

Mass Spectrometry: A Boon to Nuclear Industry

Chandramouleeswaran S and Jayshree Ramkumar^{1*}

Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India

Abstract

Mass spectrometry is a versatile technique that is used for the determination of elements at the trace and ultratrace level along with the isotope ratios. The accuracy in the quantification of isotope ratios of radionuclides is essential for environmental monitoring, migration studies, dating, determination of burn-up of fuel, nuclear material accounting and radioactive waste control. Inductively coupled plasma mass spectrometry (ICP-MS) is advantageous due to its outstanding sensitivity, precision and good accuracy for isotope ratio measurements and enhanced figures of merit for the determination of isotope ratio measurements. These advantages can be enhanced by various other variations of ICP-MS like the use of a multiple ion collector device (MC-ICP-MS). The review gives an idea of the various applications in the nuclear field and touches upon some of the important elements used in nuclear industry.

Keywords: Mass spectrometry; Inductively coupled plasma mass spectrometry; Nuclear industry

What is Mass Spectrometry?

Mass spectrometry is an analytical instrument which has been used for more than a century with its initial work on mass charge ratio being carried out by W. Wien, J.J. Thomson, and other physicists [1]. Mass Spectrometry is an analytical laboratory technique to separate the components of a sample by their mass. The sample is vaporized into a gas and then ionized. The ions are then accelerated through a potential difference and focused into a beam. The ion beam passes through a magnetic field which bends the charged stream. Lighter components or components with more ionic charge will deflect in the field more than heavier or less charged components. A detector counts the number of ions at different deflections and the data can be plotted as a 'spectrum' of different masses. Therefore it is clear that mass spectrometry performs a simple measurement of mass. The earlier work in the measurement of mass had led to the discovery of isotopes and it was in the 1930s that these measurements were correlated to the chemical structures and therefore were used extensively for biological applications for the characterization of natural products. Further progress in the field of mass spectrometry including isotopic labeling methods, hyphenated techniques and softer ionization methods made it an ideal tool for the analysis of macromolecules [2]. With the various fields that employ mass spectrometry growing in number, nuclear industry is also an important area wherein applications of mass spectrometry exist.

According to John B. Fenn, the originator of electrospray ionization for biomolecules and the 2002 Nobel Laureate in Chemistry, *mass spectrometry is the art of measuring atoms and molecules to determine their molecular weight. Such mass or weight information is sometimes sufficient, frequently necessary, and always useful in determining the identity of a species. To practice this art one puts charge on the molecules of interest, i.e., the analyte, then measures how the trajectories of the resulting ions respond in vacuum to various combinations of electric and magnetic fields. Clearly, the sine qua non of such a method is the conversion of neutral analyte molecules into ions. For small and simple species the ionization is readily carried by gas-phase encounters between the neutral molecules and electrons, photons, or other ions. In recent years, the efforts of many investigators have led to new techniques for producing ions of species too large and complex to be vaporized without substantial, even catastrophic, decomposition.* According to chemistry professor Fred W. McLafferty of Cornell University, "Scientific

breakthroughs made possible by MS have included the discovery of isotopes, the exact determination of atomic weights, the characterization of new elements, quantitative gas analysis, stable isotope labeling, fast identification of trace pollutants and drugs, and the characterization of molecular structure"

Chronological Development in Mass spectrometry

The earliest mass spectrometry was in 1897 with the discovery of electrons made by J.J. Thomson. Around 1919, the observation studies of isotopes using mass spectrometry were carried out by F.W. Aston created a mass spectrometer in which ions were dispersed by mass and focused by velocity. This design improved the mass spectrometer resolving power by an order of magnitude compared to that achieved by Thomson. These studies led to the receipt of Noble prize in Chemistry by Aston in 1922. A.J. Dempster developed a magnetic deflection instrument with direction focusing and also the first electron impact source (ionize volatilized molecules with a beam of electrons from a hot wire filament) around 1920. In the 1930's, Double Focusing Analyzer and Accelerator Mass Spectrometry came into vogue. According to Professor Klaus Biemann of the Massachusetts Institute of Technology, the double-focusing instrument (in which the ions are focused for both direction and velocity), was developed "for the purpose of accurately determining the exact atomic weights of the elements and their isotopes".

In the 1940s, Time-of-Flight Mass Spectrometry (1946) proposed by William E. Stephens of the University of Pennsylvania, and Ion Cyclotron Resonance (ICR) (1949) were built. In the 1940s the dominant commercial instrument was Model 21-101 analytical mass spectrometer, manufactured by Consolidated Engineering Corporation (Pasadena, Calif.), using Dempster's single-focusing design and was extensively used in the petroleum industry. According to McLafferty,

***Corresponding author:** Jayshree Ramkumar, Scientific officer (F), Assistant Professor Homi Bhabha National Institute, Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India-400085, Tel: 912225592224; E-mail: jrk@barc.gov.in

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"The magnetic sector type instrument was also very important in the early 1940s. This instrument was developed by Professor Alfred O. C. Nier [of the department of physics at the University of Minnesota] during World War II to do isotopic analysis, with separation of uranium-235 from uranium-238 obviously of special importance. Nier isolated by MS the first sample of plutonium (10^{-9} g), for its first actual characterization. The Calutron, a three-story-high version of Nier's sector instrument, separated uranium-235 for the first atomic bomb. The gaseous diffusion plant at Oak Ridge, Tenn., supplied uranium-235 for the subsequent explosions". There were other companies like Metropolitan Vickers in England (later Associated Electrical Industries, then VG and Micromass); Westinghouse and General Electric in the U.S. (in addition to Consolidated Engineering, mentioned above); and Atlas-Werke (later MAT [Mess und Analysetechnik]) in Germany that were involved in the manufacture of mass spectrometers. In a TOF analyzer, ions are separated based on their differences in velocities as they move in a straight path toward a collector in order of increasing mass-to-charge ratio. The advantage of TOF MS is its speed, applicability of chromatographic detection and determination of large bio-molecules. The progress was made by W. C. Wiley and I. H. McLaren of Bendix Corp., Detroit, Mich (first company to commercialize TOF mass spectrometers). According to Professor Robert J. Cotter of Johns Hopkins University School of Medicine, *"Wiley and McLaren devised a time-lag focusing scheme that improved mass resolution by simultaneously correcting for the initial spatial and kinetic energy distributions of the ions. Mass resolution was also greatly improved by the 1974 invention by Boris A. Mamyrin [of the Physical-Technical Institute, Leningrad, Soviet Union] of the reflectron, which corrects for the effects of the kinetic energy distribution of the ions."* According to Biemann, *"the performance of the initial TOF instruments was so poor that they never lived upto even single-focusing magnetic instruments this analyzer has been greatly improved recently...to almost match the most sophisticated, and very expensive, double-focusing mass spectrometers"*. Ion cyclotron resonance MS (ICR MS) involves the use of simultaneous radiofrequency electric field and a uniform magnetic field, to make the ions follow spiral paths in an analyzer chamber. The ions can be detected sequentially by scanning the radiofrequency or magnetic. However, ICR MS gained the attention of chemists in middle to late '60s through the work of D.C. Wobschall of the State University of New York at Buffalo, P.M. Llewellyn of Varian Associates (Palo Alto, Calif.) and chemistry professor J.D. Baldeschwieler. The technique is particularly applicable to the characterization of ion-molecule reactions. In 1974, M.B. Comisarow and A.G. Marshall of the department of chemistry at the University of British Columbia, Vancouver, Canada transformed radically ICR by developing Fourier transform ICR mass spectrometry (FT-ICR MS) which has major advantage of determination of multiple ions and better mass resolution.

The Reverse Geometry Double-Focusing MS and Quadrupole Analyzers become predominant in 1953. According to Biemann, *"By the 1950s it became clear that the high resolving power of the Mattauch-Herzog and Nier-Johnson geometries would be very useful for the identification of organic compounds"*.

The direct coupling of gas chromatography (GC) and TOF MS accomplished in the mid-1950s by Gohlke and McLafferty of Dow Chemical Co., Midland, Mich., in collaboration with Wiley, McLaren, and Dan Harrington at Bendix. The great utility of modern GC-MS was feasible due to the development of carrier gas separators. Quadrupole mass filter (first reported in the mid-1950s by the group of physics professor Wolfgang Paul of the University of Bonn, who shared the 1989 Nobel Prize in Physics for his work on ion trapping) was perfect

for coupling to GC. In a quadrupole device, a quadrupolar electrical field (comprising radiofrequency and direct-current components) is used to separate ions. Quadrupole MS is not very accurate and precise like double-focusing instruments but is fast and therefore best suited for GC. McLafferty says *"Certainly, the number of quadrupoles sold and in use today far exceeds the total of all other types of mass spectrometers"*.

Biemann Magnetic deflection instruments (single-focusing (of the Dempster design) and double-focusing (of the Mattauch-Herzog design but especially of the Nier-Johnson design) *"dominated high performance mass spectrometry well into the 1990s,"* articulates. *"The cheaper time-of-flight (TOF), quadrupole, and ion trap mass spectrometers evolved in parallel to the preponderant and more expensive magnetic deflection instruments"*.

The quadrupole ion trap, which can trap and mass-analyze ions using a three-dimensional quadrupolar radiofrequency electric field was first introduced developed by G.C. Stafford and commercialized in 1983 by Finnigan MAT (San Jose, Calif.), originally as a GC detector. Today, ion trap instruments are coupled to LC techniques also.

Newer ionization techniques have stretched the applications of MS. Field ionization (sample is ionized in a strong electric field gradient) first observed in 1953 by E. W. Müller was put into practice by H.D. Beckey in 1959 and used for non-volatile or thermally unstable compounds. *"Field desorption really opened the door for biological MS by demonstrating feasibility,"* says chemistry professor R.D. Macfarlane of Texas A&M University, College Station. Chemical ionization, (soft ionization occurs as a result of ion-molecule reactions when volatilized molecules are reacted by reagent gas ions) first observed in 1913 by Thomson in hydrogen gas but the chemical ionization MS was first patented in the mid-1960s by F.H. Field and B. Munson and this being milder than electron impact ionization, generates fewer fragment ions.

Tandem MS (MS-MS) involves the fragmentation of ions by "collision-induced dissociation" ("collisionally activated dissociation"), followed by analysis of the mass of resulting ions. Two mass analyzers in series (or a single mass analyzer that can be used sequentially) are needed to analyze the precursor and product ions. The amalgamation of the latest soft ionization methods with collision-induced dissociation resulted in the supremacy of Tandem MS for the analysis of mixtures. One of the most popular types of tandem MS instrument is the triple quadrupole mass spectrometer conceived by R.A. Yost and C.G. Enke. Tandem MS *"was really popularized by triple-stage quadrupoles introduced first by Finnigan and Sciex (in 1980), followed by Extranuclear and Nermag, and sometime later by VG,"* says M.S. *Story of ThermoQuest Corp., San Jose, Calif."*

Various desorption MS techniques expanded the potential of MS. The first desorption technique was the secondary ion MS (SIMS). In this a beam of ions is used to ionize molecules on a surface. Dempster first demonstrated the potential value of spark-source MS (SSMS), but that technique did not evolve until the 1950s. In SSMS, electrical discharges (sparks) are used to desorb ions from samples. The technique was widely used for trace analysis of a wide range of sample types. In the 1960s, Georges Slodzian developed the ion microscope (SIMS instrument that combined spatial and depth resolution along with isotopic analysis) to obtain high-resolution chemical images and professor A. Benninghoven developed SIMS techniques for analyzing organic compounds. Plasma desorption MS (PDMS) was developed in the 1970s by Macfarlane and uses very high-energy ions to desorb and ionize molecules. According to Macfarlane, PDMS *"was the first MS method to demonstrate feasibility for studying high*

molecular weight proteins and complex antibiotics.” Laser desorption MS (LDMS) was developed in the late 1970s by M.A. Posthumus, P.G. Kistemaker, and H.L. C. Meuzelaar and in this the sample molecules are desorbed using a photon beam. In 1981 M.Barber developed fast atom bombardment MS (FAB MS), or “liquid SIMS”, in which beams of neutral atoms are used to ionize compounds gently from the surface of a liquid matrix enabling determination of large non-volatile organic molecules. Electrospray ionization MS (ESI MS) and matrix-assisted laser desorption/ionization MS (MALDI MS) have been extensively used for the studies of biomolecules. ESI MS was designed by professor M.Dole in 1960’s but was used extensively in 1980’s by molecular beam researcher J.B.Fenn. In this, highly charged droplets dispersed from a capillary in an electric field are evaporated, and the resulting ions are drawn into an MS inlet. MALDI MS was developed by F.Hillenkamp and M.Karas in 1985 and the sample molecules are laser-desorbed from a solid or liquid matrix containing a highly UV-absorbing substance. ESI MS and MALDI MS have made MS increasingly useful for sophisticated biomedical analysis. “MALDI and ESI now promise a greatly expanded future with molecular characterization of proteins, DNA, and other large molecules, using instruments providing high sensitivity, specificity, and speed at lower cost,” says McLafferty.

Need for the Mass Spectrometry in Nuclear Industry

In the past few years, there has been an increasing focus on nuclear material and this involves the detection and measurement of trace amounts of isotopes of uranium, plutonium, thorium, fission products, etc. The determination of fission products is a major concern for the characterization and complete inventory of nuclear fuels [3-11] and burn-up determination [12]. The characterization of fission products with respect to elemental concentration and isotopic composition cannot be carried out with alpha-spectrometry alone. The low detection limits combined with a chance to obtain isotopic ratio makes mass spectrometry a very useful and potent characterization technique in nuclear industry [13-15].

Applications in Nuclear industry

The determination of fission products needs chemical separation prior to the analysis by mass spectrometry [16]. The sample matrix is destroyed by acid digestion, microwave digestion, or other techniques. Extraction of the target species is done by ion-exchange chromatography, extraction or chromatography.

The lanthanides are a major part of the stable and long-lived fission products of both U235 and Pu 239. The use of isotope dilution procedure for the determination of Nd, U and Pu is used for the computation of the burn-up of a nuclear fuel [17]. To overcome the problems associated with the separation stages using the slow classical column techniques, hyphenated techniques like HPLC-MS can be used [18]. The determination of long-lived radionuclides, (fission products/actinides) is extremely important in nuclear waste management as the actinide isotope determinations become important for waste classification [19]. Isotope speciation is very important in environmental radiochemistry for understanding transfer/migration mechanisms [20,21] and age determinations [22] and bioavailability [23,24]. The complete record of fission products and actinides can be obtained using, mass spectrometry (very good detection limits) as compared to radiometric methods [25-29]. Due to peculiar physical and geochemical reasons the Pu concentration reaches 10^{-12} to 10^{-13} g/g in soils of the Northern hemisphere [30] but the concentrations would be higher in the regions contaminated with accidental fallout from nuclear reprocessing plants and nuclear power plants, e.g. in the

Ural region (Russia) and Chernobyl (Ukraine) [31,32]. Plutonium is represented in the Chernobyl fallout by five radionuclides; four of them (^{238}Pu , ^{239}Pu , ^{240}Pu and ^{242}Pu) are long-lived alpha emitters and ^{241}Pu is a beta emitter with a half-life of ~14.4 years. In spent nuclear fuel the $^{236}\text{U}/^{238}\text{U}$ isotope ratio are higher by several orders of magnitude than in non-contaminated natural uranium ores [33-38]. Thus, knowledge of the isotopic composition of artificial actinides is important for evaluating their origin in the environment and the isotopic composition of U and Pu helps in the determination of burn-up of spent nuclear fuel. Burn-up is the most important characteristic of spent nuclear fuel that indicates the degree of utilization of uranium and also the amount of fission products and minor actinides produced during reactor operation [39]. Sector-field inductively coupled plasma mass spectrometry (ICP-SFMS) is a suitable method for actinide analysis at ultratrace concentration levels [40] but the major disadvantages are the formation of uranium hydride ions and isobaric interferences due to molecular ions of lead/rare earth elements. Therefore, matrix separation and the use of nebulizers with desolvators help to improve detection limits of the actinide isotopes [41-44]. ^{99}Tc with a long half-life of 2.14×10^5 y and relatively high fission yield can be found in the environment and it is important to explore the distribution and behavior of ^{99}Tc in the environment. The conventional methods [45,46] including the liquid scintillation counting method [47] has several disadvantages and therefore inductively coupled plasma - mass spectrometry (ICP-MS), can be used for the determination of most of the elements including long-lived radionuclides [48-53]. The post-irradiation examination of nuclear fuels gives knowledge of the inventories of actinides, fission and neutron activation products within irradiated fuels. Therefore precise and accurate isotope ratio measurements are necessary. Plutonium in fuels can be present both due to non-irradiation (MOX fuel) and irradiation of uranium oxide in light water reactors by neutron capture of ^{238}U (formed as a by-product conventional UO_2 fuelled light water reactors). There are 17 isotopes of plutonium with different half-life and the most important isotope is ^{239}Pu (half-life of 24,100 y). After reprocessing, the fissile isotopes of plutonium (^{239}Pu and ^{241}Pu) can be used in combination with depleted or natural uranium as MOX in a nuclear reactor; where the other isotopes are capable of absorbing neutrons and becoming fissile. Therefore, the determination of isotope composition of Pu in the irradiated fuels helps in the calculation of burn-up in UO_2 and MOX fuel. Therefore it is quite clear that isotopic determination is not possible using classical radio analytical methods; liquid scintillation spectrometry can determine ^{241}Pu [54]. However, the complete isotope composition of plutonium can be in principle be determined by different mass spectrometric techniques like glow discharge (GDMS), spark source (SSMS), resonance ionization (RIMS), accelerator (AMS), laser ionization (LIMS), thermal ionization mass spectrometry (TIMS) or ICP-MS. These techniques have been compared and discussed in literature [55-58]. It is seen that the ICP-MS with very low detection limits can be used for determination of isotopic composition of even long-lived radionuclides present. ICP-MS has been accepted technique for routine measurements in the nuclear industry. The American Society for Testing and Materials (ASTM) has developed and published mass spectrometric standard method for the determination of many radionuclides [57]. The determination of trace levels of actinides is compulsory for monitoring the environment in the vicinity of nuclear plants [59,60].

The constant improvements in sensitivity and interference suppression in inductively coupled plasma mass spectrometry (ICP-MS) have enabled the determination of cesium and strontium. The fission product ^{90}Sr is released into the environment primarily from

leaks, nuclear bomb testing etc. ^{90}Sr has a high fission yield (~6%), half-life of 29 years, high biological uptake and slow excretion thus making it difficult to use radiometric determination due to various disadvantages including interferences from the daughter product ^{90}Y . The procedure adopted takes time and the sample throughput is very low. However, when fast and accurate determinations are needed in crucial situations, mass spectrometry is the ultimate technique that comes to rescue of researchers. The analysis time is very short and the interferences are very less.

In the milieu of the Chernobyl accident in 1986 three radioisotopes of cesium have been monitored. In general, the determination of pure beta emitting fission products by radiometric techniques is worsened by spectral interferences from other β -emitters present in the samples and by long counting times [61,62]. Therefore ICP-MS has become an attractive alternative to radiometric determinations and has been extensively used [61-65]. However, the procedure needs a prior separation of isobaric barium and various procedures like precipitation [66], ion chromatography [9], or capillary electrophoresis [67] have been studied. The detection limits for stable cesium in the range from 2 to 20 pg/mL were achieved by ICP-MS [66,68,69].

Fission products are very important signatures of many nuclear activities [70,71] and an inventory of fission products in spent nuclear fuels is required to understand the environment around nuclear facilities [72-76]. The complete determination, both of the isotopic ratio and elemental concentration of the fission products is not possible using α , β or γ -spectrometry, and mass spectrometry though hindered by some isobaric interferences appears as an alternative and the procedure becomes more attractive when separations are carried out to remove interferences chemical separation is needed [77,78].

The experiments at lab-scale showed that chromatographic separation hyphenated to mass spectrometry can give a good measurement of these long-lived fission products in complex mixtures [79,80]. Reprocessing of irradiated nuclear fuels intended at the recovery of fissile material involves the dissolution of fuel in nitric acid to get a clear solution containing U, Pu, fission products, and a residue containing the metallic and oxide forms of some of the fission products and the separation is carried out using the Purex process [81]. The studies on the composition and dissolution characteristics of high burn-up fuels and the probable consequences on the fuel reprocessing are reported [82,83]. The analysis of fuel residues is routinely carried out by various methods including thermal ionization mass spectrometry (TIMS) [84]. The residue is found to contain Zr, Mo, Tc, Ru, Rh and Pd, trace amounts of U and Pu and natural impurities such as Fe, Cr and Ni. Spectrometric techniques for the analysis of fission products are associated with systematic errors as natural elements are used for calibration for the measurement of the nuclear-reaction produced elements. This is due to the different average relative atomic masses of the natural and reactor-produced elements.

As a rule, the relative atomic masses for polyisotopic fission elements are 1 and 2% higher than those for the corresponding natural element, owing to the neutron-rich isotopes produced by fission. The systematic errors accumulate when several elements have to be analyzed and therefore the accuracy of the sample composition determination is seriously marred. This problem is encountered in the residue characterization obtained during spent fuel dissolution. This is because the relative atomic masses of fission products Zr, Mo, Ru and Pd are higher than those for the corresponding natural elements. Inductively coupled plasma mass spectrometry (ICP-MS) has been used for the characterization of spent nuclear fuels because of its high sensitivity

and multi-isotopic capabilities [85-89]. Precise and accurate isotope ratio measurements of long-lived radionuclides present in trace and ultratrace amounts are required for analysis of various types of samples. Due to the long-term impact of long lived radionuclides (half-life >100 y) there is an on growing concern about the increasing contamination of the environment by artificial radionuclides. Therefore, best possible supervision of storage sites is possible if the analysis of the composition of waste containing radionuclides can be carried out with techniques that are highly sensitive and can handle large sample throughput [90].

In addition to the characterization of radioactive waste and environmental scrutinizing, the monitoring of the health of exposed personnel is also very important. For this various types of samples like blood, urine, feces, hair and tissue need to be analyzed and this requires a powerful and fast analytical technique that can cope with the analysis of a large number of samples within a very short time frame and give accurate and precise results. Radioanalytical methods such as α -spectrometry require prior chemical separation and enrichment and also the counting periods that are quite long ranging from days to several weeks. Moreover, ^{239}Pu and ^{240}Pu isotopes that are germane for the determination of Pu origin in radioactive waste or environmental samples (as a result of nuclear fallout from nuclear weapons tests or nuclear power plants) are difficult to analyze using radioanalytical methods. These inherent disadvantages of radioanalytical procedures make it impending to replace them with mass spectrometry. Thermal ionization mass spectrometry (TIMS) has long been recognized as being the standard technique for the isotope analysis of Pu and U in different matrices.

However, TIMS, suffers from various limitations [91]; it is restricted to elements with ionization potential >7 eV, has no multielement capability, requires time-consuming sample preparation steps. All these limitations have made it easy of ICP-MS to be considered as a universal and extremely sensitive analytical method for the isotope analysis of long-lived radionuclides. The other mass spectrometric techniques like resonance ionization mass spectrometry (RIMS) [92-95] and accelerator mass spectrometry (AMS) [96-98] can be used for ultratrace and isotope analysis of different radionuclides including the radiotoxic isotopes like ^{14}C , ^{41}Ca , ^{90}Sr , ^{99}Tc , ^{210}Pb , ^{236}U and Pu and these analysis have extensive applications in various fields like environment, cosmochemistry, radiodating, nutrition and biomedical research. Taylor et al. [99] developed a rapid method determination of ^{90}Sr in natural water, plant and sediment samples using extraction chromatography and dynamic reaction cell ICP-MS. This resulted in the removal of isobaric interference from the stable isotope ^{90}Zr . The method was validated using Cerenkov counting method and certified reference materials. The main disadvantage of using radiometric methods for determination of ^{90}Sr , was the long analysis times (several weeks). Boulyga et al. [100] reported isotopic analysis of uranium and plutonium in contaminated environmental samples. Double-focusing sector-field inductively coupled plasma mass spectrometry (ICP-SFMS) using a low-flow microconcentric nebulizer with membrane desolvation, "Aridus", was applied for isotopic measurements of uranium and plutonium at the ultratrace level.

The detection limit (3σ) for ^{236}U and ^{239}Pu after chemical extraction was 0.2 pg L^{-1} in aqueous solution and 0.04 pg g^{-1} in soil, respectively. $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratios were measured in soil samples collected within the 30 km zone around the Chernobyl nuclear power plant. The average $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratio in contaminated surface soil was 0.396 ± 0.014 . The burn-up grade and the portion of spent uranium in the spent uranium/natural

uranium mixture in soil were calculated using the iteration method. A slight variation in the burn-up grade of spent reactor uranium was revealed by analyzing $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios. A relationship between the $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratio and burn-up of spent uranium was observed. Alonso et al. [101] analyzed the dissolved spent nuclear fuel using inductively coupled plasma mass spectrometry (ICP-MS) to obtain the elemental and isotopic composition of the irradiated fuel without any chemical separation. The analysis of small spent fuel samples by ICP-MS was used to assess the type and irradiation of the fuel in pattern recognition studies.

Quantitative analysis of the fuel solutions and residues was performed only for selected elements because of the presence of isobaric interferences. For mono and poly isotopic elements, standard addition and isotope dilution methods were used respectively. Elements determined in the residues included Zr, Mo, Tc, Ru, Rh, Pd, U and Pu. Neodymium was also determined in dissolver solutions of fast neutron-irradiated fuels and the results were compared with those given by thermal ionization mass spectrometry. Günther-Leopold et al. [102] applied multicollector ICP-MS in combination with chromatographic separation techniques and laser ablation for the isotopic analysis of irradiated nuclear fuels. The advantages and limitations of the selected analytical technique for the characterization of such a heterogeneous sample matrix are discussed. Bera et al. [103] reported the analysis of dissolver solution by HPLC-TIMS to obtain the burn-up on an irradiated mixed oxide (MOX) test fuel pellet. The rapid separation procedures developed in their laboratory earlier were employed to isolate pure fractions of the desired elements. The individual lanthanide fission products (La to Eu) were separated from each other using dynamic ion-exchange chromatographic technique whereas uranium and plutonium were separated from each other using reversed phase chromatographic technique. The pure fractions of U, Pu and Nd obtained after HPLC separation procedure for "spiked" and "unspiked" dissolver solutions were used in TIMS measurements. In TIMS analysis, the fractions obtained from HPLC separation procedure on an "unspiked" fuel sample were measured. For the determination of U, Pu and Nd by isotopic dilution mass spectrometric technique (ID-MS), known quantities of tracers enriched in ^{238}U , ^{240}Pu and ^{142}Nd were added to the dissolver solution and HPLC separation was carried out. The isotope ratios viz. $^{142}\text{Nd}/(^{145}\text{Nd} + ^{146}\text{Nd})$, $^{238}\text{U}/^{233}\text{U}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ in the significant "spiked" fractions were subsequently measured by TIMS. The concentrations of neodymium, uranium and plutonium were also measured using HPLC with post-column derivatization technique. The atom % burn-up computed from HPLC and TIMS techniques were in good agreement. Rollin et al. [104] probed the dissolution rate of spent UO_2 fuel using flow through experiments under different conditions viz oxidising, anoxic and reducing. Under oxidizing conditions, the dissolution was feasible in pH range 3-9.3.

Song et al. [105] used electrothermal vaporization-inductively coupled plasma-mass spectrometric (ETV-ICP-MS) method for determination of cesium. This method was based on the selective volatilization of cesium with potassium thiocyanate (0.3 mM) as modifier and can be used for the determination of radiocesium, i.e. ^{135}Cs and ^{137}Cs , in the presence of isobaric barium using 400°C and 1100°C as pretreatment and volatilization temperatures, respectively and the limit of detection for ^{135}Cs was 0.2 pg/mL. Since the natural isotopes of Ba give isobaric interferences on the radioactive isotopes of Cs at nominal masses of 134, 135 and 137, a chemical separation of Cs from barium was necessary for the determination of the isotopic composition of Cs by mass spectrometric techniques in highly active nuclear wastes, dissolved spent nuclear fuels or radioactively

contaminated environmental samples. Moreno et al. [9] carried out the on-line separation of cesium and barium using ion chromatography (IC) and determination with an ICP-MS instrument that is coupled to the IC. Three separation schemes were compared with respect to chromatographic resolution, accuracy and precision in irradiated spent fuel samples. The IC-ICP-MS method was based on the use of CS5 cation-exchanger column and 1 M HNO_3 was used as eluent and a detection limit of 16 pg g^{-1} for total Cs with a precision of 2.5% at a concentration level of 100 ppb ($n=7$) was achieved. Pitois et al. [106] used capillary electrophoresis (CE) coupled with inductively coupled plasma mass spectrometry (both ICP-QMS and ICP-SFMS) for the determination of Cs and lanthanides. Typical detection limits of 6 ng/mL and 4 pg/mL for caesium as well as 8 ng/mL and 7 pg/mL for lanthanides have been obtained by CE-ICP-QMS and CE-ICP-SFMS, respectively. In addition to these very low detection limits, the procedure is fast (6 min for cesium and 13 min for lanthanides, respectively). Day et al. [107] developed capillary electrophoresis (CE) coupled on-line to a double focusing sector field inductively coupled plasma mass spectrometer (DF-ICP-MS) for the analysis of mixtures of lanthanides using A MicroMist AR30-1-F02 nebulizer with a Cinnabar small volume cyclonic spray chamber for the introduction of sample into ICP-MS. The CE-ICP-MS method is very fast and requires very small sample volumes (35 nL injection volume). Detection limits were found to be in the range of 0.72 to 3.9 ppb for most of the lanthanides. The method was applied to tantalum material exposed to a high energy proton beam for the production of neutrons via spallation reactions. Thus, a chemical separation step prior to ICP-MS determination was needed to avoid isobaric interferences for the accurate determination of nuclide abundances in such samples.

Comte et al. [108] developed a method for the determination of ^{79}Se in fission product solutions resulting from nuclear fuel reprocessing. ^{79}Se ($T_{1/2} = 10^6\text{ y}$) was measured using electrothermal vaporisation coupled with inductively coupled plasma mass spectrometry (ETV-ICP/MS) after a single chemical separation step using ion exchangers to separate Se from the high activity solution (10^{10} Bq l^{-1}) with a significant selenium recovery yield of 85%. The combination of ETV and chemical separation eliminated all the interferences normally associated with the determination of ^{79}Se and the concentration of ^{79}Se in the fission products solution was 0.43 mg L^{-1} . Buessle et al. [109] reported the analysis of fission products in samples from the Black Sea following their input from the Chernobyl reactor accident. The samples analyzed include discrete water samples and both suspended and dissolved phases collected by in-situ chemisorption techniques. The radiochemical scheme permits the separation and analysis of ^{134}Cs , ^{137}Cs , ^{90}Sr , ^{144}Ce , ^{147}Pm , ^{106}Ru , ^{239}Pu , ^{240}Pu , ^{242}Cm , ^{238}Pu , and ^{241}Am by mass spectrometry along with other techniques like instrumental gamma spectrometric methods. The developments are described and data are presented on some representative samples from the Black Sea. The sensitivity of the analysis for the various nuclides and sample types is summarized and questions of radiochemical interferences are addressed. Rollin et al. [18] reported the determination of lanthanides and actinides in uranium materials by HPLC-ICP-MS. The determination of Nd, U and Pu by isotope dilution analysis is well known as the classical method for the calculation of the burn-up of a nuclear fuel. Numerous isobaric overlaps restrict the direct determination of fission product and actinide isotopes by mass spectrometry and therefore an extensive chemical separation is required. For the determination of fission product isotopes in irradiated uranium fuel, high-performance liquid chromatographic (HPLC) and inductively coupled plasma mass spectrometric (ICP-MS) systems were installed in glove-boxes and

all the lanthanides were separated by HPLC and detected on-line by ICP-MS. As high U and Pu concentrations suppress the signals of trace elements in ICP-MS, a separation method to elute U and Pu first was developed. Thus it was possible to determine the isotopic composition of Nd in a high U and Pu matrix. With the same equipment, a method was developed to prevent isobaric overlaps in the mass spectrum by separating U, Am and Pu. A procedure for the simultaneous separation and determination of fission products (lanthanides) and actinides (Pu, Np, U, Am and Cm) was described by Perna et al. [110] based on the use of an anionic/cationic mixed bed chromatographic column (CS5A, Dionex), coupled on-line to an ICP-MS detector. Different parameters like oxidizing/reducing agents, nature of mobile phase etc. were varied to see the effect of these experimental parameters on the intensity and position of the chromatographic peaks. The analytical procedure developed was validated using certified materials and other independent techniques. The analytical figures of merit of the developed procedure were compared with those obtained using other commercially available ion-exchange stationary phases. The detection limits for lanthanides and actinides were 0.25 ng mL^{-1} and 0.45 ng mL^{-1} respectively with the precision of better than 5% over seven repeated measurements. The procedure was applied to the inventory of spent nuclear fuel samples. Moreno et al. [111] used IC coupled with ICP-MS to separate Np, Pu and U, using a high capacity cation exchange column (CS10), silver oxide as oxidizing agent and 40mM 2,3 diaminopropionic acid monohydro nitrate in 0.6 M HNO_3 as eluent. These conditions helped in overcoming the isobaric interferences present in the determination of isotopic composition, avoiding the influence of the tail of ^{238}U peak on ^{237}Np and ^{239}Pu peaks in presence of high uranium content and provided good resolution with a high recovery of 96-98%. Betti et al. [112] used IC-ICP-MS for the simultaneous separation and on-line detection of light fission products such as Zr, Ru, Mo, Tc, Rh, Pd, Sb and Te. The linear range and the variation coefficient were calculated for each element between 1 and $100 \mu\text{g L}^{-1}$ elemental concentrations. The detection limit of each element was calculated to be $0.5 \mu\text{g L}^{-1}$. Mo, Ru and Sb showed a linear trend over the whole concentration range $1\text{-}100 \mu\text{g L}^{-1}$, Pd, Te and Zr were linear up to $50 \mu\text{g L}^{-1}$. Becker in his review [113] reported the capability of determining element concentrations at the trace and ultratrace level and isotope ratios using mass spectrometry. The precise and accurate determination of isotope ratios of long-lived natural and artificial radionuclides is required for their environmental monitoring and health control, for studying radionuclide migration, for age dating, for determining isotope ratios of radiogenic elements in the nuclear industry, for quality assurance and determination of the burn-up of fuel material in a nuclear power plant, for reprocessing plants, nuclear material accounting and radioactive waste control. Inorganic mass spectrometry, especially inductively coupled plasma mass spectrometry (ICP-MS) as the most important inorganic mass spectrometric technique today, possesses excellent sensitivity, precision and good accuracy for isotope ratio measurements and practically no restriction with respect to the ionization potential of the element investigated—therefore, thermal ionization mass spectrometry (TIMS), which has been used as the dominant analytical technique for precise isotope ratio measurements of long-lived radionuclides for many decades, is being replaced increasingly by ICP-MS. In the last few years instrumental progress in improving figures of merit for the determination of isotope ratio measurements of long-lived radionuclides in ICP-MS has been achieved by the application of a multiple ion collector device (MC-ICP-MS) and the introduction of the collision cell interface in order to dissociate disturbing argon-based molecular ions, to reduce the kinetic energy of ions and neutralize the disturbing noble gas. The review

describes the state of the art and the progress of different inorganic mass spectrometric techniques such as ICP-MS, laser ablation ICP-MS vs. TIMS, glow discharge mass spectrometry, secondary ion mass spectrometry, resonance ionization mass spectrometry and accelerator mass spectrometry for the determination of long-lived radionuclides in quite different materials. The technique of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is quite attractive as it allows the precise measurement of the isotope compositions for a wide range of elements combined with excellent limits of detection due to high ionization efficiencies. Gunther-Leopold et al. [114] described applications of an online high-performance liquid chromatographic separation system coupled to a MC-ICP-MS in order to overcome isobaric interferences for the determination of the plutonium isotope. The described chromatographic separation is sufficient to prevent any isobaric interference between ^{238}Pu present at trace concentrations and ^{238}U present as the main component of the fuel samples.

Boron has two stable natural isotopes, ^{10}B (19.9%) and ^{11}B (80.1%). The neutron absorption properties of boron alloyed stainless steels depend on the content of the ^{10}B isotope with an absorption cross-section for thermal neutrons of more than 3.8 kilobarn (10^{-25} m^2). This isotope is an important neutron absorber used in shielding materials such as boron-alloyed steels for storage of spent nuclear fuel, reactor shielding and control, and instruments detecting neutrons [115]. Kurta et al. [116] described two methods for the rapid screening of ^{10}B enriched special steel samples with a ^{10}B isotopic fraction from 90 to 97% (taken from the production process) were compared. Both ns-LA-ICPMS and fs-LA-MC-ICPMS and evaluated the different instrumental setups for this application. Even though the micro-inhomogeneous boron distribution in the steel samples was determined by LA-ICPMS and EPMA no effect on the isotope ratios could be observed. Boron determination is not affected by isobaric interferences and by spectroscopic interferences from the elements originating from water, acid or plasma gas [117].

Conclusions

Inorganic mass spectrometric techniques find an important place in the field of nuclear industry for the direct determination of different elements in various stages. The advantages of ICP-MS when coupled to an online separation procedure increases the sample throughput to a great extent and the very low detection limits are achieved. The various determinations can be used for monitoring the environmental media or used for calculation of fuel burn-up. The importance of ICP-MS in precise isotope ratio measurements at ultratrace levels are achieved using multi collector, and/or double focusing sector field instruments.

References

1. Benyon JH, Morgan RP (1978) The development of mass spectroscopy: An historical account. *Int J Mass Spectrom Ion Physics* 27: 1-30.
2. Gross ML, Caprioli RM (2003) *The Encyclopedia of Mass Spectrometry*. Volume 1, Elsevier, Amsterdam.
3. Guillaumont R (2004) Éléments chimiques à considérer dans l'aval du cycle nucléaire. *CR Chimie* 7: 1129-1134.
4. Lee CH, Suh MY, Choi KS, Kim JS, Song BC, et al. (2000) Separation of fission products from spent pressurized water reactor fuels by anion exchange and extraction chromatography for inductively coupled plasma atomic emission spectrometric analysis. *Anal Chim Acta* 428: 133-142.
5. Wolf SF, Bowers DL, Cunnane JC (2005) Analysis of high burnup spent nuclear fuel by ICP-MS. *J Radioanal Nucl Chem* 263: 581-586.
6. Wolf SF, Tsai Y (2005) Application of ICP-MS and HR-ICP-MS for the characterization of solutions generated from corrosion testing of spent nuclear fuel. *J Radioanal Nucl Chem* 263: 575-579.

7. Becker JS, Kerl W, Dietze H (1999) Nuclide analysis of an irradiated tantalum target of a spallation neutron source using high performance ion chromatography and inductively coupled plasma mass spectrometry. *Anal Chim Acta* 387: 145-154.
8. Glagolenko I, Hilton B, Giglio J, Cummings D (2009) Fission yield measurements by inductively coupled plasma mass-spectrometry. *J Radioanal Nucl Chem* 282: 651-655.
9. Moreno JMB, Betti M, Nicolaou G (1999) Determination of caesium and its isotopic composition in nuclear samples using isotope dilution-ion chromatography-inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 14: 875-879.
10. Alonso JIG, Sena F, Arbore P, Betti M, Koch L (1995) Determination of fission products and actinides in spent nuclear fuels by isotope dilution ion chromatography inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 10: 381-393.
11. Betti M (1997) Use of ion chromatography for the determination of fission products and actinides in nuclear applications. *J Chromatogr A* 789: 369-379.
12. Koch L, Cottone G, Geerlings MW (1968) ^{148}Nd Analyse zur Abbrandbestimmung von Kernbrennstoffen. *Radiochim Acta* 10: 122-124.
13. Blair PD (1986) The application of inductively coupled plasma mass spectrometry in the nuclear industry. *Trends Anal Chem* 5: 220-223.
14. Vijayalakshmi S, Prabhu Krishna R, Mahalingam TR, Mathews CK (1992) A simple gas-liquid separator for continuous hydride introduction in ICP-MS. *At Spec* 13: 26-28.
15. Alonso JIG, Thoby-Schultzenorff D, Giovanonne B, Koch L, Wiesmann HJ (1993) Performance characteristics of a glove box inductively coupled plasma mass spectrometer for the analysis of nuclear materials. *J Anal At Spectrom* 8: 673-679.
16. HIS (1990) ASTM E 321-79 Standard Test Method for Atom Percent Fission in Uranium and Plutonium Fuel (Neodymium-148 Method). American Society for Testing and Materials, Philadelphia, PA.
17. ASTM International (1995) Standard Test Method for Atom Percent Fission in Uranium and Plutonium Fuel (Mass Spectrometric Method), ASTM E 244-80. American Society for Testing and Materials, Philadelphia, PA.
18. Röllin S, Kopajtíc Z, Wernli B, Magyar B (1996) Determination of lanthanides and actinides in uranium materials by high-performance liquid chromatography with inductively coupled plasma mass spectrometric detection. *J Chromatogr A* 739: 139-149.
19. Murray RL (1994) Understanding Radioactive Waste. 4th edition, Battelle Press.
20. Hoefs J (1987) Stable Isotopes Geochemistry. Volume 9, Springer, Berlin.
21. Shima M (1986) A summary of extremes of isotopic variations in extra-terrestrial materials. *Geochim Cosmochim Acta* 50: 577-584.
22. Faure G (1986) Principles of Isotope Geology. 2nd edition, Wiley, New York.
23. Mellon F, Sandstrom (1996) Stable Isotopes in Human Nutrition: Inorganic Nutrient Metabolism (Food Science and Technology). Academic Press, London.
24. Skipperud L, Oughton D, Saibu B (2000) The impact of Pu speciation on distribution coefficients in Mayak soil. See comment in PubMed Commons below *Sci Total Environ* 257: 81-93.
25. Crain JS (1996) Atomic spectroscopy perspectives: Applications of inductively coupled plasma-mass spectrometry in environmental radiochemistry. *At Spectroscopy Perspectives* 11: 30-39.
26. Becker JS, Dietze HJ (1998) Determination of long-lived radionuclides by double-focusing sector field ICP mass spectrometry. *Adv Mass Spectrom* 14: 681.
27. Kim CK, Seki R, Morita S, Yamasaki S, Tsumura A, et al. (1991) Application of a high resolution inductively coupled plasma mass spectrometer to the measurement of long-lived radionuclides. *J Anal At Spectrom* 6: 205-209.
28. Solatie D, Carbol P, Betti M, Bocci F, Hiernaut T, et al. (2000) Ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS) and radiometric techniques for the determination of actinides in aqueous leachate solutions from uranium oxide. *Fresenius J Anal Chem* 368: 88-94.
29. Meyers RA (2000) Encyclopedia of Analytical Chemistry: Applications, Theory, and Instrumentation. Volume 15, John Wiley & Sons.
30. Perelygin VP, Chuburkov YuT (1997) Man-made plutonium in environment — possible serious hazard for living species. *Radiat Meas* 28: 385-392.
31. Shigematsu I (1991) The International Chernobyl Project - Technical Report - Assessment of Radiological Consequences and Evaluation of Protective Measures. Report by an International Advisory Committee, IAEA, Vienna.
32. Begichev SN, Borovoj AA, Burlakov EV, Gagarinsky AJ, Demin VF, et al. (1990) Radioactive releases due to the Chernobyl accident. In: Rogers JT, Fission Product Transport Processes in Reactor Accidents, Hemisphere, New York, USA, 717-734.
33. Kirchner G, Noack CC (1988) Core history and nuclide inventory of the Chernobyl core at the time of accident. *Nucl Safety* 29: 1-5.
34. Donohue DL (1998) Strengthening IAEA safeguards through environmental sampling and analysis. *J Alloys Compd* 271: 11-18.
35. Zhao X-L, Nadeau M-J, Kilius LR, Litherland AE (1994) The first detection of naturally-occurring ^{238}U with accelerator mass spectrometry. *Nucl Instrum Methods Phys Res Sec B* 92: 249-253.
36. Berkovits D, Feldstein H, Ghelberg S, Hershkowitz A, Navon E, et al. (2000) ^{238}U in uranium minerals and standards. *Nucl Instrum Methods Phys Res Sec B* 172: 372-376.
37. Richter S, Alonso A, De Bolle W, R. Wellum R, Taylor PDP (1999) Isotopic "fingerprints" for natural uranium ore samples. *Int J Mass Spectrom* 193: 9-14.
38. Boulyga SF, Becker JS, J. L. Matusевич JL, Dietze HJ (2000) Isotope ratio measurements of spent reactor uranium in environmental samples by using inductively coupled plasma mass spectrometry. *Int J Mass Spectrom* 203: 143-154.
39. Pasukhin EM, Makarova TP, Stepanov AV, Belyaev BN (2000) Burn-up of nuclear fuel in destroyed reactor of the fourth block of the Chernobyl nuclear power plant. *Radiochem* 42: 527.
40. Becker JS, Dietze HJ (2012) Mass spectrometry of long-lived radionuclides. In: Meyer RA, Encyclopedia of Analytical Chemistry: Applications Theory and Instrumentation, John Wiley & Sons, NY, 12947-12961.
41. McLean JA, Becker JS, Boulyga SF, Dietze HJ, Montaser A (2001) Ultratrace and isotopic analysis of long-lived radionuclides by double-focusing sector field inductively coupled plasma mass spectrometry using direct liquid sample introduction. *Int J Mass Spectrom* 208: 193-204.
42. Becker JS, Dietze HJ (1999) Precise isotope ratio measurements for uranium, thorium and plutonium by quadrupole-based inductively coupled plasma mass spectrometry. *Fresenius' J Anal Chem* 364: 482-488.
43. Kim ChS, Kim ChK, Lee Ji, Lee KJ (2000) Rapid determination of Pu isotopes and atom ratios in small amounts of environmental samples by an on-line sample pre-treatment system and isotope dilution high resolution inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 15: 247-255.
44. Taylor RN, Warneke T, Milton JA, Croudace IW, Warwick PE, et al. (2001) Plutonium isotope ratio analysis at femtogram to nanogram levels by multicollector ICP-MS. *J Anal At Spectrom* 16: 279-284.
45. Holm E, Rioseco J, Garcia-Leon M (1984) Determination of ^{99}Tc in environmental samples. *Nucl Inst Meth Phys Res* 223: 204-207.
46. Holm E, Rioseco J, Ballestra S, Walton A (1988) Radiochemical measurements of ^{99}Tc : Sources and environmental levels. *J Radioanal Nucl Chem* 123: 167-179.
47. Cattarin S, Doretti L, Mazzi U (1985) Determination of ^{99}Tc in urine by liquid scintillation counting to evaluate internal contamination. See comment in PubMed Commons below *Health Phys* 49: 795-804.
48. Houk RS (1986) Mass spectrometry of inductively coupled plasmas. *Anal Chem* 58: 97A-105A.
49. Houk RS, Thompson JJ (1988) Inductively coupled plasma mass spectrometry. *Mass Spectrom Rev* 7: 425-461.
50. Kawaguchi H (1988) Inductively coupled plasma mass spectrometry. *Anal Sci Rev* 4: 339.
51. Kim CK, Otsuji M, Takaku Y, Kawamura H, Shiraishi K, et al. (1989) Application of inductively coupled plasma mass spectrometry to the determination of ^{99}Tc in soil samples. *Radioisotopes* 38: 151-152.
52. Kim CK, Oura Y, Takaku Y, Nitta H, Igarashi Y, et al. (1989) Measurement of $^{240}\text{Pu}/^{239}\text{Pu}$ ratio by fission track method and inductively coupled plasma mass spectrometry. *J Radioanal Nucl Chem Letters* 136: 353-362.

53. Kim CK, Takaku T, Yamamoto Y, Kawamura H, Shiraishi K, et al. (1989) Determining of ^{237}Np in environmental samples using inductively coupled plasma mass spectrometry. *J Radioanal Nucl Chem* 132: 131-137.
54. Lee SH, Gastaud J, La Rosa JJ, Kwong LLW, Povinec PP, et al. (2001) Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques. *J Radioanal Nucl Chem* 248: 757-764.
55. Becker JS (2002) State-of-the-art and progress in precise and accurate isotope ratio measurements by ICP-MS and LA-ICP-MS. Plenary Lecture. *J Anal Atom Spectrom* 17: 1172-1185.
56. Pillinger CT (1998) *Modern Isotope Ratio Mass Spectrometry*. Platzner IT edition, Wiley, Chichester.
57. Henry R, Koller D, Liezers M, Farmer III OT, Barinaga C, et al. (2001) New advances in inductively coupled plasma – mass spectrometry (ICP-MS) for routine measurements in the nuclear industry. *J Radioanal Nucl Chem* 249: 103-108.
58. Ache HJ (1992) Analytical chemistry in nuclear technology. *Fresenius' J Anal Chem* 343: 852-862.
59. Hembree DMJr, Carter JA, Ross HH (1995) Environmental Monitoring for Detection of Uranium Enrichment Operations: Comparison of LEU and HEU Facilities. Martin Marietta Energy System, US Department of Energy 26.
60. Warner F, Harrison RM (1993) *Radioecology after Chernobyl: Biogeochemical Pathways of Artificial Radionuclides*. Wiley, New York.
61. Ross RR, Noyce JR, Lardy MM (1993) Inductively coupled plasma-mass spectrometry: An emerging method for analysis of long-lived radionuclides. *Radioact Radiochem* 4: 24-37.
62. Garcia Alonso JI, Thoby-Schultzendorff D, Giovannone B, Koch L (1996) Analysis of long-lived radionuclides by ICP-MS. *J Radioanal Nucl Chem* 203: 19-29.
63. Smith MR, Wyse EJ, Koppelaar DW (1992) Radionuclide detection by inductively coupled plasma mass spectrometry: A comparison of atomic and radiation detection methods. *J Radioanal Nucl Chem* 160: 341-354.
64. Garcia Alonso JI, Thoby-Schultzendorff D, Giovannone B, Glatz JP, Pagliosa G, et al. (1994) Characterization of spent nuclear fuel dissolver solutions and dissolution residues by inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 9: 1209-1215.
65. Probst TU (1996) Studies on the long-term stabilities of the background of radionuclides in inductively coupled plasma mass spectrometry (ICP-MS) A review of radionuclide determination by ICP-MS. *Anal Bioanal Chem* 354: 782-787.
66. Meeks AM, Giaquinto JM, Keller JM (1998) Application of ICP-MS radionuclide analysis to "Real World" samples of department of Energy radioactive waste. *J Radioanal Nucl Chem* 234: 131-136.
67. Kirlaw PW, Castillano MTM, Caruso JA (1998) An evaluation of ultrasonic nebulizers as interfaces for capillary electrophoresis of inorganic anions and cations with inductively coupled plasma mass spectrometric detection. *Spectrochim Acta* 53: 221-237.
68. Date AR, Gray AL (1989) *Applications of Inductively Coupled Plasma Mass Spectrometry*. Glasgow, 1-42.
69. Prudnikov ED, Barnes RM (1998) Estimation of detection limits in inductively-coupled plasma-mass spectrometry. *Fresenius' J Anal Chem* 362: 465-468.
70. Warner F, Harrison RM (1993) *Radioecology after Chernobyl: biogeochemical pathways of artificial radionuclides*. Wiley, New York.
71. Von Gunten DHR (1995) Radioactivity: A tool to explore the past. *Radiochim Acta* 70: 305-316.
72. Luyck FF, Frissel MJ (1996) *Radioecology and the Restoration of Radioactive-Contaminated Sites*. NATO Series, Kluwer Academic Publishers, New York.
73. Desmet G (1990) *Transfer of Radionuclides in Natural and Semi-natural Environments*. Elsevier, Amsterdam.
74. Cecille L (1990) Proceedings of the Third European Community Conference on Radioactive Waste Management and Disposal. Luxembourg.
75. Von Gunten HR, Benes P (1995) Speciation of radionuclides in the environment. *Radiochim Acta* 69: 1-29.
76. Hunt GJ, Kereshow PJ, Swift DJ (1998) Radionuclides in the oceans (RADOC 96]97) Part 2: Distribution, Models and Impacts. *Radiat Prot Dosimetry* 75: 1-4.
77. Lieser KH (1995) Radionuclides in the geosphere: Sources, mobility, reactions in natural waters and interactions with solids. *Radiochim Acta* 70-71: 355-375.
78. Nicholson KW (1996) *Environmental Signatures of Undeclared Nuclear Facilities and Their Detection*, AEA Technology, Culham Laboratory, Abingdon, Oxon, UK.
79. Garcia Alonso JI, Sena F, Arbore P, Betti M, Koch L (1995) Determination of fission products and actinides in spent nuclear fuels by isotope dilution ion chromatography inductively coupled plasma mass spectrometry. *J Anal Atom Spectrom* 10: 381-393.
80. Barrero Moreno JM, Garcia Alonso JI, Arbore P, Nicolau G, Koch L (1996) Characterization of spent nuclear fuels by ion chromatography-inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 11: 929-935.
81. Campbell DO, Burch WD (1990) The chemistry of fuel reprocessing: present practices, future trends. *J Radioanal Nucl Chem* 142: 303-320.
82. Kleykamp H (1990) Post-irradiation examinations and composition of the residues from nitric acid dissolution experiments of high-burnup LWR fuel. *J Nucl Mater* 171: 181-188.
83. Adachi T, Ohnuki M, Yoshida N, Sonobe T, Kawamura W, et al. (1990) Dissolution study of spent PWR fuel: dissolution behavior and chemical properties of insoluble residues. *J Nucl Mater* 174: 60-71.
84. Ache HJ (1992) Analytical chemistry in nuclear technology. *Fresenius J Anal Chem* 343: 852-862.
85. Garcia Alonso JI, Thoby-Schultzendorff D, Giovanonne B, Koch L, Wiesmann H (1993) Performance characteristics of a glove box inductively coupled plasma mass spectrometer for the analysis of nuclear materials. *J Anal Atom Spectrom* 8: 673-679.
86. European Safeguards Research and Development Association (1993) 15th Annual Symposium on Safeguards and Nuclear Material Management: "Augustinianum" Rome, Italy 11-13 May, [proceedings].
87. Garcia Alonso JI, Babelot JF, Glatz JP, Cromboom O, Koch L (1993) Applications of a Glove-Box ICP-MS for the Analysis of Nuclear Materials. *Radiochim Acta* 62: 71-79.
88. Crain JS, Galiimore DL (1992) Inductively coupled plasma-mass spectrometry of synthetic elements: ^{99}Tc . *Appl Spectrom* 46: 547-549.
89. Holland G, Eaton AN (1993) *Applications of PlasmaSource Mass Spectrometry*. Royal Society of Chemistry, Cambridge.
90. Crain JS, Smith LL, Yaeger JS, Alvarado JA (1995) Determination of long-lived actinides in soil leachates by inductively coupled plasma-mass spectrometry. *J Radioanal Nucl Chem* 194: 133-139.
91. Platzner IT (1997) *Modern Isotope Ratio Mass Spectrometry*. Chemical Analysis. Volume 145, Wiley, Chichester.
92. Trautmann N, Passler G, Wendt KD (2004) Ultratrace analysis and isotope ratio measurements of long-lived radioisotopes by resonance ionization mass spectrometry (RIMS). See comment in PubMed Commons below *Anal Bioanal Chem* 378: 348-355.
93. Erdmann N, Herrmann G, Huber G, Kohler S, Kratz JV, et al. (1997) Resonance ionization mass spectroscopy for trace determination of plutonium in environmental samples. *Fresenius J Anal Chem* 359: 378-381.
94. Nunnemann M, Erdmann N, Hasse HU, Huber G, Kratz JV, et al. (1998) Trace analysis of plutonium in environmental samples by resonance ionization mass spectroscopy (RIMS). *J Alloys Compd* 271-273: 45-48.
95. Gruning C, Huber G, Klopp P, Kratz JV, Passler G, et al. (2004) Resonance Ionization Mass Spectrometry for Ultratrace Analysis of Plutonium with a New Solid State Laser System. *Int J Mass Spectrom* 235: 171-178.
96. Vockenhuber C, Ahmad I, Golser R, Kutschera W, Liechtenstein V, et al. (2003) Accelerator mass spectrometry of heavy long-lived radionuclides. *Int J Mass Spectrom* 223-224: 713-732.
97. Steier P, Golser R, Kutschera W, Priller A, Vockenhuber C, et al. (2002) Heavy-ion AMS with a "small" accelerator. *Nucl Instrum Methods Phys Res B* 188: 283-287.
98. Oughton DH, Skipperud L, Fifield LK, Cresswell RG, Salbu B, et al. (2004) Accelerator mass spectrometry measurement of $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratios in

- Novaya Zemlya and Kara Sea sediments. See comment in PubMed Commons below *Appl Radiat Isot* 61: 249-253.
99. Taylor VF, Evans RD, Cornett RJ (2007) Determination of ⁹⁰Sr in contaminated environmental samples by tuneable bandpass dynamic reaction cell ICP-MS. See comment in PubMed Commons below *Anal Bioanal Chem* 387: 343-350.
100. Boulyga SF, Becker JS (2002) Isotopic analysis of uranium and plutonium using ICP-MS and estimation of burn-up of spent uranium in contaminated environmental samples. *J Anal Atom Spectrom* 17: 1143-1147.
101. Alonso JIG, Schultzendorff DT, Giovanonne B, Glatz J, Pagliosa G, et al. (1994) Characterization of spent nuclear fuel dissolver solutions and dissolution residues by inductively coupled plasma mass spectrometry. *J Anal Atom Spectrom* 9: 1209-1215.
102. Günther-Leopold I, Kivel N, Kobler Waldis J, Wernli B (2008) Characterization of nuclear fuels by ICP mass-spectrometric techniques. See comment in PubMed Commons below *Anal Bioanal Chem* 390: 503-510.
103. Bera S, Balasubramanian R, Datta A, Sajimol R, Nalini S, et al. (2013) Burn-Up Measurements on Dissolver Solution of Mixed Oxide Fuel Using HPLC-Mass Spectrometric Method. *Int J Anal Mass Spectrom Chrom* 1: 55-60.
104. Rollin S, Spahiu K, Eklund UB (2001) Determination of dissolution rates of spent fuel in carbonate solutions under different redox conditions with a flow-through experiment. *J Nucl Mater* 297: 231-243.
105. Song M, Probst TU, Berryman NG (2001) Rapid and sensitive determination of radiocesium (Cs-135, Cs-137) in the presence of excess barium by electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) with potassium thiocyanate as modifier. *Fresenius J Anal Chem* 370: 744-751.
106. Pitois A, de Las Heras LA, Betti M (2008) Determination of fission products in nuclear samples by capillary electrophoresis-inductively coupled plasma mass spectrometry (CE-ICP-MS). *Int J Mass Spectrom* 270: 118-126.
107. Day JA, Caruso JA, Becker JS, Dietze HJ (2000) Application of capillary electrophoresis interfaced to double focusing sector field ICP-MS for nuclide abundance determination of lanthanides produced via spallation reactions in an irradiated tantalum target. *J Anal Atom Spectrom* 15: 1343-1348.
108. Comte J, Biennu P, Brochard E, Fernandez JM, Andreatti G (2003) Determination of selenium-79 in solutions of fission products after pre-treatment by ion exchange chromatography and ETV-ICP-MS. *J Anal At Spectrom* 18: 702-707.
109. Buesseler KO, Casso SA, Hartman MC, Livingston HD (1990) Determination of fission-products and actinides in the Black Sea following the Chernobyl accident. *J Radioanal Nuc Chem* 138: 33-47.
110. Perna L, Bocci F, de las Heras LA, De Pablo J, Betti M (2002) Studies on simultaneous separation and determination of lanthanides and actinides by ion chromatography inductively coupled plasma mass spectrometry combined with isotope dilution mass spectrometry. *J Anal At Spectrom* 17: 1166-1171.
111. Barrero Moreno JM, Betti M, Garcia Alonso JI (1997) Determination of Neptunium and Plutonium in the Presence of High Concentrations of Uranium by Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry. *J Anal At Spectrom* 12: 355-361.
112. Betti M, Menichetti L, Barrero Moreno JM, Fuoco R (2000) A preliminary study for the determination of long-lived radionuclides (second transition group 4-d) in environmental samples by ion chromatography inductively coupled plasma-mass spectrometry (IC-ICP-MS). *Microchem J* 67: 285-290.
113. Becker JS (2003) Mass spectrometry of long-lived radionuclides. *Spectrochim Acta* 58: 1757-1784.
114. Gunther-Leopold I, Waldis JK, Wernli B, Kopajtic Z (2005) Measurement of plutonium isotope ratios in nuclear fuel samples by HPLC-MC-ICP-MS. *Int J Mass Spec* 242: 197-202.
115. Lide DR (2002) *CRC Handbook of Chemistry and Physics*. 83rd edition, CRC Press, Boca Raton.
116. Kurta C, Dorta L, Mittermayr F, Prattes K, Hattendorf B, et al. (2014) Rapid screening of boron isotope ratios in nuclear shielding materials by LA-ICPMS – a comparison of two different instrumental setups. *J Anal At Spectrom* 29: 185-192.
117. Evans EH, Giglio JJ (1993) Interferences in inductively coupled plasma mass spectrometry. A review. *J Anal At Spectrom* 8: 1-18.