aimed tasks are connected in part to the work performed in the previous years, as well as to the work commenced in the frame of novel projects.

The primary intention in the *application and development of nuclear analytical techniques* was the development of Prompt-Gamma Activation Analysis (enhancing the sensitivity and selectivity, and enlargement of its database) and its extension to new methodology including 3D-imaging and 3D-elemental imaging.

The major tasks concerning *detection of nuclear and other materials and their isotopes*, as well as determination of their amounts, aimed at further developments of analytical methods for nuclear safeguards, by combining gamma spectrometry, neutron coincidence and delayed neutron counting, high sensitivity mass spectrometry (LA-ICP-MS), and retrospective dosimetry.

Concerning research of *radiation effects and dosimetry*, manufacturing and study of new, highly sensitive thermoluminescent and optically stimulated luminescent materials were planned, moreover developing a measurement method for the application of Sunna film dosimeters in the low dose range.

Whithin the topic „*Investigation of catalysts and catalytic processes*” the following researches were planned: testing of metal-metal (Pd, Pt, Te, Au) and metal-semiconductor (FeO_x, CeO_x) nanostructures, of silica supported model catalysts made of them, investigation of the formation of the Au-active oxide interface and their interaction in high surface area supported catalysts and model catalysts, the investigation of dry reforming of methane (important energy conversion process) on composite oxide-Ni and bimetallic catalysts, investigation of asymmetric hydrogenation of prochiral unsaturated ketones with Pd catalysts.

In connection with *environmental application of high-energy radiation and catalysis* installation of a laboratory for water analysis was intended, with elaboration and adaptation of analytical techniques to follow the efficiency of water treatments both by irradiation, and by combined treatment of irradiation and catalysis. Further, evaluation of Ru-Ir oxide/Ti monolithic catalysts was intended in wet oxidation of process waters from pharmaceutical

factories. Studies on catalytic processes and catalysts (decomposition and reduction of nitrous oxide using zeolite based catalysts, as well as $\text{NiMoO}_x/\text{Al}_2\text{O}_3$ HDS catalysts for sulphur removal) were also aimed with respect to possible environmental applications.

The *expert's services* provided for national and international authorities (predominantly for the Hungarian Atomic Energy Authority, and in a smaller proportion to the International Atomic Energy Agency) is another significant part of the Institute's activity.

Maintenance of a measuring station at the Budapest Neutron Centre supported primarily from EU sources is a further regular task. The infrastructural and professional background should be provided by the experts of the Institute for the researchers arriving here from EU states.

It is worth mentioning also here that the fiftieth anniversary of the foundation of the Institute was celebrated in 2009. Thus, the organisation and completion of the related events was also a task for 2009. A session of presentations were organised on this occasion entitled „Research in innovative environment: 50 years of the Institute of Isotopes” in the central building of the Hungarian Academy. (The programme and the presentations are also shown on the home page of the Institute.) In addition, the complete 3/4 double issue of the Magyar Kémiai Folyóirat (vol. 115, (2009)) is related to the Institute's fiftieth anniversary.

II. Outstanding research and other results, and their socio-economic impact in 2009

The circle of nuclear analytical methods has been amended, novel tools of low detection limits have been developed in the Institute. Their short description is presented separately as well.

In the field of *nuclear analytical techniques* the prominent achievements considerably expand and generalise the applicability of the PGAA method, particularly in relation with the PGAA theory, the library applicable to standard-less analysis and the developments in the data evaluation methods.

The PGAA *measurement technique* was also enhanced substantially. On the one hand a programmable beam stop was designed and built in to improve the short time activation capability, on the other hand the data analysis and the estimation of uncertainties of the data evaluation were improved. The *internal elemental distributions* of a number of complex samples were effectuated. The response function of a new gamma spectrometer was described using Monte-Carlo calculation, by which better analyses can be achieved. Spatial elemental analyses were also performed by using the newly developed techniques (PGAI and other neutron-based methods).

A *neutron coincidence counter* was designed for revealing uranium in unknown materials by an active method, applying a *cold neutron beam*. The coincidence count rate was found to be proportional to the ^{235}U content, regardless to the chemical form in the first approximation. The lower limit for ^{235}U detection was found to be 1 μg for 1000 s measurement time. This amount is lower with 1-2 orders of magnitude than that attainable by other usual neutron sources.

The nuclear analytical methods were applied successfully in various fields

The *PGAA technique* was used

- *In archaeometry*: For determination of provenance and raw material of prehistoric Hungarian, Croatian and Romanian chipped and polished stone tools; for identification of possible clay quarries of Late Neolithic ceramic findings, for non-destructive determination of alloy materials (Cu, Zn, Sn, Pb) of Renaissance brass sculptures, and for determination of elemental composition of Mesopotamian hematite based seals.
- *In Geology*: The advantages of the method were used in measuring the concentration of some trace elements (B, Cl, Gd) and hydrogen or water content, which can be measured with difficulties by other methods. In addition, all major oxides next to the rare trace elements from a bulk rock sample can be determined by the method. Among others, high pressure metamorphic rocks (Syros, Greek) were studied. It was found that the B/Be and Cl/Be ratios are in correlation with the H₂O concentration which is controlled by extraction of B and Cl during dehydration and prograde metamorphism. This helps to understand the dehydration in the metamorphic processes in the subducting slab. In other cooperation, serpentinite samples obtained from a deep sea floor drilling were analyzed. The results helped to revise the B, Cl and H recycling system during hydration and dehydration processes. Working together with Argentine researchers, boron contents of alkaline basalts were measured by PGAA from the Balaton-Highland and also from Northern-Patagonia. Results lead to the conclusion that the higher B content in the basalts of the Balaton-Highland resulted from the greater extension of the crust with greater melting of the previously metasomatised lithosphere in lower pressure environment, in comparison to the conditions under the Northern-Patagonian volcanic field.

The response of minerals for redox changes in the Boda Aleurolit Formation was investigated with another nuclear method, by the *Mössbauer spectroscopy* by determining the ratio of Fe²⁺ and Fe³⁺ ions in the minerals of the rock. The extent of weathering of the rocks in a good correspondence with the change in the Fe²⁺/Fe³⁺ ratio. Synthesized micro- and mesoporous ferrisilicates and metal-organic-framework substances of similar structure were also studied with the method. Iron ions located in different positions of the porous structure can clearly be distinguished by this technique.

In the field of *investigation of nuclear materials*

The load size of PuBe neutron sources was determined by radiography, using LINAC's bremsstrahlung and the X-ray machine of material testing at the Institute AEKI KFKI. Earlier results obtained from the estimation of these sizes and the literature value of PuBe₁₃ density, were revised in regard with the Pu content of 7 PuBe sources. Starting from the calorimetrically determined Pu masses and the stoichiometric composition of the PuBe₁₃ compound, load masses and volumes (from size), then densities were calculated. For the latter a value of 1.5 – 2.5 g/cm³ could be accepted, instead of 3.7 assumed earlier. The reason might be that the material is not dense, only a loose powder.

On the purpose to reveal the origin of seized samples a method was developed for determining 14 rare earth elements (Nd, Pm, Sm, Gd, Tb, Dy, Er, Tm, Yb, Ce, Pr, Eu, Ho, Lu) from model solution (100 ng/g U and 1 ng/g rare earth). The method is suitable for the application to real samples (uranium oxides of unknown origin) on the basis of taking the element's fingerprints.

A so-called virtual radiation source was developed in the frame of an IAEA support programme for replaying files taken by a list mode data recording system, made for neutron

coincidence measurements. The equipment can well be used for educational purposes, to demonstrate the basics of neutron coincidence measurements. By the equipment it is possible to study the signal of sources rarely or not available at all on the spot. The virtual source is easily portable, which assures liberty in the selection for sites of demonstrations and trainings.

A sample preparation method (destruction by microwaves and separation by extraction chromatography) and analysis by ICP-MS were developed for determining U and Pu isotopic composition and other actinide content of swipe samples to be used for safeguards purposes. The analytical procedure meets the requirements of the IAEA and the respective international network of laboratories (NWAL). The method is suitable for a rapid and simple preparation and analysis of swipe samples, and for detecting and revealing the origin of trace amounts of nuclear material contamination in them.

Migration of long half life fission product (^{99}Tc) and uranium isotopes has been studied in relation with perspective disposal of high level nuclear waste (spent fuel) in a geological formation. The spreading of the fission product isotope is relatively fast, its migration rate is comparable with that of strong electrolytes in aqueous media. In contrast, a large portion of uranium precipitates as U(IV) and does not participate in any migration process.

In studying *radiation effects and dosimetry*

- The conditions for the application of retrospective dosimetry had been elaborated in the institute. In this purpose a device based on optically stimulated luminescence (OSL) has been designed and completed. Adjustment, calibration were started, and test experiments were carried out.
- Principal optical properties, mainly luminescence of magnesium-borate were studied in various structures (crystalline, amorphous), doped with Eu, in the frame of a Ukrainian-Hungarian academic collaboration.
- The range of application of Sunna dosimeter films was expanded to the low dose range (5 – 500 Gy) by using OSL detection.

In the field of *studying catalysts and catalytic processes*

- the characterisation of Au nanoparticles and investigation of their adsorption and catalytic properties had been in progress further on. On the basis of study on the Au/oxide support (brookite and anatase – TiO_2 polymorphs) interactions it was established that besides the size of Au nanoparticles the crystalline structure or amorphicity of active oxide has also key importance in the CO oxidation activity. The inverse iron-oxide/Au interaction was studied in a $\text{FeO}_x/\text{Au}/\text{SiO}_2/\text{Si}(100)$ model system prepared by MBE method. The reduced surface is more active in CO oxidation than the oxidised one. CO adsorption studies followed by SFG spectroscopy showed, that in case of a thin iron oxide overlayer a part of Au sites is accessible for CO, while the thicker iron oxide overlayer completely covers the gold surface, no adsorbed CO could be detected. Au/TiO_2 prepared by deposition-precipitation (DP) using urea or NaOH were investigated in PROX reaction. The DP prepared samples were more stable against sintering than the sol prepared samples mentioned in the previous section, that was explained by the strength of the primary interactions. No significant difference was observed in the selectivity of the different samples. AuFe bimetallic particle formation was proven in Au/FeO_x system on the effect of reduction by H_2 . The reduction of

the catalyst decreased the PROX activity, that was attributed to the Au sintering.

- The methane dry reforming ($\text{CH}_4 + \text{CO}_2$) for synthesis gas production was studied on $\text{Ni/MgAl}_2\text{O}_4$ and $\text{Ni/Ce}_2\text{Zr}_2\text{O}_8$ catalysts. On $\text{Ni/Ce}_2\text{Zr}_2\text{O}_8$ the oxidation of carbon byproduct takes place at lower temperature and also the Boudouard reaction is more efficient. This is the consequence of the different structure of carbon deposits. On MgAl_2O_4 support the small Ni particles are enveloped by the CMWNT carbon nanotubes, while in case of $\text{Ce}_2\text{Zr}_2\text{O}_8$ the CMWNT has a fibrillar structure.
- *Ring opening reactions of methylcyclopentane* were investigated on bimetallic catalysts. Ca. 1-8 monolayer Ge containing PtGe catalysts have optimum catalytic activity and are more resistant towards deactivation. In case of PtIr- Al_2O_3 catalysts, if Ir was introduced in form of organic complex, Pt and Ir was deposited on the same sites and the activity and the C6 product selectivity increased.
- The asymmetric heterogeneous catalytic hydrogenation, belonging to benign or green chemistry, was tested with Pd catalysts on the proline-isophorone system. It was verified that the process depends on the catalyst, stereodifferentiation occurs on the solid surface, the optically active saturated ketone was formed not only by kinetic resolution but with the enantioselective hydrogenation of isophorone.

Application of high-energy radiation and catalysis in processes of environmental importance

- The possibilities of radiation induced decomposition of gallic acid present in high concentration in the wastewater of grape and wine processing facilities were studied. Several details of the oxidation/reduction reactions of gallic acid were cleared up by using radiation chemical techniques. A mechanism for the degradation of gallic acid induced by the ionizing radiation has been suggested.
- It was demonstrated that in the radiation induced decomposition of the highly toxic herbicide, the 2,4 dichloro phenoxy acetic acid, found almost everywhere in surface waters – depending on the conditions - hydrated electrons also contribute beside hydroxy radicals. However, $\text{O}_2^{\bullet -}/\text{HO}_2^{\bullet}$ intermediates that form in the reaction of hydrated electron and oxygen have low efficiency in the decomposition.
- The catalytic oxydation of wastewaters heavily polluted with organic impurities was studied on monoliths, and it was found that Ru oxide, Ir oxide and Ti grids are the most stable and most reactive.
- *The elimination of N_2O having green house and ozone layer damaging effect* was studied in $\text{N}_2\text{O} + \text{CH}_4$ reaction on M/H-ZSM-5 és M/Ga/H-ZSM-5 (M- Ru, Pd, Pt) zeolite catalysts. On the noble metal (Ru, Pd, Pt) containing samples besides the strong redox centres also the strong acid sites are preserved unlike in the case of Fe, Co, Mo containing systems. The Ru and Pt containing samples are more active (the temperature of the 50% conversion, T_{50} , in N_2O decomposition is 598 K, in the $\text{N}_2\text{O} + \text{CH}_4$ reaction it is 408 K) than the Fe, Co, Mo containing ones (T_{50} : 675 and 583 K in the two processes, respectively).
- *Catalytic hydrodesulfurization* processes were studied on sulfided $\text{NiMoO}_x/\text{Al}_2\text{O}_3$ catalysts of different Ni:Mo ratio. Applying ^{35}S labelled tiophene it was elucidated, that the well known recyclisation of tiophene from H_2S and butadiene takes place also between the

sulfided catalyst and the butadiene formed in the thiophene hydrodesulfurization. The differences between the thiophene-sulfur and H₂S-sulfur ↔ catalyst-sulfur isotope exchange are attributed to the energetic differences of the catalysts.

In summary, it can be concluded that the nuclear analytical techniques available at the Institute's disposal were improved and developed further in 2009. These methods, in combination with other recent techniques had been successfully applied for analysing nuclear substances as well. Thus, the Institute was able to provide the expert's services on the field of nuclear security in Hungary and in part in abroad. The merge of radiation studies with catalytic research and environmental science got an increasing accent recently. These studies are performed in part with industrial cooperations (with companies like MOL, FCSM, EGIS), with the general aim of future implementation of processes to sustain the quality of water and air in the natural environment.

III. Presentation of national and international relations

Principal support is gained for the Institute's work from its connections. This is reflected e.g. in the fact that the predominant part of the Institute's publications is coauthored by other national or foreigner researchers.

It is worth mentioning that among *national connections*

- the connections with *universities* are vivid. The researchers of the institute participate in the education – by delivering regular courses, lectures, consulting at practical work, providing tutorship for MSc reports and PhD theses. Some of the seniors of the institute contribute to the PhD courses as well. Furthermore, the joint research with the universities on different fields is also significant.
- within the other *institutional* connections that of established with the Hungarian Atomic Energy Agency (HAEA), and declared in a Memorandum of Cooperation, should be pointed at. The scientific background of the Agency, as a national authority, is supported by the Institute, primarily in the field of nuclear safeguard.

The *international connections* of the Institute are also outstanding.

- Some important ones among the *institutional connections* are
 - = The multiple connections with the International Atomic Energy Agency (IAEA). For instance the institute organised courses jointly with the Department of Safeguards Division of Technical Support (SGTS) for supervisors on nuclear security issues.
 - = The Institute is represented in organisations of nuclear security as well – institutional member in the ESARDA (European Safeguards Research and Development Association).
 - = There are Agreements of Cooperations with Max-Planck Gesellschaft (Fritz-Haber Institute in Berlin - in the field of studies of catalysts) and with the National University in Vietnam (Hanoi – in the field of various aspects of nuclear science).
- The international connections of the institute in the *field of research* are also extended. There are connections established in the field of nuclear science with some of the Joint Research Centres of EU (ITU, ISPRA, IRMM), as well as with the Lawrence Berkeley

National Laboratory, and with the National Institute of Standards and Technology in North America, or with the Institut Laue Langevin in France. There is a well-established cooperation with the Fritz-Haber Institute in Berlin on various topics in the field catalysis research. There is a long list of further bilateral connections with various institutions and universities. Some of them in the field of nuclear science ICNR – ISOE (Italy), Institute of Nuclear Sciences, Vinča, (Republic of Serbia), Ruder Bosković Institute, Zagreb, (Croatia), or the universities (from University of Tübingen, München, Cologne from Germany, Simon Bolivar University from Venezuela and University Massey in New-Zeland). On the field of catalyst's studies there are established connections with institutions in Spain and in India, and universities in Poitiers (France) or in Wien (Austria).

The cold neutron measuring facility should also be mentioned in connection with the international connections. This unique PGAA measuring facility is maintained and operated by the Institute – and a part of the measuring capacity is provided for the scientists of the EU. The visitor researchers exhaust their quotas fully always.

The international reputation of the Institute is also reflected in the practice of organizing international conferences. The 26th Miller (on the field of radiation chemistry) and the „EFNUDAT Slow and Resonance Neutrons” conferences were organized by the colleagues of the Institute in 2009.

IV. Brief evaluation of successful national and international grants

A significant part of the research activity of the Institute is based on the participation in projects. The support for obtaining appliances, consumables for the research work, and participating international conferences held abroad is mostly provided by various grants. This is particularly true in the case of the unique PGAA and NIPS cold neutron facility – where the maintenance and operation is rather expensive.

Among the *national grants*

- the **NAP-VEENEUS** grant merits an important place. This consortial project was awarded again for a support in the second three years period for development of measuring techniques with cold neutrons, commencing at 2009.
- the **OTKA projects** play also important role. 10 OTKA projects were in progress in 2009, with „large international” (ERA-CHEMISTRY), „large for young scientists” classifications among them.
- several projects announced by **HAEA** (Hungarian Atomic Energy Agency) were granted to the Institute – in particular in the field of nuclear security.

Participation in *the international projects* is also essential, the large ones are as follow:

- *EFNUDAT EU FP6 Integrated Infrastructure Initiative project (2006-2010) (European Facilities for Nuclear Data)*. The colleagues of the Institute had organised the 2nd EFNUDAT Workshop with 40 participants and 32 lectures presented (Sept. 25 – 29, 2009). The programme and lectures are available on the <http://www.iki.kfki.hu/efnudat/sciprg.shtml> web page as well. The work performed within

the project is the determination of nuclear data for design of IV generation reactors and ADS systems.

- *ANCIENT CHARM EU FP6 STREP NEST project (2006-2009) (Analysis by Neutron Resonant Capture Imaging and other Emerging Neutron Techniques: New Cultural Heritage and Archaeological Research Methods)* 3-dimensional neutron generated images of various objects of art were collected at the FRM-II reactor in Munich and in the ISIS spallation source in the closing year of the project.
- *CHARISMA EU FP7 ('Cultural heritage advanced research infrastructures: synergy for a multidisciplinary approach to conservation/restoration')* The project commenced in October 2009. It provides a mean to access sophisticated research infrastructures – included the PGAA station of the institute – for scientists from the EU countries in topics connected to the cultural heritage.
- *NMI3 – EU FP7 (Integrated infrastructure initiative (2009-2010) for neutron scattering and muon spectroscopy)* The project provides possibility to perform measurements for EU scientists on any related topic.
- *ReCosy EU FP7 CP (Redox Phenomena Controlling Systems, 2008 - 2011).* This project is related to the final disposal of high level nuclear waste. In particular, the influence of redox processes on the migration of long half life radioisotopes has been studied in geological formations (stones).
- *EU – FP7 Biodosimetric Tools for Triage to Responders* The project commenced in 2009. The aim of the project is the elaboration of methods for the first rapid screening of the extents contaminations at nuclear and radiation accidents.
- *COST - D36 WG 003/06 Interfacial functionalisation of (bi-)metallic nanoparticles to prepare highly active and selective catalysts: understanding synergy and/or promotion effect, 2007-2010*
- The Institute participates in some *projects of the International Atomic Energy Agency*:
 - = „Nuclear Forensic Methods and Techniques for Combating Illicit Trafficking of Nuclear and other Radioactive Material” (coordinated research project),
 - = a RER/8/017 „Enhancing Quality Control Methods and Procedures for Radiation Technology” (technical cooperation project),
 - = MANREAD (Minor Actinide Neutron Reaction Data),
 - = HUN8008, a technical cooperation project, which provides a mean to establish a laboratory for analysis of water.

V. The most important publications in 2009

1. Zs. Révay,
Determining elemental composition using prompt γ activation analysis,
Analytical Chemistry, 81, (2009) 6851 – 6859.
2. R. Melo, J.P. Leal, E. Takács, L. Wojnárovits,
Radiolytic degradation of gallic acid and gallic acid derivatives in aqueous solution,
Journal of Hazardous Materials, 172 (2009) 1185 – 1192.
3. L. Guczi, A. Beck, K. Frey,
Role of promoting oxide morphology in dictating the activity of Au/SiO₂ catalyst in CO oxidation,
Gold Bulletin, 42 (2009) 5 – 12.

4. Z. Paál, R. Schlögl,
Investigation of a traditional catalyst by contemporary methods: Parallel electron spectroscopic and catalytic studies on Pt black,
Surface Science, 603 (2009) 1793 – 1801.
5. H.R. Marshall, R. Altherr, K. Gmeling, Zs. Kasztovszky,
Lithium, boron and chlorine as tracers for metasomatism in high-pressure metamorphic rocks: a case study from Syros (Greece),
Mineralogy and Petrology, 95 (2009) 291 – 302.
6. J. Bagi, L. Dechamp, P. Dransart, Z. Dzbikowicz, J.-L. Dufour, J. Huszti, et al,
Neutron coincidence counting with digital signal processing,
Nuclear Instruments and Methods in Physics Research, A, 608 (2009) 316 – 327.
7. The whole 2009/3-4 issue of the Magyar Kémiai Folyóirat (vol. 115).
This special issue is devoted to the 50th anniversary of the foundation of the Institute. The issue contains 10 contributions from the authors from the Institute.