

Trends in radiochemistry at the beginning of the 21st century*

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Abstract A review on selected – the most important and most prospective – directions of the present-day radiochemistry has been presented, with a special emphasis on the research carried out at the Department of Radiochemistry, Institute of Nuclear Chemistry and Technology.

Key words radiochemistry • nuclear power • radiopharmaceutical chemistry • chemistry of radioelements • radionuclides in the environment

Introduction

Chemical studies commenced at the Institute of Nuclear Research fifty years ago were focused on practical problems connected mainly with the nuclear fuel cycle, production of radionuclides and their applications as tracers in chemistry and technology. Also fundamental studies were carried out with the use of radiotracers, in particular on the chemistry of radioelements, physico-chemical bases of separation methods, and the chemistry of “hot” atoms. All these directions matched well the development of radiochemistry in its “Golden Era” [15]. The history and achievements of radiochemical research carried out in the chemical branch of the Institute, since 1983 the Institute of Nuclear Chemistry and Technology, in particular in the Department of Radiochemistry, have been presented elsewhere [29].

After a period of some stagnancy in radiochemistry over the world in the seventies and eighties, evidence of renaissance could be observed in the 1990s. The end of the Cold War opened a new era of broad international collaborations in the areas related to the nuclear disarmament, including management and disposition of fissile materials, nuclear waste treatment, and environmental cleanup. The nuclear waste treatment is also a problem affecting the development of nuclear energy which again becomes more and more demanded over the world. Radiochemistry has gained importance not only in nuclear technology but also in other fields.

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For example, a great progress in detector technique and computer data treatment brought about an enormous development of nuclear medicine and gave new challenges to radiopharmaceutical chemistry. Successful syntheses of new heavy radioelements, as well as new discoveries in the chemistry of isotopes attract many chemists and radiochemists to these studies.

This review is devoted to some directions of the present-day radiochemistry, being considered by the author as most important and most prospective in the field, and being the object of the research interest for him and his collaborators at the Department of Radiochemistry.

Radiochemistry for nuclear power

Nuclear energy is the only reasonable alternative to the environment-unfriendly energy production based on fossil fuels. With introducing safe and effective nuclear reactors of new generations, nuclear power regains its position lessened by the Chernobyl accident [1, 13]. The problem which still remains unsolved is the safe storage of long-lived nuclear waste. The reprocessing of spent nuclear fuel has to be focused not only on the recovery of fissile materials (uranium and plutonium) for recycling but also, and first of all, on the proper treatment of the waste. That is because the main contribution to the total radiotoxicity of the fresh waste originates from radionuclides of short and medium half-lives. However, after a few hundred years the dominant contributors will be the long-lived alpha emitting isotopes of minor actinides (Np, Am, Cm and small amounts of higher actinides) and the long-lived fission products (^{99}Tc , ^{129}I), which originally make a minute fraction of the radioactivity of the waste. Two options are being considered, how to reduce the cost and to improve the safety of the management of such high-level nuclear waste. The first one is the storage of minor actinides alone, separated from fission products, which allows for a significant reduction of the volume of the very-long-lived waste to be solidified and long-term stored under special conditions (geological disposal). The other is based on the transmutation of minor actinides into short-lived nuclides using accelerator-driven systems or fast nuclear reactors [3, 5]. Because in the case of transmutation we must avoid "poisoning" of the reactor by fission products of high cross-sections for neutron capture, the minor actinides must be selectively separated from the fission products in both options. Unfortunately, similar chemical properties of the lanthanide fission products and minor actinides (except Np) make their separation (partitioning) troublesome. Various technologies of partitioning, based on hydrometallurgical processes, were developed to extract the minor actinides from nuclear waste – an acidic (HNO_3) solution as a rule, the aqueous raffinate, which remains after recovering uranium and plutonium in the solvent extraction process PUREX [23]. In some improved variants of the PUREX process also neptunium and the long-lived fission products can also be separated from the waste. However, there is still no answer generally accepted, how to extract the minor actinides from the aqueous PUREX raffinate

containing the rest of fission products. Studies on developing such methods have been carried out for decades by many research teams [23]. Two steps have been generally proposed: (1) group separation of trivalent lanthanides (Ln) and actinides (An) from the rest of fission products, and (2) selective separation of the minor actinides from the lanthanides, the latter being a few tens times more abundant than the former. In the technology being developed by the EU consortium coordinated by C. Madic, the first step consists in the group extraction of these trivalent f-electron elements as nitrates, using diamide extractants – the malonamides or diglycolamides (DIAMEX process) [21]. Various extraction systems were studied for the second step (SANEX process). To discriminate between the An(III) and Ln(III) ions various extractants – ligands with softer donor atoms (N, S) were studied. Promising results have been obtained with the use of heterocyclic N-polydentate compounds, i.e. radiation-resistant tridentate derivatives of triazinyl-pyridines [21] and related tetradentate extractants [14]. Very selective separations of An(III) from Ln(III) have been reached, with the separation factors of the order of tens and even hundreds. Recently, a research team of the Institute of Nuclear Chemistry and Technology joined the project, basing on their previous expertise in the chemistry [29, 32] and solvent extraction separations [8, 29] of the f-electron elements.

To-day, the more and more important role in studying the actinide chemistry and the processes of their solvent extraction is played by computational chemistry [30]. A review on the computational chemistry in modelling solvent extraction of metal ions has been published [26].

Apart from hydrometallurgical, also pyrometallurgical processes are considered as a tool for separating the long-lived radionuclides from nuclear waste [3, 5, 21], which points to this new area for radiochemical studies directed to modern technologies of reprocessing spent nuclear fuel.

Another radiochemical problem related to nuclear energy is water clean-up in nuclear power stations, i.e. removal of radionuclides from reactor cooling water, from water in the fuel storage pools, and from low-level aqueous waste released from nuclear stations. Ion-exchange filters are broadly used for this purpose.

Radiopharmaceutical chemistry

With no doubt, the greatest challenge to radiochemistry of to-day comes from nuclear medicine, both diagnosis and therapy. Precise measurements of biodistribution within a living organism of radiopharmaceuticals – the radiolabelled molecules that participate in biochemical processes – make it possible to image certain functional disturbances in the organism, i.e. to diagnose its disease much earlier than morphological changes appear, able to be detected using the methods of classical medicine. This fact is invaluable for early diagnosing and successful curing cancer metastases.

Rapid development of nuclear diagnosis observed in the last decades is not only due to the progress in detectors and imaging systems [9] and in computer data

treatment, but also to the progress in chemistry and radiochemistry. Radiochemical aspects of nuclear medicine, both diagnostic and therapeutic, include selection, production and separation of radionuclides, followed by radiolabelling chemistry: the production of radiopharmaceuticals. In this respect, the most important for nuclear diagnosis appeared the very convenient availability (at reasonable price) of generator-produced ^{99m}Tc , and also a great progress in the coordination chemistry of technetium. ^{99m}Tc is a gamma emitting radionuclide of the decay properties favourable for imaging by single photon emission computerized tomography (SPECT). Numerous ^{99m}Tc labelled radiopharmaceuticals of the 1st generation have been developed and used for imaging of the functioning of human organs (heart, brain, kidney etc.). Also various receptor specific radiopharmaceuticals of the 2nd generation have been developed, consisted of ^{99m}Tc complexes attached to biologically active molecules such as peptides, antibodies, small neuroreceptor targeting molecules, etc. [2, 4]. Some of these radiopharmaceuticals are used for tumor imaging.

Recently, another method of imaging gains a tremendously growing interest. This is positron emission tomography (PET) based on the coincidence detection of two photons emitted in the opposite directions upon positron annihilation. By using short-lived cyclotron-produced radionuclides, mainly ^{18}F [33], PET is much more expensive than SPECT, but its high resolution makes the method very attractive for nuclear medicine, in particular when combined with computerized tomography (PET-CT). In the majority of clinical PET applications, the organic molecule 2- ^{18}F fluoro-deoxy-D-glucose (^{18}F FDG) is used, which is increasingly consumed by tumor cells (glycolytic metabolism). Also the other most often used PET radiopharmaceuticals, labelled with ^{18}F ($t_{1/2} = 1.9$ h) and with ^{11}C , ^{13}N and ^{15}O of still shorter half-lives, are the organic species. However, the increasing availability of positron emitters of metallic character, e.g. ^{45}Ti , $^{60,61,62,64}\text{Cu}$, $^{66,68}\text{Ga}$, ^{86}Y , ^{89}Zr , ^{90}Nb etc. [20], makes important further studies on the coordination radiochemistry of these metal ions, focused on potential applications of their complexes in PET imaging.

The second branch of nuclear medicine is radionuclide therapy which employs the toxic effect of nuclear radiation on pathological conditions as cancer and rheumatoid arthritis. Radiopharmaceuticals labelled with particle-emitting radionuclides are used, which locate selectively in disease sites and deliver almost all radiation to the sites. This maximizes destruction of cancer cells and minimizes radiation dose to normal tissues. Depending on the dimensions of the disease sites, e.g. large tumors or small metastasis cancer cells, various radionuclides are used, differing in kind and energy of radiation, which determines the range of radiation in the tissue. The ranges vary from millimeters for high-energy β^- emitters (e.g. ^{90}Y , ^{188}Re), mm fractions for soft β^- emitters (e.g. ^{177}Lu , ^{131}I), a few cell diameters (tens mm) for α emitters (e.g. $^{212,213}\text{Bi}$, ^{211}At), to subcellular range for low-energy Auger-electron emitters (e.g. ^{67}Ga , ^{103m}Rh , ^{123}I) [38]. The resulting variety of radionuclides used for therapeutic purposes

is another challenge to radiochemists who have to develop various types of therapeutic radiopharmaceuticals, from organic molecules to metal complexes bound to tissue-specific biomolecules [20, 38].

The Polish production of radiopharmaceuticals and radionuclides for medical uses has mainly been developed and assisted with the own research by the Radioisotope Centre POLATOM [24]. Studies on radiopharmaceutical chemistry have also been commenced at the Institute of Nuclear Chemistry and Technology [27, 31], supported in part by the European Commission within the Marie Curie Action for the Transfer of Knowledge (6th Framework Programme).

Chemistry of radioelements

Recent discoveries, or rather successful nuclear syntheses of new superheavy radioelements, the transactinides, allow nuclear chemists not only to complete the Periodic Table, but also to perform elementary chemical studies with the new elements. Because the half-lives of the known longest-lived isotopes of the superheavy elements are very short, rarely exceeding 1 min, very fast recoil techniques were developed for their separation, as well as the gas-phase chemistry – fast separation technique in fully automated apparatus – for identification. Apart from that, also liquid-phase radiochemical studies, based on column chromatography, solvent extraction, etc. were carried out either manually or in automated apparatus. Because of the extremely low yields of the nuclear syntheses (one atom at a time), a new fundamental and experimental approach, single atom chemistry based on very simple chemical experiments, has been developed [36]. Chemical studies become more accessible due to the fact that some isotopes of the superheavy elements appear relatively long-lived (hours). The single-atom-chemistry studies are usually preceded by model experiments with the short-lived isotopes of lighter analogs of superheavy elements [34]. The knowledge of chemical properties of the heaviest elements is not only of fundamental interest, in particular for testing the role of relativistic effects in chemistry, but is extremely important for identification of the new nuclei which are detected by means of their decay radiation.

Although significant deviations from the periodicity of the chemical properties observed down the Groups in the Periodic Table, the elements from 104 (Rf) to 108 (Hs) show some chemical similarity to their lighter analogs in Groups 4 to 8, respectively [19]. This is in agreement with theoretical predictions taking relativistic effects into account [30]. On the other hand, the first chemical investigations on the element 112 show that relativistic effects significantly change its properties when comparing to its lighter analog – mercury [37].

Relativistic effects affect the chemical properties of other heavy radioelements as well [19]. This has also been shown by the works from our Department [29], in particular on the unusual hydrolysis of Ra^{2+} [40] and Ac^{3+} ions, and on the experimental determination of ionic radius of No^{3+} [7].

Radionuclides in the environment

Studies on the behaviour of radionuclides and radioelements in the environment, including radioanalytical chemistry of trace elements, seem to be the most popular kind of research in applied radiochemistry. The studies are rarely based on simple radiometric measurements, in most of them radiochemical techniques are used to separate and/or preconcentrate a given radionuclide present in trace amounts in a large sample. In particular, studies on chemical speciation of the trace radionuclides or radioelements meet an increasing interest.

There are numerous aspects of such studies, both practical and cognitive. Monitoring of radioactive contamination of water and food is a routine procedure for environmental radiation protection [22]. Studies on the distribution and migration of natural radionuclides in the environment allow us to detect environmental hazards, e.g. surface contaminations from radium-bearing coal-mine waters [10], and bring important information on the sources of contamination of the environment [6]. Studies on the migration of cosmogenic radionuclides make it possible to study and to model geochemical processes, e.g. circulation of phosphates (^{32}P) in ecosystems [35]. Determination of anthropogenic radionuclides in environmental samples brings information on the sources of contamination, e.g. nuclear reactor operation, nuclear accidents, testing and production of nuclear weapons, etc. [16, 22].

In order to detect radionuclides in ultra-trace levels, highly sensitive analytical methods must be used. Numerous radiometric techniques have been developed, e.g. determination of radium isotopes based on measuring of radon emanation [18]. Long-lived radionuclides, e.g. ^{129}I or ^{238}U , can be successfully determined using radiochemical neutron activation analysis, commonly used for non-radioactive trace elements [12]. Proper certified reference materials [12] as well as inter-laboratory comparisons [28] are of great importance for the assessment and control of the quality of the analytical data from a given laboratory. However, it is worth mentioning that radiometry is no more – as it was in the early days of radiochemistry – the most sensitive method of analysis. Some non-radiometric methods based on mass spectrometry, e.g. ICP-MS, have become competitive or even more sensitive than the radiometric ones in detecting ultra-trace amounts of medium- and long-lived radionuclides [12]. The progress in this area is very fast.

Concluding remarks

The present paper does not encompass all the areas of modern radiochemistry and nuclear chemistry. For example, very interesting problems have been neglected, related to newly discovered mass-independent isotope effects [17] and to new applications of stable isotopes in material science, environmental studies, food authentication, and medical research. These problems have also been studied at the Institute of Nuclear Chemistry and Technology [11]. There is no doubt that

radiochemical researches and closely related studies in nuclear chemistry, directed towards various applications in nuclear medicine, nuclear technology, environmental problems, etc. should be developed both over the world and in our country. An obstacle for that can result from the decreasing number of experts in the field of these sciences, including academic teachers, and from still a low interest of students [25]. The remedying programmes have been commenced over the world [39]. A similar action should also start in Poland as soon as possible.

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