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Analytical radiochemistry of neutron activated samples in practice

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Abstract
Analytical radiochemistry of neutron-activated samples, as practiced during past decades at the Jožef Stefan Institute Ljubljana, is outlined. The paper reviews achievements made in both elemental analysis and analyses of long-lived radionuclides, in variety of sample types. The presented analytical procedures include application of diverse chemical separations, multiple irradiations of samples, use of various nuclear reactions and detection modes for particular measurands, and determination of elements that are difficult to be determined by neutron activation analysis (NAA). Useful practical applications of neutron-activated tracers for chemical yield determinations, as unique feature of radiochemical NAA in comparison with non-nuclear analytical methods, are also addressed.

Keywords Analytical radiochemistry · Neutron activation analysis · Radiochemical separation · k_0-RNAA · Radioactive tracer

Introduction

The Journal of Radioanalytical Chemistry (JRC) was founded by Professor Tibor Braun in 1968. Accidentally, the first scientific paper on radiochemical neutron activation analysis (RNAA) in Slovenia was prepared at the same time by Professor Ladislav Kosta and Dr. Anthony R. Byrne. The concerned research work emerged from the first activities around the newly commissioned 250 kW TRIGA Mark II research reactor of the Jožef Stefan Institute (JSI), Ljubljana, and that particular paper was published in the year 1969 [1]. Over the next 50 years, the above authors as well as their colleagues and successors, gathered within the radiochemistry research group at the JSI TRIGA reactor, have published numerous scientific papers, many of them in the Journal of Radioanalytical (and Nuclear) Chemistry. The coincidental appearance of JRC and the first published paper by Kosta and Byrne on RNAA therefore offers a good opportunity to look back and review the most important achievements of the JSI group in radiochemistry, involving unique challenges and possibilities of utilizing neutron-activated nuclides for analytical purposes.

According to the International Union of Pure and Applied Chemistry (IUPAC), the term analytical radiochemistry (synonym: radioanalytical chemistry) is defined as "that part of analytical chemistry in which the application of radioactivity is an essential step in the analytical procedures" [2]. Analytical radiochemistry can be understood as a rather broad field of chemistry, ranging from the analyses of natural and man-made radionuclides (with radiochemical separations mostly in connection with the final detection of emitted α- or β- particles) to the analyses of elements or radionuclides following neutron activation of target nuclides. The later one is also referred to as RNAA and is mostly (but not exclusively) related with final measurement γ-rays emitted by the formed radionuclide.

Neutron activation analysis (NAA) is nowadays a well-established nuclear analytical method for quantitative determination of elements in vast kinds of materials. It is particularly valuable as it (1) is based on a physical principle very different from other competitive analytical techniques, (2) exhibits, if performed under well-controlled conditions, broad signal linearity ranging from the detection limit up to 100% mass fraction of a measurand, and (3)

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offers, based on isotopic detection nature, possibility for determination of radionuclides.

Comparison of chart of the nuclides and periodic table of the elements clearly shows higher number of analytical measurement possibilities when involving nuclides of an element, in comparison with single-element only determination, which is usually the case in applying non-nuclear analytical techniques. In addition to the existing nuclides, the use of neutron activation that involve various nuclear reactions (depending on the particular element/nuclide), offers numerous analytical measurement possibilities with respect to the selected nuclear reactions, activation and decay modes, half-lives of the formed radionuclides and types of radiation emission measured. Critical examination of chart of the nuclides, combined with consideration of the factors listed above, offer many analytical opportunities, sometimes involving several independent approaches. Many radioanalytical approaches with respect to the factors listed above, have been utilised at the JSI during the last decades and some of them, mostly nonconventional in analytical radiochemistry community at large, are briefly reviewed further below. More experimental details for the particular procedures discussed can be found in the cited literature.

Radiochemical neutron activation analysis for determination of the elements

As a general rule, the applied radiochemical procedure must allow for: (1) the radionuclide of interest be isolated in high yield and with high purity, (2) the radionuclide of interest be detected with as high efficiency as possible, considering also background and (3) the procedure be applicable to a wide range of material types and radionuclide concentrations. Radiochemical separation makes use of differences between the distribution coefficients of the individual constituents of a mixture between two phases. The separation may involve (1) isolation of a major constituent with traces remaining in a solution, (2) isolation of trace constituents with major constituents retained in the solution and (3) separation of trace constituents from one another after isolation. The separation can further involve (1) specific isolation of a single constituent from the solution, (2) group separation of all trace elements and (3) masking of interfering constituents for complete specificity.

There are two conceptually diverse approaches to RNAA with respect to timing: either to perform radiochemical separation prior to neutron irradiation or to perform the separation after the irradiation, the latter one often referred to as chemical neutron activation analysis. The first approach is obviously advantageous as it makes use of unique advantage of working with activated radionuclide of the element to be determined, evidenced by the absence or at least minimisation of potential contamination during the chemical separation process. Furthermore, inactive carrier of the element to be determined can be added after neutron irradiation, to overcome the element's unpredictable behaviour at very low concentrations. Weakness of this approach is if the time required for the radiochemical separation is too long in comparison with the half-life of the induced radionuclide (e.g. in the range of several minutes). In such case, a pre-irradiation separation should be applied. Then the comparative advantage of NAA is lost, as the measurement encounters the same problems as other, non-nuclear techniques, such as the problem of blank, the risk of contamination, etc.

Whenever the separation is applied, chemical recovery should be known, either in advance by carrying out pre-experiment or, better, by simultaneous determination along with the analytical measurement. NAA allows for two unique possibilities: determination by re-activating the previously added inactive carrier or by using radioactive tracer. The radioactive tracer could be commercially purchased or locally produced by irradiating suitable target. Some examples are shown further below.

Whenever RNAA is applied, the sample should in most cases be first mineralised and brought into a liquid form. Dry or wet ashing, total dissolution with mineral acids and application of fusion are the most frequently used options. In this step, particular care should be taken to avoid losses in case of volatile elements such as iodine, mercury and selenium. In case of Hg, for instance, separation by volatilisation is one of the possible options [1].

Isolation of a major constituent is usually applied when its activity interferes with the signals of measurands, either by nuclear interference reactions, overlapping gamma-ray peaks, or by increasing the background radiation. Typical examples are ^{82}Br, ^{42}K, ^{24}Na and ^{32}P in various, mostly biological materials. Those radionuclides can be separated by simple separations using selective sorption on inorganic ion exchangers [3–6]. In case of alloys or metals, major constituents can effectively be removed by applying electrolysis [7]. For analysing groups of elements by RNAA, there are many procedures available, mostly based on ion exchange chromatography [8–11]. However, for achieving the lowest possible detection limits and minimising measurement uncertainty at given experimental conditions, single element or small group separation followed by either direct gamma-ray measurement or further isolation of single elements, is required.

Such approach has been vastly used at JSI, with post-irradiation separations whenever possible. Most frequently, solvent extraction has been applied, as it is fast and highly selective, if applied under well-controlled conditions.

Extraction of iodides into toluene has been applied for As and Sn [12, 13], extraction of carbamates for Cd, Co, Cu, In, Mn and Zn [5, 14–16], extraction with 4-nitro-o-phenylene diamine (4-NDP) for Se [17] and extraction with N-benzoyl-N-phenylhydroxylamine (BPHA) for V [18, 19]. Less frequently, ion exchange chromatography has been used, as e.g., for Co and Ni [20]. Other separations have involved determination of I and Se by selective extraction of elementary iodine into CCl_4 and Se(IV) with 4-nitro-o-phenylenediamine (4-NPD) [21].

Radiochemical isolation of a single element does not necessarily needs to be followed by gamma-ray measurement. As the detection efficiency for gamma rays on semiconductor detectors is relatively low (typically $< 1\%$, depending on photon energy), the isolated radionuclide of high radiochemical purity can be measured by e.g., beta-particles counting, where the detection efficiency can reach almost 100%. An example of such RNAA procedure is determination of tin by liquid scintillation counting of ^{121}Sn [22].

Multiple irradiation followed by radiochemical separation

Simultaneous determination of several elements, where the induced radionuclides have different half-lives, can be carried out by multiple irradiation of the same sample. Such procedure was developed for the determination of vanadium (^{52}V, $t_{1/2}$ = 3.75 min), arsenic (^{76}As, $t_{1/2}$ = 26.4 h) and molybdenum (^{99}Mo, $t_{1/2}$ = 2.75 d) [23]. Iodine and selenium can simultaneously be determined in biological materials by long irradiation (to induce long-lived ^{75}Se ($t_{1/2}$ = 120 d) activity), cooling (to allow medium-lived nuclides to decay away), short irradiation of the same sample (to induce short-lived ^{128}I ($t_{1/2}$ = 25.0 min) activity), followed by radiochemistry [24]. The procedure is based on sample ignition in an oxygen flask, followed by selective sequential extraction of elemental iodine into chloroform and Se(IV) with 4-nitro-o-phenylenediamine (4-NPD) [24]. Another scheme is concerned with RNAA of Hg, U and I. The sample is first irradiated for about 20 h to induce activities of ^{197}Hg and ^{235}U fission product ^{133}I. After cooling period of about two days, the same sample is re-irradiated for about 2 min to activate iodine (^{128}I). The sample is then ignited using oxygen flask and iodine is extracted as above, while Hg is extracted as iodide into toluene [25].

Application of different nuclear reactions to determine two elements by separating only one

Reactors having relatively high fast neutron flux, such as the JSI TRIGA Mark II with the fast flux in the same range as the thermal one, offer possibility for analysing nuclides that are activated by fast neutrons. In case of favourable nuclear parameters (cross section, isotopic abundance, gamma-ray energy and intensity), a nuclear reaction with fast neutrons yields an induced radionuclide, which is an isotope of different element that the target one. In such case, it is possible to determine two elements by chemically isolating only one. Sometimes, even reactions with thermal neutrons leads to such radionuclide pairs via further decay of the induced radionuclide. Some examples of such nuclear reactions are shown in Table 1.

An example of applying such approach is radiochemical separation of cobalt by anion exchange chromatography for the determination of Co and Ni in biological materials [20].

Speciation studies

NAA is an element specific technique, so the measurement result does not depend on chemical or molecular form of the element to be determined. However, it can be applied as a hyphenated technique, i.e., as an element specific detector in species analysis. Moreover, neutron activation can also be used to produce labelled species. Such approach was developed for arsenic species, involving ion exchange chromatography as a separation step. NAA was used as an element specific detector for determination of inorganic arsenic, monomethyl arsonic acid, dimethylarsinic acid and arsenobetaine, and neutron irradiation was applied to produce the ^{76}As labelled species. The labelled species, could later be used to validate the column separations [26].

Table 1 Some examples of nuclear reactions yielding radionuclides of the same element

Nuclear reactions	Radionuclide pair
^{27}Al (n, γ) ^{28}Al; ^{29}Si (n, p) ^{29}Al	^{28}Al, ^{29}Al
^{55}Mn (n, γ) ^{56}Mn; ^{54}Fe (n, p) ^{54}Mn	^{56}Mn, ^{54}Mn
^{59}Co (n, γ) ^{60}Co; ^{58}Ni (n, p) ^{58}Co	^{60}Co, ^{58}Co
^{109}Ag (n, γ) ^{110m}Ag; ^{110}Pd (n, γ) ^{111}Pd → ^{111}Ag	^{110m}Ag, ^{111}Ag
^{123}Sb (n, γ) ^{124}Sb; ^{124}Sn (n, γ) ^{125}Sn → ^{125}Sb	^{124}Sb, ^{125}Sb
^{238}U (n, f) ^{131}I; ^{127}I (n, $2n$) ^{126}I	^{131}I, ^{126}I
^{197}Au (n, γ) ^{198}Au; ^{198}Pt (n, γ) ^{199}Pt → ^{199}Au	^{198}Au, ^{199}Au
^{231}Pa (n, γ) ^{232}Pa; ^{232}Th (n, γ) ^{233}Th → ^{233}Pa	^{232}Pa, ^{233}Pa
^{237}Np (n, γ) ^{238}Np; ^{238}U (n, γ) ^{239}U → ^{239}Np	^{238}Np, ^{239}Np

Elements that are difficult to be determined by NAA

Lead and thallium are two elements usually not considered determinable by NAA. Nevertheless, radiochemical procedure involving nuclear reactions with fast neutrons (^{204}Pb (n, $2n$) ^{203}Pb and ^{203}Tl (n, $2n$) ^{202}Tl) was developed and successfully tested on environmental samples [27].

Radiochemical k_0-neutron activation analysis

The k_0-method of NAA was launched in the mid-1970s by Simonits et al. [28]. After several years of its continuous improvement and validation, the k_0-NAA has become widespread as an analytical tool for panoramic analyses of various kinds of samples, as it allows for determination of more than 60 elements. At JSI, k_0-NAA was introduced at the end of 1980s and applied, as in vast majority of other laboratories, in its instrumental, non-destructive form (k_0-INAA) [29]. However, k_0-INAA is in practice limited in number of measurands and their respective detection limits by interferences, due to matrix elements, as well as inter-element and background effects. To overcome those problems, the method can also be applied in its radiochemical form (k_0-RNAA). Such approach may be particularly useful in case of characterising mineral samples, as described in more detail in [30].

A study was carried out with colleagues from Ss. Cyril and Methodius University in Skopje, on arsenic (realgar and orpiment) and antimony (stibnite) minerals [31]. High concentrations (> 50%) of As and Sb in those minerals and the resulting high background activities of ^{76}As and $^{122/124}$Sb, made the determination of medium-lived radionuclides at lower mass fractions impossible or having high detection limits. Therefore, post-irradiation solvent extraction of their iodides into toluene was applied prior to gamma-ray spectrometric measurement of trace elements of interest, to extend the number of elements detected and/or to improve detection limits for their determination [12, 31, 32].

The induced radionuclide ^{59}Fe interferes in the determination of many elements in iron minerals. Therefore, the separation of iron by isoamyl acetate or diisopropyl ether (DIPE) from hydrochloric acid solution, prior to gamma-ray spectrometric measurement, was applied for k_0-RNAA of iron minerals (pyrite, chalcopyrite and hematite) [33]. In case of chalcopyrite, copper as a matrix element also interfered in the determination of many trace elements. Therefore, a refined post-irradiation separation scheme was developed, involving first the removal of copper by electrolysis, followed by the liquid–liquid extraction of iron by DIPE. The applied separation allowed for studying content of up to 50 elements in chalcopyrite [34].

For verification of the applied k_0-RNAA procedures, different certified reference materials or reference materials were used [35–40].

Radiochemical neutron activation analysis for determination of radionuclides

Radionuclides can be determined either by direct activity measurement, usually termed as “radiometric analysis” or by measurement of their mass. However, the required sensitivity usually limits the choice of mass measurement to spectroscopic techniques, mass spectrometry and (NAA). Radiometric methods are less favourable for long-lived, low specific activity radionuclides, where mass-based (“atom-counting”) techniques might be more advantageous. NAA is therefore favourable when the radionuclide to be determined has a large neutron capture cross section for formation of a product nuclide of relatively short half-life with good measurement properties, preferably for gamma-ray spectrometry. In the most favourable case, INAA is appropriate for the determination of some radionuclides, such as ^{238}U and ^{232}Th via ^{239}Np and ^{233}Pa, respectively, in many materials at natural levels. If post-irradiation radiochemical separation of the formed radionuclide is needed to improve the signal/noise ratio and the sensitivity, the procedure is advantageous to radiometric determination, as the added carrier could be used to optimize and control chemical recovery and the procedure is not subject to blank corrections. Blank is namely the factor limiting sensitivity and accuracy of most other non-nuclear techniques.

The advantage of NAA with respect to radiometric determination can be expressed in terms of an advantage factor (AF). The AFs for some radionuclides, calculated for specific measurement conditions of the JSI TRIGA Mark II reactor, are shown in Table 2.

Table 2 Advantage factors for some long-lived radionuclides [41]

Nuclear reaction	AF
^{238}U (n, γ) ^{239}U	7.0×10^6
^{238}U (n, γ) ^{239}U → ^{239}Np	8.0×10^5
^{232}Th (n, γ) ^{233}Th → ^{233}Pa	4.0×10^5
^{230}Th (n, γ) ^{231}Th	27
^{237}Np (n, γ) ^{238}Np	640
^{231}Pa (n, γ) ^{232}Pa	106

As shown in Table 2, extremely high AF values are for NAA of ^{238}U and ^{232}Th, and lower but still favourable for ^{237}Np, ^{231}Pa and ^{230}Th.

A method for the simultaneous RNAA of uranium and thorium at trace levels in biological samples was developed, based on a technique referred to as LICSIR, where a double neutron irradiation is employed. In the first, long irradiation, ^{233}Pa ($t_{1/2}$ = 27.0 d) is induced by neutron capture of ^{232}Th and the sample is then cooled for several weeks. Afterwards, a second short irradiation is performed to induce ^{239}U ($t_{1/2}$ = 23.5 min), followed by a rapid sequential solvent extraction separation of ^{239}U with tri-n-butyl phosphate (TBP) and ^{233}Pa with tri-n-octyl phosphine oxide (TOPO) [42]. Chemical yields of ^{239}U and ^{233}Pa are measured using ^{235}U and ^{231}Pa tracers.

Analysis of uranium can be accompanied by simultaneous RNAA determination of manganese and vanadium from the same test portion, using carbamate and BPHA solvent extractions, respectively [43, 44].

Several methods for determination of ^{237}Np in soil and sediment samples were developed [41, 45–48]. One of the procedures makes use of a pre-irradiation RNAA. First ^{237}Np is isolated from a sample by either ion exchange chromatography or extraction chromatography. The isolated Np fraction is then neutron-irradiated, inducing the ^{237}Np (n, γ) ^{238}Np ($t_{1/2}$ = 2.2 d). The recovery of radiochemical separation is determined by adding known amount of ^{239}Np prior to the sample decomposition. However, separation of neptunium from uranium before irradiation is required as ^{237}Np is also formed by: ^{235}U (n, γ) ^{236}U (n, γ) → ^{237}U ($t_{1/2}$ = 6.75 d) → ^{237}Np and ^{238}U (n, 2n) ^{237}U → ^{237}Np [45, 48, 49].

Another long-lived radionuclide of interest has been ^{129}I. The developed RNAA procedure comprises (1) a preconcentration step involving sample decomposition by alkaline fusion, followed by iodine extraction into chloroform and subsequent trapping on activated charcoal; (2) neutron activation via the nuclear reaction ^{129}I (n, γ) ^{130}I; and (3) post-irradiation radiochemical separation of I, involving combustion of the charcoal in an oxygen atmosphere and iodine extraction into chloroform. The procedure allows for simultaneous determination of stable iodine via the nuclear reaction with fast neutrons ^{127}I (n, 2n) ^{126}I, thus also obtaining the ^{129}I/^{127}I isotopic ratio in the measured sample [50].

Neutron-activated tracers for chemical yield determination

Accurate determination of chemical yield in a separation procedure is of utmost importance as it increases accuracy of measurement and minimizes measurement uncertainty.

Table 3 Commercially available radioisotopic tracers for chemical yield determination applied for RNAA at JSI

Measurand	Tracer	References
Cd	^{109}Cd	[15, 27]
Co, Ni	^{57}Co	[15, 20]
I, ^{129}I	^{131}I	[50]
Pb	^{210}Pb	[27]
^{232}Th	^{231}Pa	[42]
^{237}Np	^{239}Np	[48]
^{231}Pa	^{233}Pa	[41]
V	^{48}V	[19]

For best result, the chemical yield should be determined for each particular measurement and its determination in separate experiment(s) used only in case that the firs approach is not feasible. The yield of RNAA may be determined by classical analytical methods such as gravimetric or spectrophotometric measurement of inactive carrier, added to the sample after neutron irradiation. However, NAA offers unique possibility of either re-activating the added carrier or by addition of radioisotopic yield tracer(s).

Some commercially available radioisotopic chemical yield tracers used for RNAA at JSI are shown in Table 3. However, many radionuclides to be used as tracers can be produced by neutron irradiation of suitable target nuclides, via nuclear reactions induced either by thermal or fast neutrons. The ones, so far produced and applied for RNAA at JSI are listed in Table 4.

Special case is the use of ^{235}U tracer for the RNAA of uranium via ^{239}U measurement. Natural uranium can be added in higher amount as a carrier, simultaneously serving also as the chemical yield monitor by measuring ^{235}U content at its 185.7 keV gamma-ray line [42, 44, 49].

Conclusions

Analytical radiochemistry of neutron-activated samples has played, apart from the general decline of NAA, a significant role in elemental analysis and measurements of long-lived radionuclides, in various kinds of samples. Although RNAA is particularly suitable in providing highly accurate measurement results at lowest detection limits, it may also serve as a valuable tool in providing useful data for a number of elements at higher concentration levels. The isotopic nature of neutron-activated nuclides, the availability of various nuclear reactions and related activation-decay schemes, the possibility of applying various counting techniques (gamma-ray spectrometry, alpha-particle spectrometry, beta-particle counting) and the variety of available radiochemical procedures for the same measurand,

Table 4 Neutron-activated tracers for chemical yield determination applied for RNAA at JSI

Measurand	Tracer	Nuclear reaction	Purification	References
As	^{77}As	^{76}Ge (n, γ) ^{77}Ge → ^{77}As	Selective solvent extraction of iodide	[51]
Co	^{58}Co	^{58}Ni (n, p) ^{58}Co	Ion exchange chromatography	[16]
Cu	^{67}Cu	^{67}Zn (n, p) ^{67}Cu	Ion exchange chromatography	[15]
Hg	^{203}Hg	^{202}Hg (n, γ) ^{203}Hg	Not needed	[25]
Mn	^{54}Mn	^{54}Fe (n, p) ^{54}Mn	Ion exchange chromatography	[44]
^{237}Np	^{239}Np	^{238}U (n, γ) ^{239}U → ^{239}Np	Ion exchange chromatography or extraction chromatography	[48]
^{231}Pa	^{233}Pa	^{232}Th (n, γ) ^{233}Th → ^{233}Pa	Ion exchange chromatography	[41]
Sb	^{125}Sb	^{124}Sn (n, γ) ^{125}Sn → ^{125}Sb	Selective solvent extraction of iodide	[51]
Se	^{81m}Se	Enriched ^{80}Se (n, γ) ^{81m}Se	Not needed	[52]
U	^{238}Np	^{237}Np (n, γ) ^{238}Np	Not needed	[49]

makes NAA a challenging analytical tool. The availability of neutron-induced radioisotopic tracers for chemical yield determinations makes the method highly competitive, compared with other analytical techniques, for accurate, low-uncertainty measurements of many elements and long-lived radionuclides. It is therefore reasonably expected that the RNAA technique will remain preserved and exploited in the dedicated institutes in future.

It is hoped that the practices and examples presented in this paper will contribute to maintaining the knowledge in analytical radiochemistry of neutron-activated samples and in disseminating its potential to the interested researchers and students.

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