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Review

Application of flow analysis in determination of selected radionuclides

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ABSTRACT

The subject of this article is the review of developed applications of flow analysis methods for determination of radionuclides hard-to-detect in reactor cooling waters (^{90}Sr, ^{239,240}Pu, and ^{241}Am), and also ^{99}Tc, which are released to the environment primarily through nuclear fuel processing. Flow analysis, which developed for decades parallel to flow methods of chemical synthesis, is widely employed in modern chemical analysis, mainly for environmental, food analysis and pharmaceutical applications. It allows the simplification of design of analytical instruments and procedures, the shortening of analysis time, improvement of precision, and often the automation of whole analytical procedure. All those factors can be also advantageous for determination of critical radionuclides for process needs and protection of environment. The review is based on 84 references, published mainly in leading analytical journals.

Contents

1. Introduction

Flow analysis is considered an efficient and universal method of chemical analysis. Its wide range of advantages as compared to other analytical methods is the argument for its increasing use. Thus, a relatively simple instrumentation may be distinguished, which provides usually low sample consumption, together with a possibility of its on-line processing in the flow system by effortless extension of the construction with additional units. Analytical flow systems present an opportunity to implement numerous measurement concepts, which are not always possible to achieve with common laboratory methods. Generally, this refers to a variety of measuring system constructions which are adapted to an analysts' ideas and assure that a sample in the flow is processed chemically on-line, *e.g.*, by derivatization, separation, and even by multistage

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reactions, but also physically, for example by sample preconcentration. Moreover, almost all kinds of chemical and physicochemical detection may be employed in flow systems, depending exclusively on the analyst's needs and choice. Another essential feature of the flow analysis is its automation ability, understood as full control over the fluid flow, its volumes, flow rates, timing, and detection conditions. This improves the efficiency of measurements, provides a good reproducibility of results, and also minimizes the human error influence by mechanization of all the performed processes.

The development of the flow analysis laboratory methods began with the research conducted in the 1950s by Skeggs, who introduced the air segmentation of liquids in order to reduce sample dispersion in analytical systems, designed to analyze body fluids (SFA – *segmented flow analysis*) [1]. A significant technological progress of flow methods came through with Ruzicka and Hansen who were pioneers in the field of *flow injection analysis* (FIA) [2]. The operational principle of FIA technique is based on recording the transient signal with a detector, which corresponds to the analyte concentration in the injected sample, instead of recording a steady-state signal in SFA systems. Both types of flow systems are based on connecting all stages of sample processing and detection into one system, where they take place one after another in the flowing stream. A basic FIA fluidic system is equipped with a pumping device – the most common one is a peristaltic pump – which provides flow of a liquid, a tubing manifold, an injection valve with an injection loop to load a sample into the system, and a detector. A schematic illustration of a FIA measuring system is shown in Fig. 1A. After a sample is injected into the flowing carrier stream, it moves downstream and interacts with an introduced reagent in a reactor coil to produce a detectable form by a chemical reaction. In a more complex FIA setups there are also different modules for on-line sample processing incorporated into the flow system.

A sequential injection analysis (SIA) is considered to be a new generation of the FIA method, which – compared to FIA – can be considered more flexible because it introduces reverse flow; the change of the flow direction is programmed and usually controlled by a computer [3]. The most essential advantage of this system in comparison with FIA systems is essential reduction of the reagent consumption. An SIA analyzer (Fig. 1B) consists of a syringe pump, a multi-position rotary valve, a tubing manifold with a holding and a reactor coil, and a detector. What distinguishes the SIA from the FIA is the system's heart: a multi-position valve, used for selecting samples or reagents to enter into the holding coil or into the reactor coil in another position of the valve. Again, a chemical reaction takes place in the reactor coil and a formed compound is delivered to the detector [4].

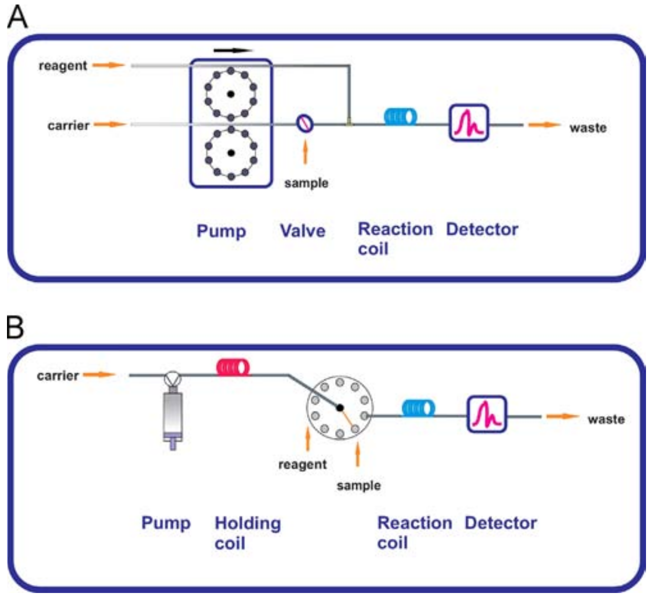


Fig. 1. Schematic diagrams of typical flow injection analysis (FIA) system with sample injection (A) and sequential injection analysis (SIA) system (B).

The flow methods in chemical analysis have been developed for over 50 years along with other numerous highly specialized systems. This includes *e.g.*, the MCFIA – a *multi-commuted flow injection analysis* [5–7], the MSFIA – *multi-syringe flow injection analysis* [8–10], the MPFS's – *multi-pumping flow system* [11–13] and the most recent option: the LOV – *lab-on-valve* systems [14,15]. Currently, flow analysis is widely applied in chemical analysis of environmental samples as well as geological, industrial, or clinical ones.

The implementation of this technique for determination of radionuclides is a relatively new, and a not very common field of application, although the first approach in developing flow systems used for radiochemistry was proposed by Ruzicka in the late 1960s [16]. The first reported example of using FIA in radioanalysis was for measuring vanadate by passage through a microcolumn of silver powder labeled with silver ^{110m}Ag by Grudpan and Nacapricha in 1991 [17]. Three years later, the term *radiometric flow injection analysis* (RFIA), relating to FIA systems combined with radiometric detectors, was coined by Myintu et al. [18]. They also proposed two subdivisions of the RFIA: the *flow injection activation analysis* (FIAA) and *the flow injection radiorelease analysis* (FIRRA) [18,19]. In the first method, the injected sample is directly transported to a neutron irradiation flow cell to form a radionuclide for detection. In contrast, in the radiorelease technique the sample mixes with a radioactive reagent and by their chemical reaction the portion of activity is released. The application of this method was well described in the abovementioned studies on vanadate determination [17]. The flow-injection radiorelease analysis was based on the reduction of vanadate to vanadium (IV) by [^{110m}Ag]-radiolabelled acidified solution, and as a result the released activity of radiosilver was proportional to the concentration of vanadium.

Regardless of the suggested classification and terminology, each radioanalytical analysis is a multistage process which usually includes: a sample pretreatment, isolation from sample matrix or separation from others components of a sample, preconcentration, and the final step – detection. If all stages were connected together on-line in one analytical system controlled by a computer, it would presumably be a fully mechanized or even an automated system. The current constructions of flow systems confirm such an assumption. However, it is not always possible. For example, it is impossible when the sample pretreatment is complicated and it is difficult to automate this operation (such as in the case of an evaporation process) or also, when a chosen type of detection is time-consuming (*e.g.*, gas proportional counter often requires a few hours or even days for detection of low activity samples). In such cases, one of the stages of the process has to be carried out off-line.

2. Detection methods employed in radiometric flow analysis

Detection of radionuclides is the most essential part of an analytical procedure. Its physico-chemical nature, which determines transformations of unstable nucleus into stable ones by radioactive decays, has a great impact on difficulties with determination of radioisotopes. A spontaneous transformation of a radioisotope constitutes a “fingerprint” of the particular radionuclide; first of all, radioactive decay has a rate specific for the radioisotope, known as half-life time, $T_{1/2}$. And, what is essential, it causes the emission of particles of different energy, which is a principle for the determination of radioisotopes.

The flow analysis is a compatible technique, connectable with broad detection options – both optical and electrochemical. A choice of detection type depends primarily on the nature of the sample analyzed. Generally, for radiochemical substances only several kinds of detectors are used: (i) radiometric; (ii) mass spectrometric; and (iii) spectrophotometric ones.

2.1. Radiometric detection

The radiometric detectors that were used earliest in flow analysis systems are the low background proportional counter, scintillation detector and semiconductor detector [20]. When radiometry developed, liquid scintillation and spectrometry dedicated for certain decays become more common. The choice of radiometric detection depends on types of the emitted radiation α, β or γ.

The utilization of the α decay makes the radionuclide de-excite and emit α particles of characteristic energy. This type of nucleus transformations exists for example in uranium radioisotopes $^{233-238}$U. Alfa-emitting radionuclides can be measured directly by using α-spectrometry [21–24]. Another detectors applied to alfa-emitters determination are proportional counters, ionization chambers, and liquid scintillation counters (LSC), which are suitable especially for flow analysis [25–27].

The process of β decay leads to radionuclide de-excitation, accompanied by emission of β^- particles (electrons) or β^+ particles (positrons). However, the energy distribution of different beta-emitters is continuous, therefore these particles do not have the specific values of energy. Accordingly, determination of this type of emitters requires a chemical separation of these radionuclides from the others present in the sample. The detectors of β^- radiation are beta counters, the well-known Geiger–Müller counters, liquid scintillation counters (LSC), or Cherenkov radiation cells [28–34].

As far as γ radiation is concerned, it almost always accompanies α and β^- as well as β^+ emission, and can be usually measured by γ-spectrometry or, rarely in flow analysis, by crystal scintillator with NaI, ZnS and semiconductor detectors *i.e.*, silicon or germanium detectors. It is worth noting that due to their excellent energy resolution, semiconductor detectors can be chosen for analysis of multi-component mixtures of radionuclides. Determinations of gamma emitters are considered not to be labor-intensive and they are relatively fast since sample pretreatment is not necessary. However, the detection efficiency is not impressive and generally depends on the distance between a sample and the detector. Determinations with use of γ-spectrometry are performed for radionuclides with suitable energy, *i.e.*, ^{60}Co, ^{137}Cs or ^{241}Am. This type of detection can be successfully employed in flow analysis, which was proved by Myint et al. [35]. The researchers constructed the radiometric flow injection analyzers equipped with gamma-spectrometry for the radiochemical determination, which were multifaceted according to the impact of experimental parameters [35]. The study highlighted the essence of apparatus parameters *i.e.*, internal tube diameter or flow parameters such as flow rate or sample volume, which have an influence on the dispersion present in the RFIA set-up. It has been proved that the dispersion increases with increasing internal tube diameter, regardless of the volume of the sample introduced, or flow rate.

The FIA system equipped with NaI (Tl) γ-scintillation detector was reported for ^{60}Co and ^{137}Cs determination [36]. The developed method achieved the desired results in an analysis of model radioactive wastewaters in the reverse FIA system, where in that case a sample is used as a carrier. Such concept of measurements does not require any reagent apart from water for dilution, but it could be only applicable when a large amount of sample is available. Hence, according to the authors, it could be appropriate for determination of ^{60}Co and ^{137}Cs in real samples of radioactive wastewaters. It was found that the peak magnitude, understood as the activity counts in time, increases as the volume of injected water increases. Having the calibration curves of peak height of the radionuclides allows measuring the specific activity of real radioactive wastewaters due to determination of the peak height of injecting the same amount of water into carrier stream.

Radiometric detection has found its place among the other detection methods commonly introduced into the flow systems that are more widely recognized [37]. This detection is considered as utilitarian tool for monitoring radioactivity, which ensures safety through operating with radioactive substances in a closed, and increasingly automated, flow system. Grudpan et al. [38] designed four types of radiometric cells intended for flow analysis. The flow cells were made using tubing (40 cm length and 1 mm inner diameter) for end-window and liquid-type Geiger–Müller counters, and for cylindrical and well-type scintillation [NaI/Tl] counters. They were examined for the effects of flow parameters (length of the mixing coil, flow rate) to the height of the peaks or dispersion. The results demonstrated that dispersion increases with the length of the mixing coil – among the tested detectors the lowest dispersions observed for the well-type detector. Moreover, the peak height decreases with increasing flow rate. The proposed flow cells provide simple and inexpensive devices for application in automated flow systems, which can be used as an alternative to the withdrawn liquid-type GM counters.

Nowadays, radiometric technique is considered a traditional counting technique. Its main disadvantage is the long analysis time required for detection – it varies from several hours to as long as several days – but also the necessity of radionuclide separation. Nonetheless, a large majority of radioactivity laboratories are still equipped with several such detectors. Obviously, easy application and relatively low instrument costs are taken into account in designing measuring systems. Radiometric detection techniques are being willingly introduced to flow analysis, yet due to long determination time they are used mostly off-line. Without regard to this difficulty, radiometric techniques frequently accompany highly specialized methods of detection for analytical purposes.

2.2. Spectrophotometric detection

Spectrophotometric measurements usually require significantly more inexpensive instrumentation and as an analytical method, spectrophotometry is not less efficient, an alternative to detection of radioactive elements, which can be employed in the flow system. The basis of determinations is usually the reaction of a determined element with a complexing agent. This leads to formation of a color product, detectable by a conventional spectrophotometer. The complexing reagents include, first of all, the compounds of a cyclic structure, among which the most frequently used ones are Chlorophosphonazo-mN, Chromazurol S (CAS), and Arsenazo III [39–47]. The short time needed for forming a color complex assures a sampling rate and also that kind of analyzes are characterized by excellent precision and accuracy. However, the mentioned complexing agents are not selective. For example, the Arsenazo III can be used as group reagent for spectrophotometric detection of Th, Zr, U, Cd, Zn, Ca, hence it is important to include a separation process into this kind of determinations.

The studies on application of flow injection techniques with spectrophotometric detection reported so far, are focused mainly on uranium determination. The method was successfully adapted for instance in determination of uranium in seawater [42]. The measurement procedure was based on a multi-stage analysis carried out in a completely automated flow system. Firstly, the injected sample was directed to the separation column filled with high-selective polymer resin Bio-Beads SM-2, modified by dodecylamidoxime. Afterwards, the adsorbed uranium was eluted by 0.01 M hydrochloric acid solution and then reacted with Chlorophosphonazo III to form a detectable complex. Possible interferences of calcium and magnesium presence were additionally masked. The reported limit of detection was 0.13 μg L^{-1}. Spectrophotometric determination of uranium was successfully applied to investigate environmental samples, not only liquid [42–46] but also the solid ones, for example geological samples, which needed additional electro-oxidative leaching process [44]. In the latter case the solid sample of ore was placed inside an electro-oxidative leaching cell, consisting of graphite electrodes and integrated with flow system, where it was mixed with the electrolyte solution with the passing nitrogen. Electro-oxidative leaching process provided electrochemical conversion of a slightly soluble U(IV) into more soluble species U(VI) and thereby improved the uranium extraction to the liquid phase. After the leaching was performed, the obtained solution was subjected to spectrophotometric determination of uranium.

The enhancement of detection parameters and determination of uranium at ultra trace levels (ppt) were achieved with the use of high-performance flow apparatus MSFIA–MPFS [45]. The detection system was coupled to a long path-length liquid wave-guide capillary cell (LWCC). The effectiveness of the usage of LWCC is related to its construction. It is a long (50–250 cm) fiber capillary with a lower refractive index connected to a light source. The sample passes through the LWCC while its concentration is determined by measuring its absorbance in the capillary. In accordance to the Lambert–Beer law, the absorbance is increased proportionally to the length of the optical path, hence the advantages such as a significant sensitivity enhancement and a lower detection limit are understandable.

The Arsenazo III forms complexes with uranium as well as with thorium, therefore it was used in simultaneous determinations of both these elements [46]. The most important part of the study was not only the detection stage, but also the separation of elements on column with the UTEVA-resin^{TM}. This process was based on a multi-stage procedure of sample dilution and preconcentration, and adjusted for a given analyte. In spite of this being virtually laborious, the analyzes were performed rapidly and efficiently in a completely automated system, which did not require human intervention. In fact, a wide concentration range of both elements can be determined: thorium 0–1200 μg L^{-1}; uranium 0–2000 μg L^{-1}, and the limits of detection were 60 ng L^{-1} and 5.9 ng L^{-1}. The proposed flow system proved to be a proficient tool for determination of thorium and uranium concentration in water samples.

The spectrophotometric detection is a convenient technique. Its usability is supported by satisfactory detection parameters, which allow analyzing the environmental samples as well, by using a conventional spectrophotometer, available in all analytical laboratories. Such type of detection offers simple and rapid measurements, which can be additionally supported by automation of the analytical system. Moreover, an improvement of the limit detection and determinations at ultra trace level can be achieved by coupling to LWCC and the analyzes still remain relatively affordable in comparison with ICP-MS. However, as opposed to mass spectrometry, the spectrophotometric detection is not a universal method – there are few complexing agents which form colored complexes with other radioactive elements. Additionally, these reagents are not adequately selective and preliminary sample components separation is required. And, most importantly, in terms of radiochemical analysis, the spectrophotometric detection is only useful for determination of total element content, without distinguishing its nuclides.

2.3. *Mass spectrometric detection*

A new quality in radionuclide detection has been achieved by application of mass spectrometry, which faced successfully the problems encountered in the conventional radiometric determinations. Firstly, the time required for an analysis was reduced to as short as several minutes. Secondly, the use of a highly specialized instrument enhanced the detection parameters significantly; the method sensitivity increased and the limit of detection improved by few orders of magnitude, allowing the performing a trace (ng L^{-1}) and even an ultra trace analysis (pg L^{-1}). Mass spectrometry, and inductively coupled plasma mass spectrometry (ICP-MS), most commonly used for elemental analysis, allow to conduct the measurements of both liquid and solid samples relatively easily and directly without a necessity of their previous treatment. Hence, ICP-MS is frequently applied in investigation of different environmental samples [48–55]. An invaluable advantage of the discussed technique is its capability to perform a multi-element analysis, also that of radionuclides, mostly the long-lived ones. This is justified by the fact that ICP-MS detection is limited by the amount of analyte nuclides present in a sample. The shorter the radionuclide's half-time, the faster its concentration level in the sample, and the lower limit of detection is required for its determination.

Considering that the concentrations of radionuclides in the environmental or geological samples are generally low, the concentrations of the short-lived radionuclides are often not high enough to be determined by ICP-MS. Despite this, mass spectrometry is still one of the most applicative and a desired tools for radiochemical analyzes, and it is continually developing. There are intense studies carried out towards the improvement of detection parameters, but also for the purpose of reduction of the required sample volume by the application of the high-efficiency nebulizers. For instance, there were four types of nebulizers examined for flow measurements: a conventional Meinhard nebulizer with a Scott-type spray chamber, a MicroMist microcentric nebulizer with a mini-cyclonic spray chamber, an ultrasonic nebulizer with an aerosol desolvation unit (USN), and a direct injection high-efficiency nebulizer (DIHEN) which were used to introduce and atomize samples of long-lived radionuclides ^{226}Ra, ^{230}Th, ^{237}Np, ^{238}U, ^{239}Pu, ^{241}Am [57]. Among them, the most satisfactory results were achieved for measurements with the ultrasonic nebulizer (USN): the highest sensitivity and the lowest limit of detection. However, considering that USN required a significantly large sample volume, a MicroMist nebulizer proved to be much more suitable.

A significant improvement of detection parameters was obtained as a result of application of a grounded platinum electrode (GE), which accounted for the elimination of secondary discharge between the cone and the plasma, and it also prevented the capacitive coupling [57]. In all the cases, an adaptation of the GE improved the method's sensitivity and lowered the limit of detection by an order of magnitude. Additionally, the authors checked the measurement's efficiency of the highly specialized DIHEN nebulizer coupled to double-focusing sector field ICP-MS, but also to a quadrupole-based ICP-MS. The first system provided higher sensitivity in determination of long-lived radionuclides and moreover, the application of GE contributed to an improvement of the results. Nevertheless, the studies by Schaumloffel et al., who also compared the detection parameters obtained by application of different types of nebulizers to measure a concentration of uranium and plutonium in flow system, gave impressive results by using a microconcentric nebulizer with a desolvator (DS-5) [58].

Additional valuable feature offered by ICP-MS is a quantitative analysis by determination of radioisotope ratio [59,60]. This method is being applied increasingly for instance in geochronological dating, archaeometry, or in provenance studies. Until now, the main limitation of the method was the time required to prepare a sample for measurement, and laborious separation of matrix components, which was additionally very expensive. The introduction of all these processes in the flow system and the complete automation of the method caused a significant improvement.

The reported studies prove that ICP-MS is a powerful tool for determination of long-lived radioisotopes, and it gives an opportunity to conduct multi-elemental analyzes at trace level. Additionally, coupling with more sophisticated devices such as the grounded electrode ensures high sensitivity even at an ultra trace level (pg L^{-1}). Furthermore, there are a number of examples in literature proving the ICP-MS to be a widespread detection technique introduced into flow systems (FI–ICP-MS) to facilitate a complete automation of determination process [49,50,58,61].

Despite the numerous advantages of ICP-MS mentioned above, some limitations of this method should be also pointed out. They include numerous types of interferences, such as the non-spectral ones, derived from the contamination of the sample or the measuring instrument, and the spectral ones, related to the occurring isobaric ions *i.e.*, $^{241}Pu/^{241}Am$, or to the forming of polyatomic ions *i.e.*, $^{239}Pu/^{238}UH^{+}$. The importance of this problem can be exemplified by difficulties found in determination of plutonium isotopes, where the presence of isobaric ions such as ^{238}U, $^{238}UH^{+}$, $^{238}UH_2^{+}$ or ^{241}Am in plasma overlaps the spectra of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu. Even worse, in case of the ^{238}Pu radionuclide, the half-time is very short and its concentration in the environmental samples is relatively low. All that, along with the high concentration of ^{238}U, which is the main spectral interference of ^{238}Pu, makes the detection of that radioisotope with mass spectrometry impossible in the environmental samples. In order to cope with this, however, numerous new procedures of radionuclide separation are being developed [51,56]. In the case of plutonium determination, the electrochemical detection based on the measurement of the reduction Pu(VI) can be applied [62]. This method was also employed in the flow-injection system, where detection limit of 0.82 μg L^{-1} was reported.

3. Methods of sample preparation

Most analytical procedures involve several sample processing steps prior to the detection. They may include, when necessary, sample dissolution, extraction or mineralization, sample clean-up, pH adjustment, the analyte preconcentration and mixing with different reagents, or analyte derivatization. All these processes are performed mostly manually, but usually that causes a risk that the obtained results be vitiated by human errors, such as transferring a wrong quantity of the sample, not ensuring the same reaction conditions or introducing impurities. This affects the accuracy and precision of determination, and results in poor reproducibility. Additionally, these steps are distinctly time-consuming and labor-intensive. In case of radiochemical determinations, carrying out the classical analytical processing of radioactive samples threatens the human health by exposure to direct contact with radioactive substances. A significant improvement in this field is made, by performing all sample processing steps on-line in mechanized or automated flow systems.

3.1. Off-line procedures in determination of radionuclides

Despite numerous advantages offered by flow analysis, it is rather rarely implemented in sample preparation for determination of radionuclides. The reason for this may be the same as in most cases when radiometric detection cannot be carried out in flow systems: sample processing requires too much time to be performed in flow conditions. A similar situation is often encountered *e.g.*, in analysis of environmental samples, which requires many hours of pretreatment: mineralization, clean-up and preconcentration. For instance, for determination of total content of uranium in rocks and solid, a multistage process of sample preparation has to be employed [63]. First sample is mineralized in strong acidic conditions (HF/HNO_3), which lasts 20 h in 160 °C. The application of drastic chemical and temperature conditions makes it impossible to integrate the sample preparation into the flow analysis. Only mineralized and dissolved samples are injected into FIA system.

A similar situation occurs when a sample requires a long and often repeated process of preparation that involves the use of instruments, which are impossible to integrate with the flow system. An example is the multi-step preparation processing of soil samples, which requires grinding as well as blending and then fusions [54]. Only a fused sample is repeatedly filtered and mixed-acid digested to be introduced into the flow system. The time-consuming process contradicts the flow analysis idea to improve an analytical process by total automation.

In some cases, even liquid samples cannot be processed on-line in the flow system because their preparation procedures require operations that are very difficult or impossible to carry out in flow conditions. These include, for instance preconcentration by evaporation, co-precipitation or above-mentioned sample mineralization in drastic conditions [41,58,63]. Schaumlöffel et al. [58] developed a flow system dedicated for analyzes of environmental (tap water) and biological samples (urine). The analyzed samples required different procedures of preparation, hence the sample preparation step was excluded from flow system, and a developed versatile nFI–ICP-SFMS (nano-volume flow injection system and inductively coupled plasma double focusing sector field mass spectrometry) was capable of measuring both types of samples. The treatment of urine samples needed pre-concentration by evaporation, which is genuinely complicated in conditions of continuous flow, and similarly the co-precipitation process, which was applied for preparation of water samples. The precipitates could accumulate and clog the channels of the apparatus. For that reason, such processes are not desirable for use in flow analyzers. Obviously, in some cases processes, which are difficult to be carried out on-line can be replaced, for instance, pre-concentration by evaporation can be replaced by solid phase extraction, or other.

3.2. On-line sample processing in FIA determination of radionuclides

The complete automation of the analysis dedicated to radionuclide determinations results in improvement of functional parameters by increasing reliability of the results, and also reducing the time of measurements, and makes them less laborious and safer because of less exposure to radioactivity. Numerous steps in sample processing can be introduced into flow system and serve up to carry out even the multi-elemental analyzes. As far as determination of radionuclides is concerned, the most critical part seems to be the radionuclide separation from other sample components, mainly from the radioactive interferences.

The basic techniques for radionuclide isolation in flow systems include liquid extraction [57,64], adsorption on activated alumina [57] or other sorbents discussed below. Due to the fact that the determination of radionuclides almost always requires preconcentration, sorbents that can simultaneously meet both the selective separation of the analyte and the preconcentration are searched for. For this purpose, the most effective ones were chromatographic resins based on ion exchange reactions, chelating sorbents, and sorbents for extraction chromatography.

The ion exchange resins are popular choices for the analytical process due to numerous advantages. Among them, there are high capacity for efficient separation, low expenses, and availability. The basic principle of separation is ion exchange reaction between ions of the stationary phase and those present in the solution. As an example, the anion exchange resin Amberlite IRA-400 can be

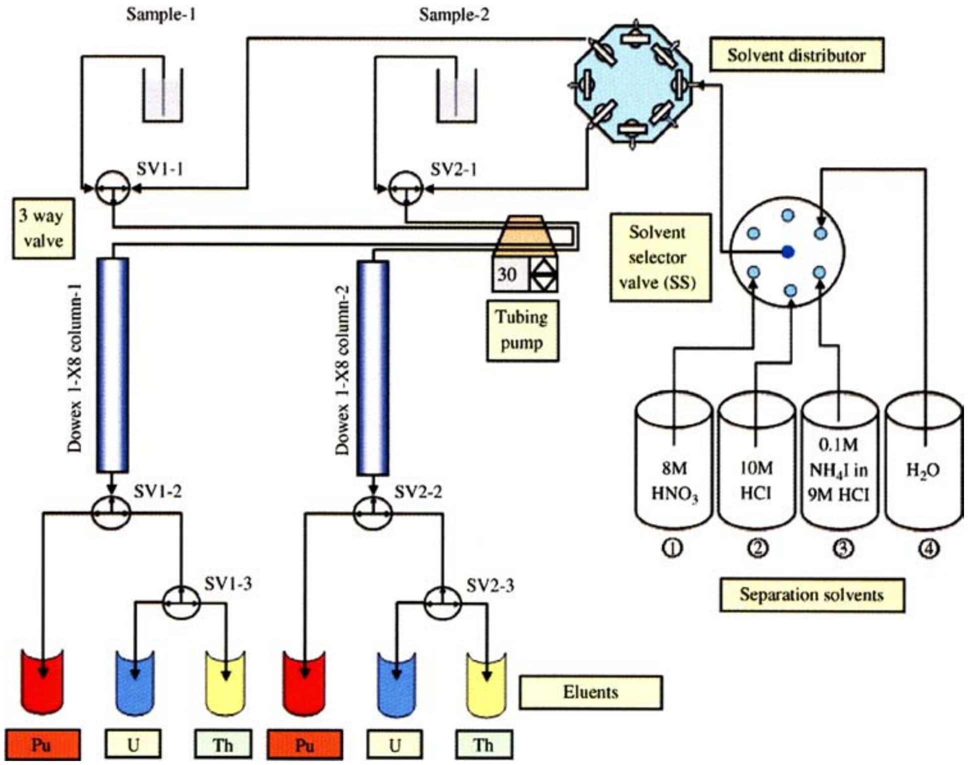


Fig. 2. Schematic diagram of SIA system designed for Pu, ^{210}Po and ^{210}Pb separation from environmental sample using anion exchange resin for off-line alpha spectrometry measurements and liquid scintillation counting [22].

indicated, which was used in determination of technetium [53]:

$$RN(CH_3)_{3^+}\,Cl^-\,(solid) + TcO_{4^-}\,(solution) \leftrightarrow RN(CH_3)_{3^+}\,TcO_{4^-}\,(solid) + Cl^-\,(solution)$$

Other examples of ion exchange resins used in determination of radionuclides include: Dowex 1-X8 [22,65], Duolite A101 [66], BioRad^{TM} resin [67] or AG MP-1M [30], AG1-X4 [61] (anion resins) and Dowex 50-X12 [69] (cation resins). A schematic diagram of sequential injection system for separation of Pu, ^{210}Po and ^{210}Pb employing Dowex-1-X8 anion exchange resin is shown in Fig. 2. The separation was conducted parallel in two lines simultaneously for two samples.

In flow systems, the commonly used separation materials are solvent impregnated resins, which function as liquid extraction stationary phase covering the inert solid support, porous silica or organic polymer. They provide fast, selective, and effective isolation of target radionuclides from sample matrix. It is commonly recognized, that first extraction resins were developed by Hortwitz et al. in early 1990s for actinides separation [68]. But importantly, the application of synthetic ion-exchange resins (Dowex 50) had already been described by Seaborg et al. for separation and identification of transuranium elements in 1950s [69]. Only a properly selected strong extractant can be successfully employed for separation and preconcentration of a particular radionuclide. Currently, there is a large variety of commercially available extraction resins for the specific separation of different radionuclides of Ra, Sr, Tc, U, Th, Cm, Pu, Am, Np, *etc.* The most known and common are TRU-resin^{TM}, TEVA-resin^{TM} and UTEVA-resin^{TM}. In chemical composition, the TRU-resin^{TM} is octylphenyl-N, N-di-isobutyl carbamoylphosphine oxide dissolved in tributylphosphate, which can be applied in transuranium elements separation, mainly americium and plutonium. A comparison of automated and manual techniques of separation can be found in literature [70]. The authors draw attention to the development of separation techniques used for radionuclides that have recently been carried out based on manual extraction chromatography, which required an introduction of the sample and the solvent on the top of the open column. The separation was processed under gravity flow, was excessively long, and required intensive labor. The next step was to use combinations of methods based on precipitation, solvent extraction, or ion exchange, in order to improve the separation performance, although there were still labor- and time-consuming, and at worst it posed a risk of exposition by direct contact with a radioactive sample. Against this background, the closed columns filled with chromatographic resins seem to be invaluable. Moreover, they can also be integrated into the flow system and subjected to complete automation.

The TEVA-resin^{TM} (TetraValent Actinides) can be employed for the separation of tetravalent actinides using extraction materials an aliphatic quaternary ammonium salt Aliquat 336 N as liquid. It is most widely used in flow systems for determination of technetium [28,50,54,67,71]. Its highly specialized variant, UTEVA-resin^{TM}, adsorbs uranium isotopes and several tetravalent actinides selectively. Also, commercial sorbents dedicated for selective retention of other elements such as *e.g.*, Sr-resin^{TM} for strontium, were employed in flow injection systems [17,31–33,59]. As it can be found in the literature, the resins are frequently designed and synthesized for a certain group of radionuclides, such as the commercial Ln-resin^{TM} (Lanthanides), used for separation of lanthanides, but they can be also employed for isotopes that do not belong to the dedicated group. For instance, the mentioned Ln-resin was successfully applied in FIA determination of ^{226}Ra [48].

There are different technological developments connected to using flow-through extraction columns with solid sorbents or extraction resins in flow injection systems. For instance, Egorov et al. [23] developed a multipurpose flow analyzer for determination of different radionuclides in nuclear waste. The developed SI-RSC system was equipped with a renewable separation column, which, depending on particular target analyte, was automatically packed with Sr-resin^{TM} for selective determination of strontium, TEVA-resin^{TM} for technetium, and TRU-resin^{TM} for americium. The concept of full automation of the radionuclide separation process was successfully applied to multiple analyzes. The SI-RSC analyzer was developed for automatic packing and emptying of the separation column. With use of the renewable column, there is no need to change the instrument, and the time needed to change the resin and conditions is saved. Among the advantages of the developed technique, the lack of necessity to wash all the components of the sample but the one of interest is mentioned. Certainly, it is useful when several components of the sample are difficult or impossible to remove. In addition, what is emphasized, the carryover on the column from one separation to another is eliminated.

The flow analysis is a useful tool in the hands of analysts, and it improves determinations of radionuclides by constructing various configurations of measuring systems. In addition, their effectiveness creates a promising prospect for the application of this type of analysis for continuous monitoring of the radioactive content in the reactor coolant. Determination of radionuclides in the reactor coolant can be used *e.g.*, to evaluate the integrity of the fuel rods. In the literature, there are so far a few publications related to this research subject [72,73], however there is no information on the application of flow techniques for this purpose.

The radionuclides ^{90}Sr, ^{99}Tc, ^{239}Pu, ^{240}Pu and ^{241}Am are considered ones of the major reference elements in the reactor coolant. The achievements reported so far in the literature will be reviewed below for determination of ^{90}Sr, ^{99}Tc, $^{239-240}$Pu, ^{241}Am in different samples with taking advantage of automated flow analysis techniques.

4. Flow analysis in determination of strontium

The strontium isotopic composition includes 23 radioisotopes, but only four of them are stable (^{84}Sr, $^{86-88}$Sr). Among the rest of the radionuclides, the most common in the environment are ^{89}Sr and ^{90}Sr, of which the latter is usually a target radionuclide in analytical determinations. Their presence in natural surroundings is attributed to anthropogenic reasons such as intense development of nuclear engineering in power plants and medical applications, but it can also indicate nuclear weapon testing. Radioactive ^{90}Sr is highly dangerous because of its chemical properties, which allow it to replace calcium as ^{90}Ca analog for example in human body, especially in bones. This may represent a particular risk of cancer disease. Furthermore, the discussed radionuclide is a natural component of alkali soil and exhibits high mobility in the environment. All those factors determine a necessity of environmental determination of radiostrontium, including monitoring of the nuclear waste for radioecology reasons as well as radiation protection.

From the physical point of view, ^{90}Sr is a pure β emitter with a relatively long half-time of 29 years, after which it decays into another short-lived β emitter ^{90}Y. Portable proportional counters are commonly employed instruments for ^{90}Sr determination. Nevertheless, bearing in mind the probable presence of ^{90}Y in the samples, and the detector's lack of capacity to determine different β radiation emitters, it is necessary to include a separation step in the analytical procedure. The most commonly used separation methods in ^{90}Sr investigation include liquid extraction, ion chromatography and extraction chromatography, and the latter is the one that is most frequently employed. It is based on the application of synthetic Sr-resin™, developed by Hortwitz [74] for selective retention of strontium. In chemical terms, Sr-resin™ is a 1 M crown-ether (4,4′(5′)-di-t-butylcyclohexano-18-crown-6) disolved in 1-octanol and sorbed on an inert support. Mainly, Sr-resin™ is used for separation of strontium, however it is also applicable as a separation resin for lead/plutonium and barium/radium.

For the first time in flow injection measurements, its use was reported by Grate et al. [31], who developed a SIA system for determination of ^{90}Sr in nuclear waste. In on-line separation step, the Sr-resin™ was used to eliminate ^{90}Y and other interfering radionuclides. The interfering ions were eluted with nitric acid, and strontium – with deionized water. Then, in the next step, the eluate was mixed with scintillation liquid and transported to the flow-through liquid scintillation counter. The developed procedure was characterized by low detection limit (2.62 Bq of ^{90}Sr) and the analysis time was 40 min. The applied separation method was simpler than the separation by ion chromatography, which required maintaining the pH conditions.

A different approach towards the radionuclide separation in flow systems, was reported by Miró et al. [64]. A developed procedure of ^{90}Sr determination in environmental samples was based on a flow system with sequential injection, where separation of different matrix components was carried out by a wetting-film extraction. The film coated the walls of a tubular open reactor, and it was composed of 4,4′-(5′)-bis(tetra-butylcyclohexane)-18-crown-6(BCHC) in 1-octanol, which retained strontium ions selectively in accordance with the following reaction:

$$Sr^{2+} + 2NO_{3^-} + BCHC \leftrightarrow Sr(BCHC)(NO_3)_2$$

The sample acidification with 8 M nitric acid assured that the strontium formed an inclusion complex and also eliminated potential interferences, especially from potassium and lead ions, which can be retained by the film. The results obtained by using a proportional counter as a detector were in activity range 0.07–0.30 Bq in the analyzed water, milk, and soil samples. Although the developed method is a good example of miniaturization of analytical system with reduced reagents consumption and short analysis time, the amount of labor and time required to prepare the reactor for the analysis, and its durability for application in routine environmental monitoring on a far greater scale were not discussed

For the same purpose of ^{90}Sr determination in samples of water, milk, and soil a multisyringe flow injection analysis (MSFIA) system was reported [32]. A developed system can be considered semi-automated, as the sample processing, separation, and concentration processes were carried out on-line in flow conditions, while the detection step with the ICP-AES spectrometer and the proportional counter, occurred off-line. The detection limit of total strontium was reported as 10 μg L^{-1} (0.01 Bq). Despite the fact that the obtained detection limit was rather poor, the performed study turned to be an effective attempt to employ other flow techniques in radiochemical measurements of low-activity environmental samples.

Over the years, a further progress of instrumentation for flow analysis resulted in development of procedures for ^{90}Sr determination with the detection limit at ng level and the lowest detected activity of radiostrontium was decreased down to 0.008 Bq [33]. What has to be admitted, is that the construction of the system was miniaturized with use of LOV (Fig. 3). The analytical procedure included a couple of stages. Firstly, the column in the LOV was loaded with Sr-resin™ and conditioned. Then, a sample was injected and its on-line processing – the separation and preconcentration – took place in the LOV. Similarly to the previous experiments, the strontium was retained on the column, while interferences were eluted by 8 M nitric acid. The analyte was removed from the column with 0.01 M nitric acid. The detection of strontium was carried out by ICP-AES, but ^{90}Sr activity was measured with a low background proportional counter. The advantages offered by the combination of LOV–MSFIA were also used for the determination of other radionuclides in environmental samples [47,52].

The overview of the reported studies indicates the improvement of flow techniques and their implementation in radiostrontium determination. It is important that the current rapid

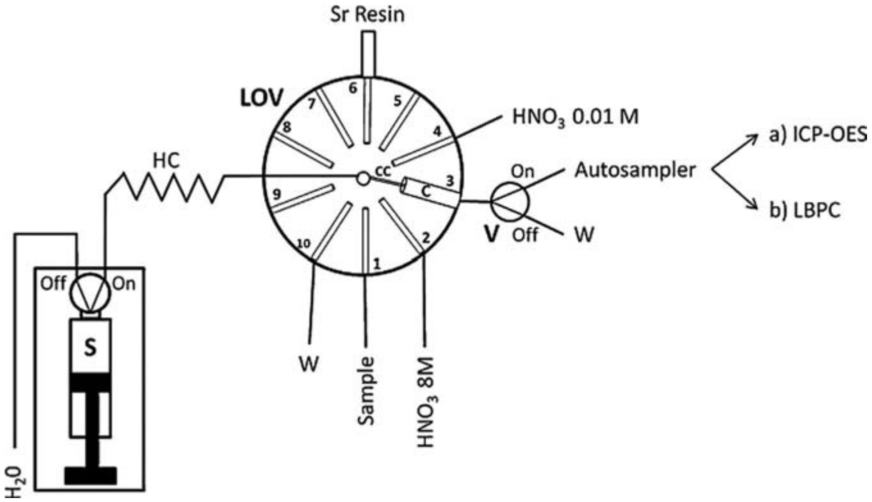


Fig. 3. Schematic diagram of lab-on-valve SIA system for strontium isolation and pre-concentration with (a) ICP-OES detection for total Sr determination and (b) low background proportional counter (LBPC) detection for ^{90}Sr determination. S – syringe; LOV – lab-on-valve; HC – holding coil; V – solenoid valve; C – column with Sr – extraction resin; CC – central conduit; W – waste [33].

technological development allows producing smart, proficient systems, which are able to carry out even 5 analyzes per hour with small reagents and resin consumption. Moreover, the sample volume decreased to even 0.1 mL, which proves a reduction of cost and amount of radioactive waste.

5. Flow analysis in determination of technetium

Despite the fact that the concentration of natural technetium in the environment is not high enough to be detected with use of conventional measurement techniques, the determinations of technetium nuclides are considered to be among the most common determinations of radionuclides. The monitoring of ^{99}Tc presence in the environment serves to evaluate radiological safety, as the main source of its occurrence is artificial production in nuclear power plants, spent fuel reprocessing, or application in nuclear medicine, where ^{99m}Tc is used for diagnostic purposes. Moreover, the observation of technetium in the environment might indicate nuclear weapons testing. The abundance of ^{99}Tc is a result of its characteristic feature, namely its long half-life $T_{1/2}=2.12\times10^5$ years. It also has an appreciable mobility in water as pertechnetium anions TcO_4^-, as well as in soil where it enters plant roots easily. It proves the necessity of the determination of total technetium in environmental and geological samples, as well as in the industrial ones, which refer to the operation of nuclear power plants [75].

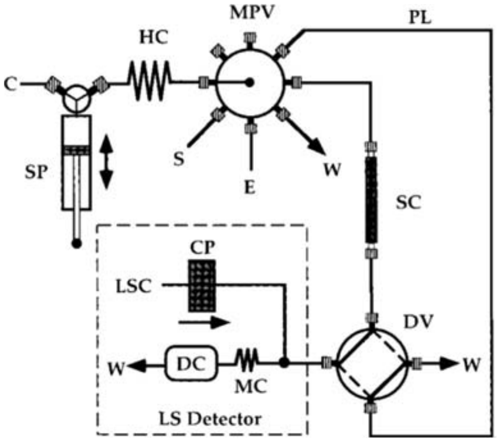
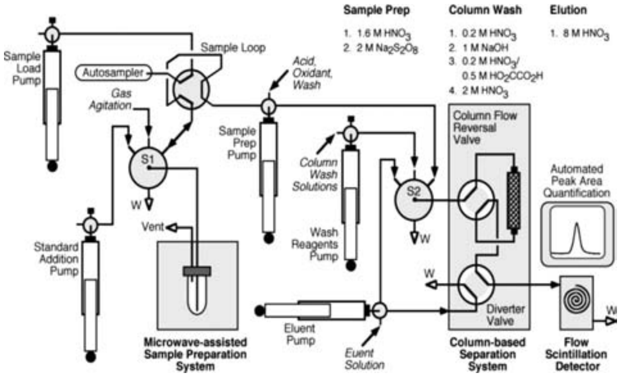
The ^{99}Tc is a pure β-emitter so it is impossible to use direct nondestructive γ spectroscopy for its detection because of the lack of observed γ emission. The ^{99}Tc might be however easily determined with use of other radiometric techniques, such as Geiger–Müller counters or scintillation counters. Unfortunately, the radiometric measurements are considered to be inconvenient because of its long-time requirement. Its long half-life period and specific activity (0.64 Bq ng^{-1}) allow an efficient use of mass spectrometry. As mentioned above, in this detection numerous interferences should be taken into account, especially the isobaric ones from radionuclides ^{99}Ru or ^{98}Mo^{1}H. This requires a separation of the matrix components and a preconcentration for detection.

The majority of separation techniques used for technetium analyzes in FIA systems are based on the use of anion exchange chromatography of TcO_4^- ions which are present in oxygenated water conditions, and have high affinity for anion column *i.e.*, BioRad™ resin [67] or AG MP-1M [30]. The sample diluted with acid is introduced on the column and pertechnetium ions, as well as other anions, are retained on the column. The removal of other sample elements is possible by washing the column with different solutions, such as water or diluted acid solutions. Then, the TcO_4^- ions are eluted only when high concentrated nitric acid (12 M) is passing through the column [30,67]. Extraction chromatography methods with synthetic resin (TEVA-resin™) columns are also commonly used. The pertechnetium ions are retained on resin while the interfering elements of the sample are being removed with 0.1 M HNO_3 solution. For analyte elution, the pertechnetate retention decreases with increasing nitric acid concentration, and the retained Tc(VII) can be eluted by using 6–12 M nitric acid [28,50,54,67,71].

The manual multi-stage procedure of technetium determination makes it laborious and time-consuming, whereas performing every individual step in automated FIA system makes it considerably easier. The first effective attempt to design a flow system intended for determination of radionuclides in soil was published by Hollenbach et al. [54]. After the off-line sample preparation (grinding, blending, fusion, and filtration) the isotopes and matrix components were separated in the TEVA-resin™ and then the eluted extract was preconcentrated and transported directly to an ICP-MS detector. The reported LOD 11 mBq g^{-1} was not very impressive and was comparable to those obtained by using radiometric methods off-line, but the measurements were faster, less laborious, and they generated less radioactive waste.

A better results were reported by Egorov et al. [28], who developed a SIA system for ^{99}Tc determination in nuclear waste. In the developed system, the separation column packed with TEVA-resin™ was used, and the measuring procedure involved radiometric LSC detection in stopped-flow mode. The evaluated LOD was 1.1 Bq g^{-1} and the time of analysis was limited to 40 min for the first sample and to 20 min for the subsequent ones. While maintaining all the advantages of flow analysis, this approach additionally enhanced method efficiency and reduced the scintillation liquid solution consumption. Fifteen years later, the same research group reported ^{99}Tc determination in nuclear waste by applying different methods of on-line sample pretreatment [30]. The constructed flow injection system incorporated the microwave assisted sample treatment, developed earlier [29]. In the first stage of sample preparation all the possible chemical species of technetium were oxidized to pertechnetium ions by peroxydisulfate solution. Then TEVA-resin™ was replaced by polymeric analytical grade anion exchange resin AG MP-IM, which ensured

Table 1
A comparison two flow analysis systems for determination of ^{99}Tc with liquid scintillation detection [28,30].

Schematic diagram of manifolds		
Description	SIA analyzer for stop-flow measurements [28]: C – carrier (water); SP – syringe pump; HC – holding coil; S – sample line; E – eluent lines; W – waste; MPV – multi-position valve; SC – TEVA resin column; PL – purge line; DV – two-way diverter valve; LSC – liquid scintillation cocktail; CP – cocktail pump; DC – detector flow cell; MC – mixing coil	Continuous flow process monitor incorporating micro-wave sample preparation [30]. The distribution valves on the ends of the syringe pumps are simplified for the diagram: some of them have more than three ports to provide access to more than one reagent solution. S1 and S2 – multi-position valves, W – waste
Separation	Extraction resin TEVA	Anion exchange resin AG MP – 1 M
Sample volume (μL)	1.0 mL	286 or 495 μL
LOD	1.1 Bq/mL	23.5 Bq/mL
Analysis time per sample	40 min/20 min	12.5 min

an effective separation process in a short time, whereas an additional reduction of time was achieved by an implementation of a reversing elution. The nitric acid was used as an eluent. The column was repeatedly washed with oxalic acid solution to bind tetravalent actinides into nitrato complexes and, in the final stage, by 2 M nitric acid to eliminate interferences from ^{121m}Sn and ^{121}Sn. A final detection of ^{99}Tc was achieved with a flow-through solid scintillator detector. What is noticeable while comparing the working parameters of both developed flow systems [28,30], is a decrease of the detection limit to 23.5 Bq mL^{-1}, and also the accuracy and precision improvement (< 10% RSD). Moreover, the performed analyzes were more efficient – the duration of one measurement was reduced to 12.5 min, which was almost three times shorter than in the procedure [28] from fifteen years earlier. A comparison between specifications of two flow-injection systems developed for determination of ^{99}Tc is shown in Table 1.

A completely new and innovative idea was to develop a preconcentrating microcolumn sensor sensitive to ^{99}Tc, which was introduced into the flow system, as shown in Fig. 4 [76]. The idea was to elaborate a rapid method of radiometric detection, which was based on a microcolumn, packed with a mixture of anion exchange resin and scintillating plastic beads. The column was placed in a transparent flow cell, which was located between two photomultiplier tubes. At the time of retention of pertechnetate ions on the resin, the radioactive decay of ^{99}Tc produced the quantifiable scintillation pulses, which provided the basis for radiometric detection of radioactive technetium. The developed system was used successfully for determination of technetium-99 in groundwater. The limit of ^{99}Tc detection was reported as ten times lower than the standard limit in drinking water (about 0.0033 Bq mL^{-1}). A noticeable disadvantage of this method is the time required for analysis (about 3.5 h) and sometimes the required sample volume (about 130 mL).

The developments reported above seem promising for application of continuous monitoring of ^{99}Tc presence in nuclear waste,

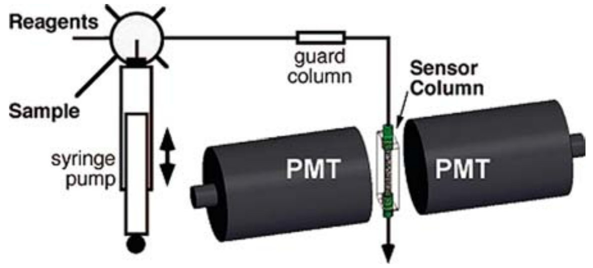


Fig. 4. The configuration of radiometric preconcentrating minicolumn sensor for ^{99}Tc sensing in groundwater, consisting of a transparent flow cell containing the packed bed placed between two photomultiplier tubes [76]. The sensor assembly is shown connected to the fluidic system consisted of syringe pump and a six-position distribution valve. The guard column contains hydroxylapatite to adsorb organic matter.

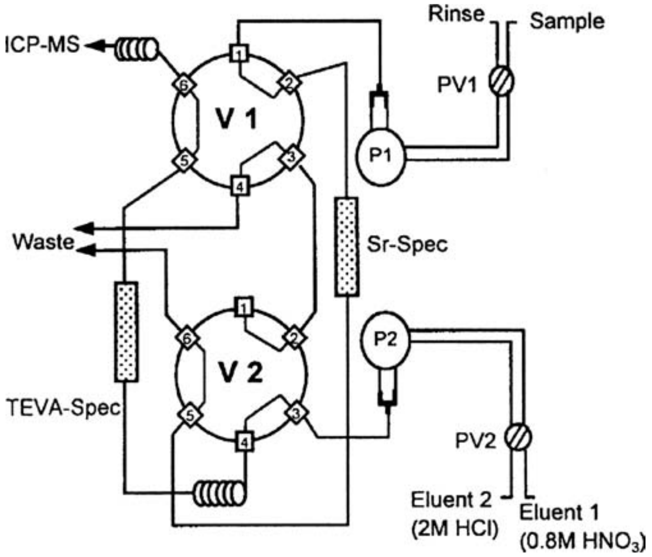


Fig. 6. Schematic diagram of flow system for on-line sample preparation with two column with extraction based sorbents (Sr-Spec and TEVA-Spec) for determination of Pu isotopes in environmental samples using isotope dilution method with high resolution ISP-MS detection [56]. P1 and P2 – peristaltic pumps, V1 and V2 – two position valves, PV1 and PV2 – pinch valves; eluent 1 – 0.8 M nitric acid, eluent 2 – 2 M hydrochloric acid, rinse – 4 M nitric acid.

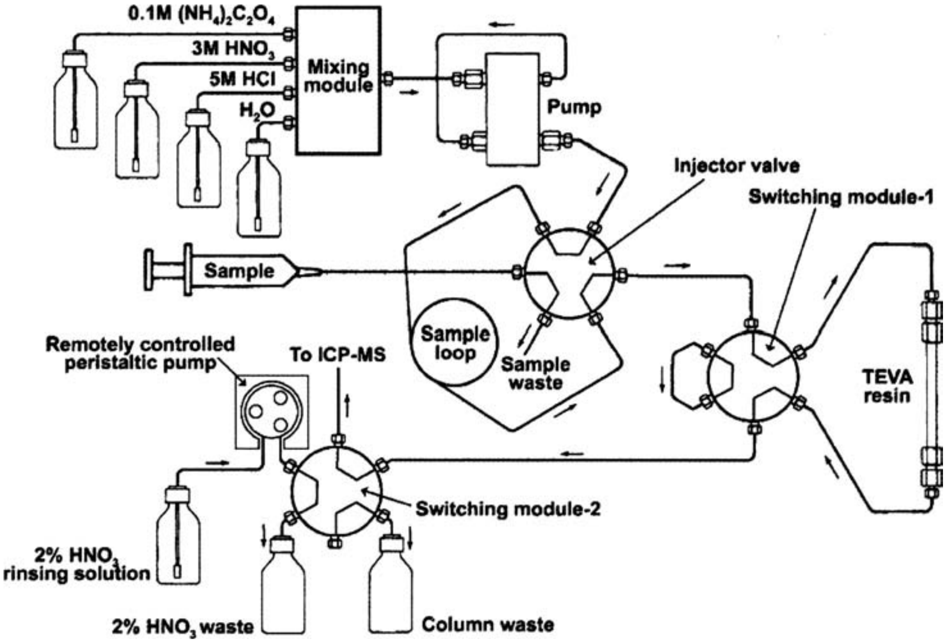


Fig. 5. Schematic diagram of flow injection system for on-line preconcentration and separation of ^{239,240}Pu isotopes in urine using extraction chromatography with TEVA resin and ICP-MS detection [78].

where concentrations of radionuclides are high. It is still needed, however, to develop more efficient flow injection systems for analyzes of low-active environmental samples.

6. Flow analysis in determination of plutonium and americium

The plutonium monitoring in the environment is necessary as it is harmful to human health because of its ability to accumulate in the internal organs and bones, where it is highly carcinogenic. Its presence in the natural environment results from human activities, mainly military ones – especially when in 1945 a nuclear bomb was dropped on Nagasaki and it introduced about 3 kg of ^{239}Pu to the atmosphere. Despite the passage of time, the effects of this incident still are and will be noticeable, because the half-life of ^{239}Pu is 2.41×10^4 years.

There are 20 radionuclides of plutonium, among which the most stable are $^{238-242}$Pu and ^{244}Pu. The majority of them do not exist naturally in the environment and they are produced artificially. This is related to the operation of nuclear power plants and associated with nuclear fuel processing or possible nuclear accidents [77]. These aspects determine the need for continuous monitoring of plutonium radioisotopes – mostly ^{239}Pu and ^{240}Pu. The attention is also increasingly focused on the need for plutonium radionuclide determination in biological materials as well, especially the biomonitoring of persons exposed to radiation [78,79]. This requires efficient and accurate analytical methods, which allow the detection at the sub-μBq L^{-1} level.

A significant contribution to these needs is the development of various flow injection systems for determination of plutonium isotopes with various designs, different detections, and sample processing steps. The flow-injection system shown schematically in Fig. 5 was developed for Pu isotopes determination with on-line preconcentration and separation of isotopes on TEVA resin and ICP-MS detection [78]. The developed system allowed to analyze urine samples at the desired trace level (^{239}Pu at 0.21, and ^{240}Pu at 0.19 mBq L^{-1}) in 14.5 min. Outstanding results were also reported on the analysis of urine in the bead injection system and lab-on-valve employing extraction chromatographic sample processing, also with TEVA resin and ICP-MS detection [79]. The bead injection variant of flow system refers to the concept of renewing the sorbent, instead of the common use of extraction column. This methodology has been already used in flow systems for the determination of radionuclides in small sample volume (250 μλ) [56] (Fig. 6), nevertheless it can be also adapted in a microflow system for processing large-sized (1 L) samples [79].

The FIA system was also developed for determination of plutonium isotope rations by ICP-MS employing on-line electrochemically modulated separations (Fig. 7A) [60]. For determinations at very low levels of analytes, a flow-through voltammetric cell was used to accumulate plutonium by anodic oxidation of Pu(III) to Pu(IV and VI), and then to release them at controlled potential. Due to more negative potentials required for U(IV), the separation of Pu from uranium interference was possible. The efficiency of that procedure is illustrated in Fig. 7B, which shows the ICP-MS response recorded after accumulation and release of ^{239}Pu and ^{240}Pu in the presence of excess of uranium. The limit of detection for ^{239}Pu determination was evaluated as 0.055 fg.

The determinations of plutonium isotopes are often combined in one analytical procedure with the determination of americium ^{241}Am, which is derived from β^- decay $^{241}_{94}\mathrm{Pu} \xrightarrow{\beta^-} {}^{241}_{95}\mathrm{Am}$. Apart from ^{241}Am, the second most occurring radioisotope of this element is ^{243}Am. The presence of ^{241}Am in environment, as in the case of plutonium radionuclides, is entirely anthropogenic and it has long half-life of 432 years. The simplest method for the detection of the mentioned radionuclides is to use radiometric techniques.

Considering that they are all alpha emitters, α-spectrometry seems to be the most suitable for this purpose. Unfortunately, it provides only a measurement of the activity of ^{241}Am and the activity of the sum of ^{239}Pu and ^{240}Pu, because their energies are too similar (5.16 and 5.17 MeV, respectively) to be distinguished by the detector. Furthermore, the measurements may be affected by a number of interferences *e.g.*, ^{210}Po, ^{224}Ra or ^{229}Th. The accurate determination of radionuclides requires including a separation process.

One of the first attempts to design a flow-injection analysis for the determination of plutonium and americium was reported by Egorov et al. [21]. The developed system was based on radiometric detection of radionuclides separated on a column with TRU-resin^{TM}. In this case, actinides in trivalent oxidation state, such as americium are not retained on TRU-resin^{TM} in strong acid media, whereas tetravalent and hexavalent actinides are strongly retained. For the separation process, the oxidation of Pu(III) to Pu(IV) by solution of HNO_3-$NaNO_2$ was applied. The oxidized plutonium was strongly bound to the column, while the Am(III) was eluted by hydrochloric acid 4 mol L^{-1}. Among the tested eluents, the best extracting solution for selective elution of plutonium from the column was 0.02 M solution of titanium(III) in 4 M hydrochloric acid, and Am–Pu elution was completed in less than seven minutes. It was demonstrated that the americium fraction did not contain plutonium, and in the plutonium fraction only 0.2% of americium was detected by γ spectrometry. In further studies, the same authors investigated the effect of column length

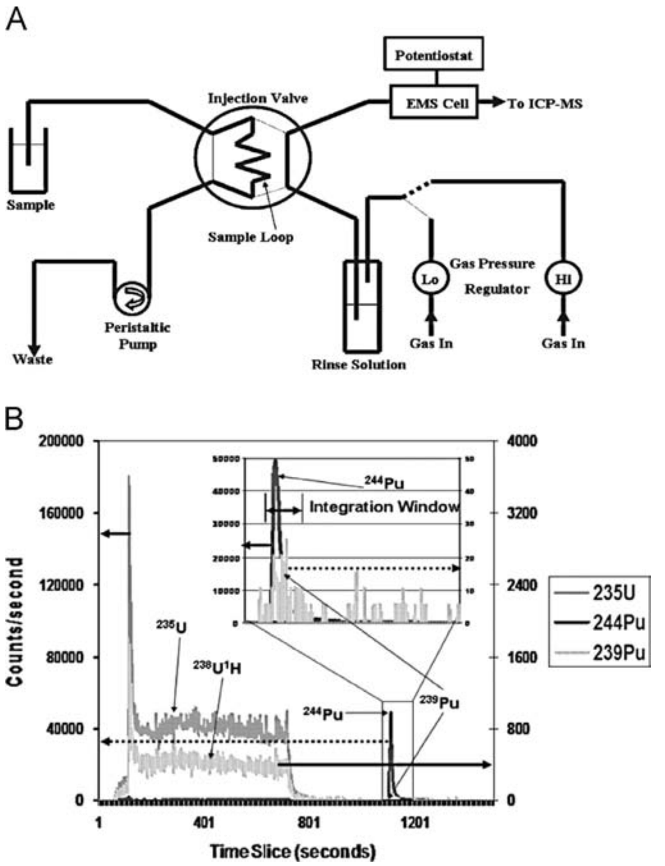


Fig. 7. Schematic diagram of FIA system with ICP-MS detection for determination of plutonium isotope ratio using on-line electrochemically modulated separations (A) and signal recordings corresponding to isotopes of uranium and plutonium temporal ICP-MS response, when using electrochemical accumulation of plutonium (B) [60].

and flow rate [27]. Kaye et al. [24] reported the analysis of soil samples using a similar methodology, except for the plutonium elution. They applied a solution of 0.1 M hydroquinone in a 4 M HCl solution to elute plutonium fraction from the column.

The SIA system with the on-line flow-through liquid scintillation detector, employing a column with TRU-resin (Fig. 8**A**) was developed for simultaneous determination of Am, Cm, and Pu isotopes in nuclear waste samples [70]. Several procedures were optimized for individual and group actinide elution. As an example of the obtained separations, the alpha energy spectra are shown for the trivalent actinide fraction (Fig. 8B), and the plutonium fraction (Fig. 8C).

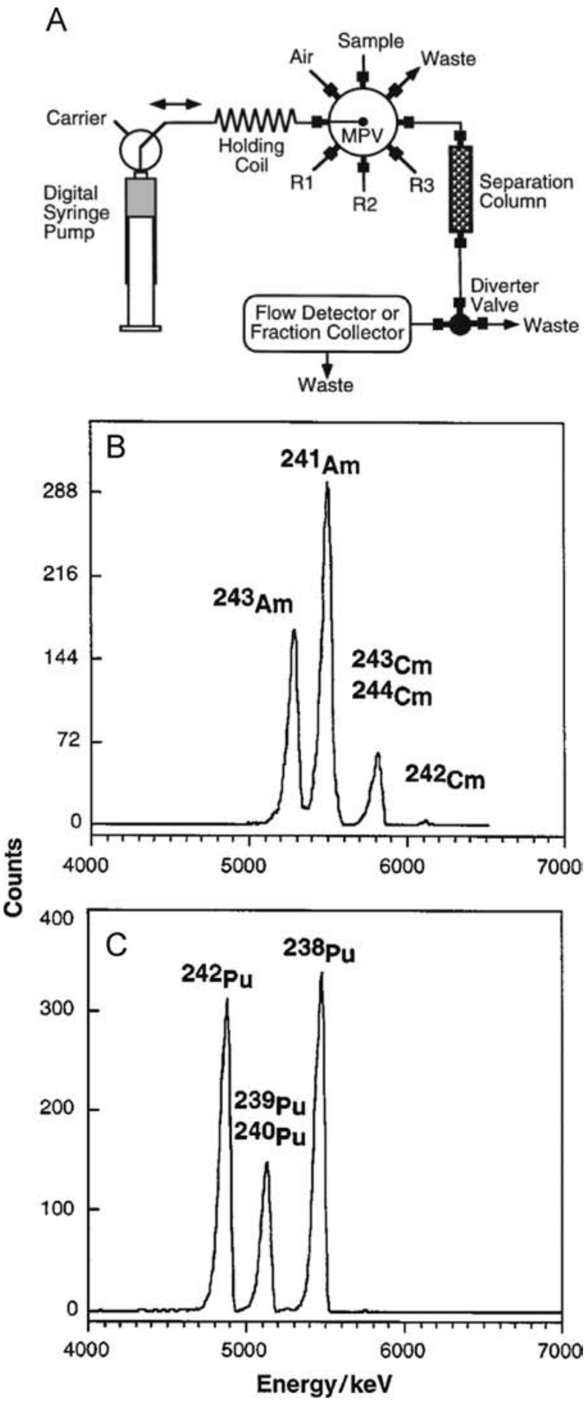


Fig. 8. Application of SIA system with on-line extraction chromatography using TRU resin in separation of actinides with the alpha spectrometry detection employing flow-through liquid scintillation detector [70]. (A) – schematic diagram of SIA system, (B) – alpha energy spectra for analysis of nuclear waste sample using Am/Cm–Pu separation procedure, and (C) – alpha spectra corresponding to plutonium fraction.

Fajardo et al. [26] improved the efficiency of flow injection simultaneous determinations of Am and Pu by the use of MSFIA–MPFS system (Fig. 9**A**). The limit of detection 0.004 Bq mL^{-1} was obtained with a multiplanchet low-background proportional counter and the developed system was successfully used in analysis of real environmental and biological samples.

As it was mentioned, another approach of improving the detection parameters and reducing the analysis time is to replace the time-consuming radiometric detection with a highly efficient and sensitive ICP-MS detection [56,58]. Unfortunately, these measurements posed also some difficulties with spectral interferences of both isotopes plutonium and americium. The separation of sample components did not always solve the problem. For example, when low-active environmental samples were being analyzed, the concentration of uranium (^{238}U, $^{238}UH^{+}$, $^{238}UH_2$) – the main interference – was even 10^8 higher, which made the accurate determination of plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu) practically impossible. In order to eliminate this problem, Kim et al. [56] developed sequential separations of uranium and plutonium on Sr-resin^{TM} and TEVA-resin ^{TM}, and employed isotope dilution technique with high resolution ICP-MS detection. Similarly, the determination of ^{241}Am can be affected by isobaric and polyatomic interferences, *e.g.*, ^{241}Pu, $^{209}Bi^{16}O_2^{+}$, $^{206}Pb^{35}Cl^{+}$. However, as opposed to the discussed plutonium isotopes, ^{241}Am can be also measured by γ-spectrometry. Still, the sensitivity of this detection is rather low, and in both cases, α-spectrometry is a much more reliable choice for the determinations of the low-activity samples.

7. Conclusions

The conventional methods of determination of radionuclides can last up to several days and require a lot of work to prepare a sample for measurements. Flow analysis is an attractive concept, which replies to the demand of continuous radioactivity monitoring. Applications of flow analysis in determination of radionuclides for different purposes have been developed for more than 20 years, and they were already the subject of several reviews in different journals [20,80,81], and also a book chapter [4].

However, this overview discusses also the most recent trends in development of flow methods for the purpose of radionuclides determinations. Over the years, the method has been appreciably developed and gained a lot of improvements for entirely automated measurements; especially the employing of extraction resins invented for specific separation of radioisotopes in the on-line sample processing. Also, especially in the recent years, significant steps have been made towards the miniaturization of flow analyzers, for instance by application of LOV valves (LOV). This leads to a lower consumption of reagents, but also reduces the generation of toxic waste. The advanced flow systems have enhanced considerably the detection parameters: accuracy, repeatability, and sensitivity, and they have allowed determinations even at ultra trace levels. The time required to carry out an analysis has been significantly reduced, and additionally, such devices as MSFIA have significantly increased the sampling-rate of the performed measurements. Additionally, possibility of conducting the analyzes of radioactive materials without direct contact with them, which reduces the risk of analysts, may be considered an invaluable advantage of using flow system automation. Table 2 is submitted in complement and summary to the information of flow methods developed for determination of discussed radionuclides: ^{90}Sr, ^{99}Tc, $^{239+240}$ Pu and ^{241}Am with an indication of applied experimental parameters (method of separation, sample

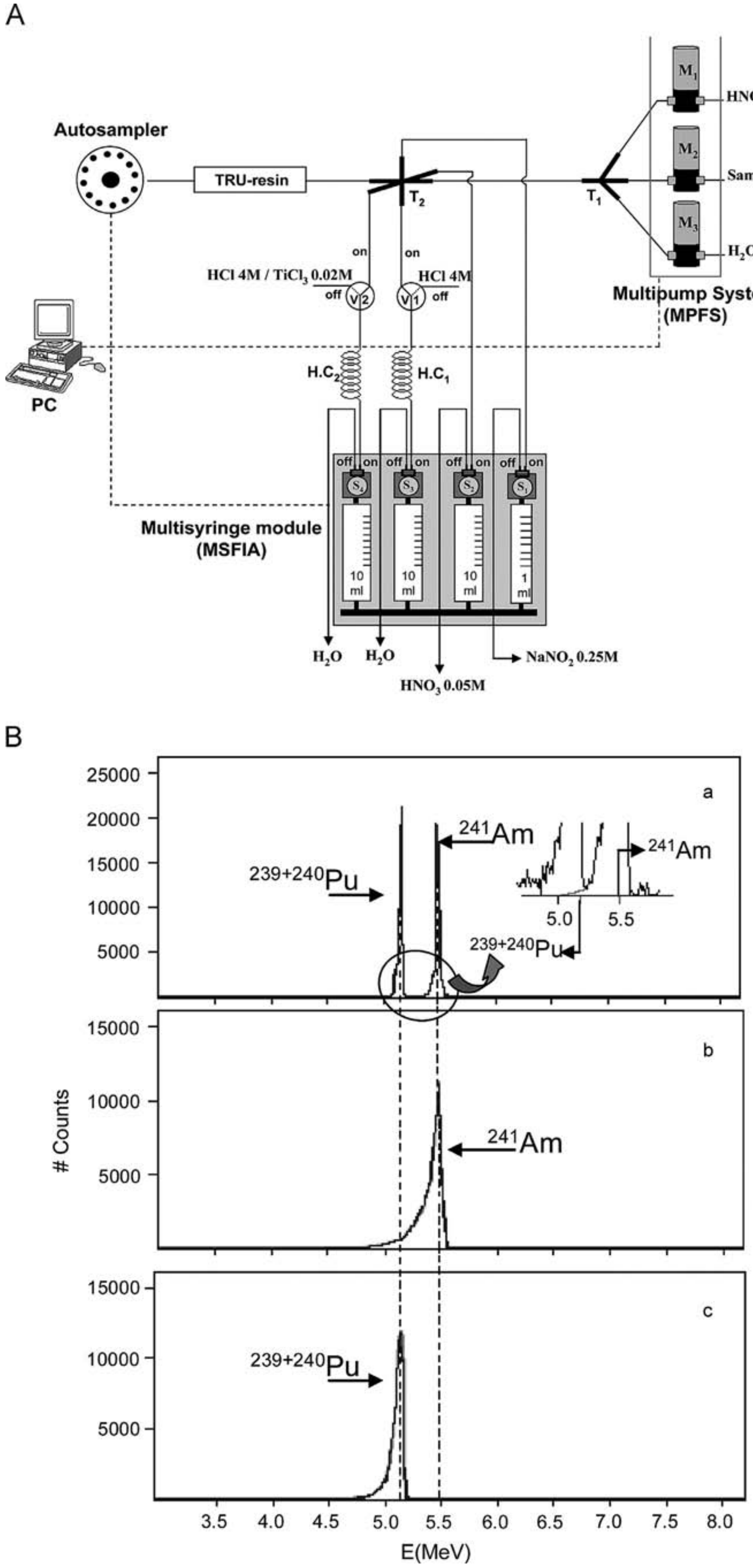


Fig. 9. Schematic diagram of MSFIA–MPFS flow system developed for the separation and preconcentration of americium and plutonium, and their determination with radiometric detection (A), and α spectrum of separation process: (i) before separation; (ii) and (iii) after separation [26]. Counting time: (a) 6×10^5 s and (b) and (c) 3×10^5 s. The ^{241}Am activity was 1 Bq mL^{-1} and $^{239+240}$Pu activity – 1 Bq mL^{-1}.

Table 2
Flow analysis methods developed for determination of ^{90}Sr, ^{99}Tc, $^{239+240Pu}$ and ^{241}Am with different detection.

Analyte	Sample	Type of flow system	Sample volume (mL)	Separation method	Detection method	Limit of detection (Bq/g)	Ref.
^{90}Sr	Water and soil	MSFIA	2	Sr-resin	ICP-AES proportional counter	0.01	[32]
	Water	LOV	0.1–8	Sr-resin	ICP-AES proportional counter	0.008	[33]
	Water and soil	SIA	2	Liquid–liquid extraction	proportional counter	0.07–0.30	[63]
	Water	SIA	350	SuperLig 620	Cherenkov radiation counting	7	[34]
	Nuclear waste	SIA	0,1	Sr-resin	LSC	2.62	[31]
^{99}Tc	Soil	FIA	10	TEVA	ICP-MS	0.011	[54]
	Soil	FIA	23	TEVA	HR-ICP-MS	0.00005	[50]
	Nuclear waste	SIA	1	TEVA	LSC	1.1	[28]
	Nuclear waste	Continuous flow	0.495	AG-MP-IM	Flow-through soild scintialltor	23.5	[30]
$^{239+240}$Pu	Soil	SIA	200	Anion-exchange resin	α-Spectrometry	N.d.	[22]
	Soil and sediment	FIA	2.4	Sr-resin TEVA	HR-ICP-MS	0.0000092 (^{239}Pu) 0.000025 (^{240}Pu)	[56]
	Seawater	FIA	0.25	Co-precipation	ICP-MS	0.0000023 (^{239}Pu) 0.0000084 (^{240}Pu)	[53]
	Urine	FIA	1.063	TEVA	ICP-MS	0.00021 (^{239}Pu) 0.00019 (^{240}Pu)	[78]
$^{239+240}$Pu + ^{241}Am	Standard solutions	FIA	0.25	TRU-resin	Radioactivity detector	N.d.	[21]
	Blood, urine and vegetables	MSFIA–MPFS	1	TRU-resin	Proportional counter	0.004	[26]
	Standard solutions	FIA	0.25	TRU-resin	Liquid scintillator	N.d.	[27]

MSFIA – multisyringe flow injection analysis; LOV – lab on valve; SIA – sequential injection analysis; FIA – flow injection analysis; MPFS – multipumping flow system; ICP-AES – inductively coupled plasma atomic emission spectroscopy; ICP-MS – inductively coupled plasma mass spectrometry; HR-ICP-MS – high resolution inductively coupled plasma mass spectrometry; LSC – liquid scintillation counting; N.d. – not determined.

volume, type of detection) that would allow a comparison of the effectiveness of each method (limit detection).

Despite those numerous advantages offered by flow analysis, this technique is still not widely used in laboratories and neither is it applicable for routine determinations. Among the reasons, there is difficulty of performing all processes of sample preparation, such as mineralization of solid samples, on-line in flow analyzers. Furthermore, it is noted that a repeated use of separation resin causes its degradation, and it can be a source of contamination for other samples. In turn, changing the new resin and preparing the column for radionuclide separation is also time-consuming and labor-intensive. In addition, the fact that the systems are designed mainly for the analyzes carried out in a small scale is also criticized, because it is difficult to include them in full-scale monitoring.

Flow analysis has a solid place among other methods of modern analytical chemistry [82,83]. Further improvement is continuously needed for the flow systems dedicated for environmental samples in order to perform determinations of radionuclides in a very low-activity samples accurately and efficiently, employing also recent trends *e.g.*, in development of radiation spectrometers [84]. Regardless of the indicated drawbacks, the flow techniques have become increasingly competitive to the traditional format of radionuclide analyzes. A continuous development of flow methods will certainly result in their further improvement in order for them to be a useful and multi-purpose tool for performing safe determinations of radioisotopes in all areas of their occurrence.

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