METHODS FOR NUCLEAR MATERIAL CONTROL USED IN THE
BASIC PRODUCTION OF A TYPICAL RADIOCHEMICAL PLANT

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Techniques for destructive and non-destructive assay of the component and isotopic composition of nuclear materials are described, namely, gravimetric, titrimetric, coulometric, mass-spectrometry, as well as those based on the registration of neutron and γ-radiations. Their metrologic characteristics are described. The techniques described are suggested to be used for MC&A purposes at the model radiochemical plant for processing irradiated fuel subassemblies from power reactors. The measurement control program is also described. This program is intended for the measurement quality assurance in the framework of MC&A system.

INTRODUCTION

This paper is mainly based on the materials of work performed Contract # B802819 between SSC-VNIINM and Brookhaven National Laboratory. The work completed in 1997, was dedicated to the development of requirements to measurements of bulk fissile materials (FM) for MC&A as applied to the model radiochemical plant.

The basic measurement techniques, designed in the Analytical Division of SSC RF - VNIINM and introduced into practice after the commissioning of the first domestic radiochemical plant RT-1, were considered and described in the course of developing the requirements to the methods of FM measurements. The FM measurement techniques are enumerated and briefly described. In the paper Consideration is given not only to their physical and chemical principles, but also to the sequence of analytical operations implemented in the technique.

The techniques are described in relation to the particular materials analyzed in the corresponding material balance areas with the indication of the accuracy achieved, along with its comparison with the recommended international target values and with the conclusion about the level of consistency between the achieved values of accuracy and international criteria.

In those cases where the analysis techniques do not agree with the recommended international target values in terms of the accuracy criteria, the reasons for these conditions are indicated and recommendations on their improvement are given.

1. DESTRUCTIVE ASSAY TECHNIQUES

1.1 Isotopic composition analysis by a mass-spectrometric technique

The mass-spectrometric technique is used in order:

- to determine the content of uranium, plutonium and neptunium in the starting nitrate solutions;
• to determine uranium and plutonium isotopic composition in the end products (uranium and plutonium dioxide fusion cake).

The isotopic composition of uranium and plutonium (both metal compounds) is analyzed by means of a mass-spectrometric technique with the use of thermoionization mass-spectrometers MI-1201 commercially available (resolution is not less than 500) and MI-3306 (resolution is equal to 800). The resolution is determined as a ratio M/ΔM, measured at the level of 10% of the peak height.

The metal Pu samples to be analyzed are dissolved in nitric acid; the plutonium dioxide samples are dissolved in the mixture of concentrated nitric acid and hydrofluoric acid or hydrochloric and iodhydric acids. After that the sample solutions are transformed into the nitrate form by means of evaporation with concentrated nitric acid. The plutonium solution in 0.1 M HNO₃ is applied onto the ion source. 1-3 mg uranium or plutonium are applied onto the ion source evaporator.

The U, UO₂, U₃O₈ samples are dissolved in nitric acid, evaporated up to wet salts and dissolved in 0.1 HNO₃.

For the isotopic analysis the plutonium samples are first of all subject to purification from americium by means of a chromatographic technique. The presence of other actinides does not impact the results of a mass-spectrometric isotopic analysis of standard plutonium.

The isotopic sensitivity of the analysis is equal to 5x10⁻⁴ and 2x10⁻⁷ at.% for MI-1201 and MI-3306, respectively (detection limits). The result error depends on the type of the instrument and on the isotopic content and covers the range of 0.008-0.02% (MI-1201) and 0.005-0.01% (MI-3306).

The metrological support for this technique is based on the system of state and sector reference samples of uranium isotopic composition which cover the entire range of isotopic content required.

The capability of mass-spectrometric methods for isotopic analyses is also used in the isotopic dilution technique in order to determine the uranium and plutonium content in various materials and solutions. In case of isotopic dilution a certain amount of the element under determination is introduced into the sample. The isotopic composition of this element differs from the composition in the sample ("tag"). the variation in the isotopic composition is measured by mass-spectrometer. After that the content of the element is calculated. The following isotopes are used as "tracers": U-233, U-235, U-238, Pu-242 (in case of high enrichment in these isotopes).

A relative error of the results obtained by means of isotopic dilution ranges from 1% to 1.5%.

1.2 Potentiometric titration technique

The technique is used in order to determine uranium:
• in the starting nitrate solutions in the products of the first and second cycles of extraction;
• in the end product in the form of uranium fusion cake.

1.2.1 Uranium potentiometric titration: the Davies-Grey method

Uranium (VI) is reduced to uranium (IV) with iron (II). The excess of iron (II) is oxidized with nitric acid in the presence of Mo (VI) as a catalizer. Uranium (IV) is titrated with potassium dichromate (K₂Cr₂O₇) in the presence of vanadyl sulfate as an indicator. For this purpose a Russia lab titrator T-108 with ionometer EV-74, is used. A platinum electrode EPV-1 (TU 25-05.2143, Russia) is used as an indicator and a mercuric/mercurous sulfate electrode (Hg/H₂SO₄) or a silver-chloride (EVL-1M1 or EVL-1M3, Russia) are used as a reference electrode. One of these reference electrodes used in the redox titration method have the advantage over calomel electrodes in a more distinct fixation of the titration end point.
5 ml 1,5 M/L sulfaminic acid solution and 40 ml 85% phosphoric acid solution are added to the sample solution which has about 300 mg uranium. The solution is stirred after the addition of each reagent. Then 5 ml 1M/L iron (II) sulfate solution is added and the sample is being held up for 0.5 - 1 min. The vessel walls are washed with 10 ml oxidizing mixture (the mixture consists of 8 M/L nitric acid, 0.15 M/L sulfaminic acid and 0.4% ammonium molybdate) and the solution is stirred vigorously avoiding any splashes. After the dark-brown colour is vanished (20-40 s) the solution is being held up for 3 min and then 100 ml water and 110-130 mg vanadyl sulfate are added and right after that titration starts. For this purpose electrodes are installed into the sample vessel and the stirrer and ionometer are switched on. The ionometer covers the range of “-1+4” in case of the mercury-mercurous sulfate electrode and the range of “4+9” in case of the silver-chloride electrode. Then at a high speed the dispensing burette doses about 90% equivalent volume of titrant. After that the buretter is switched over to a low speed and external control. The “START” key is pressed and the process of titration starts. It will last till the preset potential is achieved (70-160 mV with regard to the Hg/H₂SO₄ electrode and 550-600 mV with regard to the silver-chloride electrode). As soon as the “end” lamp flashes the readings of equivalent volume in the burette display are registered in the log. The time span between the moment when the sample is ready and the moment when the titration is over should not exceed 7 min. During titration it is necessary to register the titrant solution temperature, which is needed for the calculation of uranium mass fraction in the sample being analyzed. A relative error of this method is equal to 0.3%. Plutonium does not affect the measurement.

1.2.2 Plutonium potentiometric titration: by the McDonald-Savage method

The method can be used in order to determine Pu:
- in nitrate feed solutions,
- in products of the first and second extraction cycles.

Plutonium is oxidized to the VI-valent state with cerium nitrate. The excess of cerium nitrate is reduced with sodium arsenite in the presence of osmium tetroxide as a catalizer. The excess of sodium arsenite is decomposed with potassium permanganate. The excess of potassium permanganate is reduced with oxalic acid. The final stages of Pu determination consist in Pu (VI) reduction to Pu (IV) with a standard solution of Fe (II), a small excess of which is determined by the back titration with a standard solution of potassium bichromate. The titration end point is determined potentiometrically.

In order to determine plutonium we use a redox titration by the Davies-Grey method. However we think that in the future it will be possible to use the titration by the McDonald and Savage method which is described here based on the information from the USA. No data on the relative error of this measurement are available.

1.3 Coulometry in determination of uranium and plutonium

This method is used in order to determine U and Pu:
- in nitrate feed solutions
- in products of the first and second extraction cycles
- in the end product in the form of plutonium dioxide and uranium fusion cake.

The controlled - potential coulometry (CPC) makes it possible to make precision analyses without any preextraction of the components and can achieve a high selectivity. The titration end point (TEP) is determined directly from the current value without any special indication system.

One of the methods within the framework of CPC technique is a potential - scanning coulometry (PSC). In this case the valency transfer potential is gradually varied starting with the
initial valency potential. By means of that it is possible to significantly reduce background currents and thus to increase sensitivity and accuracy of measurements.

The analytical control is carried out step-by-step in the following way:

- The amount of sample measured very accurately is introduced into the electrolytic cell and diluted with a background electrolyte. The preliminary reduction of uranium and plutonium is carried out with a gradual decrease in the potential from $+0.5V$ to $-0.17V$. This value is maintained to the residual current which does not exceed $1mA$. Then uranium and plutonium are jointly oxidized with a gradual increase in the potential up to $+0.90V$. This value is maintained till the residual current is equal to $10mA$.
- Then plutonium is selectively reduced with a gradual decrease in the potential to $+0.5V$, with the residual current of $10mA$.
- Plutonium is selectively oxidized with a gradual increase in the potential up to $+0.90V$, the residual current being equal to $10mA$.

The duration of each step and current integrals which passed through the cell during this stages are measured. The data obtained are used with the aim to calculate the analysis results with the help of certain constants, parameters and results of out-of-process measurements. A relative error of this method is $0.3\%$.

The specific feature of this method is actually absolute automation of electrochemical analysis and mathematical processing of the obtained values, their filing and possible application in the computer nuclear material control and accounting system.

1.4 Direct U and Pu measurements by injection-spectrophotometry

This method is used in order to measure U and Pu

- in the products of the first and second extraction cycles.

The method consists in injecting the sample solution into the carrier flow (nitric acid, 3M) and measuring the U and Pu inherent light absorption at various wave lengths, in particular at $416\text{ nm}$ and $563\text{ nm}$, respectively.

The device used for this purpose consists of separate components of a liquid chromatograph “TŠVET-306” made in Russia:

- vessels for a carrier solution,
- a pump to supply the carrier solution with the required speed into the analytical line (BPZh-49 type),
- a sample injector which consists in a 6-way gage tap with a dose metering loop (30 ml) and two positions: “sampling” and “analysis”,
- a spectrophotometer SF-00 (Russia) which contains a monochromator with a spherical mirror ($F=160\text{ mm}$) and a diffractional lattice (1200 pieces/mm) with a flow-through vial of $15\text{ mm}$ in length and $25\text{ ml}$ in volume. It serves in order to get the electrical signal proportional to the value of luminous radiation transmission,
- a logarithmic amplifier (UL-02 type) to transform signals from the spectrophotometer in order to get the output signals proportional to the optical density of the solutions being analyzed or to the concentration of metals under measurement within the interval of $0.01\text{-}1.28$ units.

The device provides the level of zero signal fluctuation noise not higher than $0.005\text{ mV}$ in the dry cell and the detection limit of benzene of $5\times10^{-7}\text{ g/ml}$.

Analysis. The carrier (nitric acid 3M solution) goes through the device with the volumetric velocity of $5\text{ ml/min}$ and with the “sampling”cock position of the tap. Through the metering loop the carrier is supplied to the analytical line and the loop is washed and filled with the solution.
being analyzed. Then the tap is switched over to the "analysis" position and the sample is forced out from the loop to the flow-through vial of the spectrophotometer by the carrier flow. The solution optical density is registered first at the wave length of 416 nm and then, at the second sample injection, of 563 nm. The time required for changing the wave length and setting the base line does not exceed 5 min.

The uranium and plutonium concentrations in the solutions being analyzed are determined by means of the graduation curve and calibration factor obtained on the basis of standard solutions with the definite content of these metals in them. The relative error of this method does not exceed 1%.

The specific features of this method consist in its very rapid determination, no need in sample preparation small volume of samples (several tens of microliters), easy automation.

1.5 Extraction chromatography/spectrophotometry techniques

The method is used to measure uranium and plutonium in raffinates and liquid waste.

The aqueous and organic solutions of uranium, neptunium and plutonium have a specific colour, thus making it possible to determine these elements and to identify their various valency forms.

Spectrophotometric methods of direct determination of uranium, neptunium and plutonium are mainly used in order to solve particular analytical tasks due to low sensitivity and selectivity of these methods.

Spectrophotometric methods of U, Np and Pu determination based on the formation of intensively stained complex of these elements with organic reagents have assumed a significant importance for analytical purposes. Arsenazo III and xylenol orange are used most frequently as these reagents. As the arsenazo group agents form the stained compounds with many elements in the degrees of oxidation +4 and +6, it is necessary to preliminary pre-extract the element being analyzed from the solution in order to purify it from different hindering components and impurities. In order to selectively extract and purify U, Np and Pu from the solutions and materials being analyzed the chromatographic methods are often used, in particular, the method of extraction chromatography with "solid-extractants". Solid extractants are in the form of granulated porous polymers impregnated with the extrantant. The extrantant mass content in the solid extractant can achieve high values, exceeding 50%.

The spectrophotometric determination of uranium (III) with arsenazo (III) is usually carried out at pH = 5.5. For this purpose the solution aliquot (about 5 ml) which contains 5-50 mg of uranium is placed into a measuring flask (25 ml). Then 15 ml of acetate buffer with pH 5.5 and with sodium ethylenediaminetetraacetate (trilone B) are added. After that 1 ml saturated sulfanilic acid solution and 2 ml 0.1% arsenazo (III) aqueous solution are added. The tag is reached by means of certain addition of distilled water. Then the solution is stirred and left for 15-20 min. After that the optical density is measured with the spectrophotometer at the wave length of 650 nm in the vials with the length of 50 mm based on the comparison with the arsenazo (III) solution. The uranium content is determined with a graduation curve.

The method sensitivity is equal to 1 |ag. The relative error of this method is 10%.

Uranium in the organic solutions is reextracted with of acetate buffer solution which contains arsenazo (III). Then the optical density of the product is measured of two wave lengths: 750 nm and 650 nm, based on the comparison with the reextrantant solution. The relative error is equal to 5%.
1.6 Gravimetry for uranium measurement

This method is used in order to determine uranium in uranyl fusion cake.

This method is based on the following: the sample is dissolved in nitric acid, uranium is precipitated at pH = 2.25-2.50 in the form of uranyl ethylenediaminetetraacetate which in 10-15 min after addition of hydrogen peroxide is transformed into uranium peroxide. The following introduction of formate buffer solution provides the optimum pH and a quantitative precipitation of uranium within the next 15-20 min. Uranium determination is performed by the calcination of the precipitate and its weighing in the form of U₃O₈.

A certain amount of fusion cake (uranyl nitrite hexahydrate) which contains about 0.5 g uranium is weighted with the error not more than 0.0005 g, put into the can, then 10-20 ml 1 M nitric acid and 20-40 ml distilled water are added and the solution is heated up to boiling. The solution is diluted with distilled water up to 100 ml and then 5 ml solution of diammonium salt of ethylenediaminetetraacetic acid, 0.5 ml thymol blue solution and ammonia solution (1:6) are added till the time when the colour changes from pink to orange. In this case uranyl ethylenediaminetetraacetate of a light yellow colour is precipitated. Then 15-20 ml of hydrogen peroxide are added. After that the solution above the precipitate should become pink. In 10-15 min 15 ml of buffer solution are added and in another 15 min the solution is filtered through the two-layer paper filter “white strip”. The precipitate is washed by means of decantation. The precipitate is transferred onto the filter and washed with 50-100 ml washing solution. The washed precipitate together with the filter dried out. The dried filter placed in the preliminary weighed crucible is installed into the muffle furnace with the temperature not higher than 300°C. Then the temperature increases up to 900-1000°C and is maintained at this level for an hour. Then U₃O₈ formed in the result of all these procedures is cooled in the exsiccator and weighed. In parallel with this analysis a control test is performed for each stage of the analysis. The relative error of the method is 0.3%.

1.7 Measurement of \(^{237}\text{Np}\) concentration in solutions with the methods of extraction chromatography, isotopic dilution and gamma-spectrometry

The method is used with the aim to determine neptunium concentration in the solutions of Pu product.

It is rather difficult to determine Np concentration in solutions which have a complex salt composition and contain uranium, plutonium and fission products, without its pre-extraction and purification from impeding impurities. The analysis which involves chemical procedures usually assumes either actually complete extraction of the nuclide to be analyzed (and that is a rather labour-consuming and complicated task), or controlling its chemical yield by the method of isotopic dilution. The isotopic dilution technique permits exclude the errors in measurement results which occur due to the analyzed nuclide losses in the purification process. Below is the description of the technique for measuring \(^{237}\text{Np}\) concentration in solutions which is based on the combination of methods of extraction chromatography, isotopic dilution and \(^{237}\text{Np}\) and \(^{239}\text{Np}\) - gamma-radiation spectrometry by means of a semiconductor gamma-spectrometer. Trioctylamine is used as an extrantant. This extrantant allows to achieve a high level of purification of Np extracted from the solution from U, Pu and gamm-emitting fission products. \(^{239}\text{N}\) in its radioactive equilibrium with the mother \(^{243}\text{Am}\) is used as a tracer.

The analysis is performed in the following way. The aliquot with the volume of 1-2 ml is taken from the solution being analyzed. Then 2 ml \(^{243}\text{Am}\) solution is added to this aliquot and carefully stirred. Next comes the addition of 0.1 ml Fe (II) sulfamate solution. The final solu-
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tion is left for 2-3 min and then transferred into the chromatographic column and filtered with the speed of 1 ml/min. When this procedure is over the column is washed with three portions of 3 ml 1.5 M/L nitric acid each. Neptunium extracted by trioctylamine is eluated with 2 ml 0.3 M/L H$_2$C$_2$O$_4$ solution in a special vial made of organic glass.

The $^{237}$Np concentration in the eluate is determined by gamma-spectrometry. By means of the gamma-spectrometer of high resolution $^{237}$Np gamma-radiation with the energy of 86.5 keV and $^{239}$N gamma-and/or X-radiation with the energy of 228.2 or 277.6 keV or (106.1 + 103.7) keV are registered. maximum $^{239}$Np yield is gamma-radiation with the energy of (106.1 + 103.7) keV. But it is necessary to take into account the contribution of $^{237}$Np gamma-radiation with the energy of 106.1 keV.

The $^{237}$N content in the solution being analyzed is calculated by means of the following formula:

$$m_{^{237}} = \frac{G_{^{237}}}{G_{^{239}}} \cdot \frac{N_{^{237}}}{N_{^{239}}} \cdot m_{^{243}},$$

where $G_{^{237}}$, $G_{^{239}}$ are graduation factors which are determined during graduation based on the results of multiple measurements;

$N_{^{237}}$ - a number of pulses in the $^{237}$N peak at the energy of 86.5 keV during the time of measurement;

$N_{^{239}}$ - a number of pulses in the $^{239}$Np peak during the time of measurement;

2,347 is a $^{239}$Np half-life, days;

t - the time period since the beginning of extraction till the beginning of measurement, days

$m_{^{243}}$ is the $^{243}$Am mass added as a tracer into the solution being analyzed, mg.

Graduation is carried out by means of reference solutions with the known concentration of $^{237}$Np being in the equilibrium with $^{233}$Pa and reference solutions of $^{243}$Am in the equilibrium with $^{239}$Np. The solutions are placed into the vials identical to those which are used for the analysis and the measurements are performed in the same geometry. The graduation factors are calculated by means of the formulae:

$$G_{^{237}} = \frac{m_{k}^{^{237}}}{N_{^{237}}^{k} \cdot 0.87}; \quad G_{^{239}} = \frac{m_{k}^{^{243}}}{N_{^{239}}^{k}},$$

where $m_{k}^{^{237}}$, $m_{k}^{^{243}}$ are $^{237}$Np and $^{243}$Am masses, respectively, in the reference solutions, mg;

$N_{^{237}}^{k}$, $N_{^{239}}^{k}$ are numbers of pulses in $^{237}$N and $^{239}$N peaks, respectively, during the time of measurement;

0.87 is a coefficient which takes into account the contribution of $^{233}$Pa gamma-radiation into the $^{237}$Np peak.

The relative error of this technique within the range of $^{237}$Np content in the sample being equal to 1 - 200 mg is from 30% to 6% at the confidence probability of 0.95.

There is another available technique similar to the one described above with the only difference which consists in the fact that $^{237}$Np is used as a tracer.
2. NDA METHODS

2.1 X-ray fluorescence technique

This method is used in order:
- to measure U, Pu, Np concentrations in the feed solution;
- to measure U, Pu, Np concentrations in the extrantant products.

The X-ray fluorescence method can be applied both for the feed analysis and the analysis of U, Pu and Np products.

The method consists in excitation of heavy element atoms by X-ray tube irradiation or with an isotopic source and in registration of characteristic radiation of K, L or M series.

The most commonly accepted excitation source is a X-ray radiation generator through isotopic sources are currently used with increasing frequency. The detection systems available are both with the wave length dispersion and with energy dispersion. Detection is mainly carried out in the L-area.

In case of the wave length dispersion a high resolution is provided, but at the same time it is accompanied with a low detection efficiency. And vice versa, the energy dispersion option provides a better efficiency but worse resolution. The spectrometer with the wave length dispersion within the range of U/Pu ratio from 50 to 300 provides the relative standard deviation of about 0.5% in the result of measurement results.

The spectrometer with the wave length dispersion and with X-ray tube excitation was designed and used in operation for a certain period of time at the reprocessing plant.

The X-ray fluorescent method can be recommended to be used for the analysis of both feed solutions and the product of the first extraction cycle and U, Pu and Np products.

2.2 Gamma absorption method for controlling U and Pu solution concentrations

This method is used in order:
- to control U and Pu concentration in the process solutions.

In order to nondestructively control U and Pu concentration in process solutions of radiochemical fuel-element fabrication plants the method of gamma absorptiometry is widely used. It is based on measuring the of external source radiation attenuation by a solution layer depending on the uranium concentration in it. The advantage of this method consists in the fact that it is not sensitive to the isotopic composition of the material being measured. There is no serial production of gamma absorptiometers as devices for assaying U and Pu concentrations. They are usually designed as applied to the requirements of each specific task.

$^{241}\text{Am}$ is used as a gamma-radiation source in the absorptiometers applied for the process control. Scintillation counters with a thin scintillator are usually used as detectors. The solution layer thickness between the source and detector is chosen depending on the range of uranium concentrations measured in the test point and is a fixed value in the gamma absorptiometer design.

For the conventional one-beam absorptiometer the dependence of U or Pu concentration ($C_{NM}$) in the solution on the number of registered pulses is described by the formula:

$$C_{NM} = \frac{\ln(N_0 / N)}{\rho x (\mu_{NM} - \mu_s)} - \frac{\mu_s}{\mu_{NM} - \mu_s},$$

where $N_0$ is the number of registered pulses without any source;
$N$ is the number of registered pulses with the source available;
r is the solution density, g·cm$^{-3}$;
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x is the solution layer thickness, cm;

\( m_{NM} \) is the mass factor of the source gamma-radiation absorption by U or Pu, cm\(^2\cdot g^{-1}\);

\( m_s \) is the mass factor of the source gamma-radiation absorption by the carrier, cm\(^2\cdot g^{-1}\).

The dependence \( C_{NM} = f(N) \) is well-defined if \( r \) and \( m_s \) are constant. In practice it may not be so and thus it requires a thorough analysis of corresponding errors.

2.3 Neutron methods of control

The techniques based on detection of inherent neutron radiation of nuclear materials makes it possible to measure process product characteristics directly related to the fissile material mass. These characteristics are as follows: mass, concentration or distribution of fissile material in the particular equipment. Some of these techniques can be used with the aim to measure technological process characteristics related to the fissile material amount in the equipment. As compared to other NDA methods these techniques are distinct in the relative simplicity of methodological solutions and equipment being used, thus allowing a high reliability of their running to be achieved. The feasibility to implement this method under the conditions of high radiation fields directly in the process lines makes this method be the most important and widely used tool for remote control of technological process at radiochemical and chemical-metallurgical plants. The physical basis of this method consists in measuring neutron radiation of process products. Under the particular geometrical conditions and with the reproducible nuclide composition this radiation value can be related to the NM mass or concentration. Transuranium nuclides are the principal source of neutron radiation for the process products at radiochemical plants. In the feed solution of VVER spent fuel or spent fuel subassemblies this is curium, and in case of low burn-up these are plutonium isotopes. After solution purification from fission products and transplutonium nuclides the principal neutron source is plutonium. In the course of uranium affinage the uranium neutron radiation can be used for the purpose of control (due to \(^{238}\)U spontaneous fissioning). Neutron counters and fission chambers are used as neutron detectors.

The following techniques are used or can be used for purposes of control and accountancy of bulk nuclear materials:

- measurement of NM mass (concentration) in tanks;
- measurement of the amount of unsolved fuel on cladding;
- measurement of NM distribution in the extraction equipment;
- measurement of NM mass in the sorption equipment and monitoring of process dynamics;
- monitoring of spent fuel dissolution dynamics.

Besides, the neutron radiometric methods are used to monitor Pu content in solid radioactive waste; though for this purpose evidently it will be more reasonable to use methods based on neutron coincidence or active methods with the application of a neutron generator or isotopic source or their combination.

In some cases neutron radiation measurements are accompanied with the measurement of gamma-radiation. For instance, the amount of unsolved fuel on cladding can be accounted based on neutron and gamma-radiation. Gamma radiation can be also converted into neutron radiation by means of a beryllium radiator.

2.4 Measurement of Pu content with gamma-spectrometry and neutron coincidence technique

The method is used in order:

- to analyze the end product in the form of plutonium dioxide,
- to determine Pu concentration in waste.
The principal NDA methods currently in use for measuring Pu mass in various Pu bearing materials are neutron coincidence counting and calorimetry; their accuracy is quite competitive with destructive methods. However these methods require certain data on isotopic composition of Pu being analyzed. These data can be obtained by non-destructive gamma-spectrometric methods with the use of semi-conductor gamma-spectrometers of high resolution with codes such as MGA, PC/FRAM, etc. for gamma-spectra processing.

The passive neutron coincidence method is based on the selective registration of neutrons generated in one event of spontaneous fission of Pu even isotope nuclei (\(^{238}\text{Pu}, \(^{240}\text{Pu}, \(^{242}\text{Pu}\)). These prompt neutrons are correlated in time, whereas (\(\alpha, n\))-reaction neutrons form the background randomly distributed in time. The required selectivity is achieved by means of registration of neutron pulse coincidences within the time interval which depends on the physical properties of the detection system.

Methods and tools for NM assay based on double neutron coincidences have been widely used, since Development and application in the Los Alamos National Laboratory of shift register package and the mechanism of semi-empirical correction of neutron multiplication in samples measured. Neutron coincidence counters based on the shift register have been demonstrating a very successful operation for the MC&A purposes for about 20 years.

The principal contribution into the neutron spontaneous fission counting comes from \(^{240}\text{Pu}\) both in case of Pu from the fuel with a low burn-up value, where the content of this isotope covers about 6%, and in case of Pu from the fuel with a high burn-up value, when its content runs to \(\sim 15\%-25\%\). For the sake of convenience the value called \(^{240}\text{Pu effective mass (}^{240}\text{Pu}_{\text{eff}}\)) is used. \(^{240}\text{Pu}_{\text{eff}}\) mass is the mass of \(^{240}\text{Pu}\) which gives the same coincidence count as a real sample with the above-mentioned even isotopes. If the isotopic composition of Pu in the sample to be analyzed is known or measured than one can calculate the \(^{240}\text{Pu}_{\text{eff}}\) value as a fraction of the total Pu mass using the formula:

\[
f\left(^{240}\text{Pu}_{\text{eff}}\right) = f\left(^{240}\text{Pu}\right) + 2.52 f\left(^{238}\text{Pu}\right) + 1.68 f\left(^{242}\text{Pu}\right),
\]

where \(f(\text{Pu})\) is mass (or atomic) fraction of Pu even isotopes which can be obtained in the result of gamma-spectrometry measurements. The coefficients 2.52 and 1.68 take into account the difference in the numbers of specific neutron production in spontaneous fission neutrons per a unit of mass of \(^{238}\text{Pu}\) and \(^{242}\text{Pu}\) relative to \(^{240}\text{Pu}\). The value \(f\left(^{240}\text{Pu}_{\text{eff}}\right)\) is given by the codes MGA and PC/FRAM as a result of measurements.

Having measured the spontaneous fission neutron count rate in the sample being analyzed \(n_{sf}\) we can get the value of \(^{240}\text{Pu}_{\text{eff}}\) mass is grams via the formula:

\[
m_{\text{Pu}} = m_{^{240}\text{Pu}_{\text{eff}}} = K \cdot n_{sf},
\]

where \(K\) is a graduation factor in g·s, which is determined during of neutron coincidence counter calibration by measuring a count rate of spontaneous fission neutrons from Pu standard sources with the known isotopic composition (the known values of \(m_{^{240}\text{Pu}_{\text{eff}}^\text{in grams}}\)).

The total Pu mass in the sample being analyzed in grams is determined with data on neutron coincidence counts and gamma-spectrometry by means of the formula:

\[
m_{\text{Pu}} = m_{^{240}\text{Pu}_{\text{eff}}} / f\left(^{240}\text{Pu}_{\text{eff}}\right).
\]

However, a significant drawback of such a combined method is that the gamma-spectrometry technique is capable to determine the relative content of all the Pu isotopes with the exception of \(^{242}\text{Pu}\) which cannot be distinguished in the spectrum due to a very low intensity of its gamma-radiation. Because of that the content of this isotope is calculated based on the correlation with
other isotopes. A lot of different investigations resulted in a great number of algorithms for determining $^{242}\text{Pu}$ content. However each of them taken separately is applicable for a rather limited group of Pu samples depending on the reactor type, burn-up value, initial enrichment in terms of $^{235}\text{U}$ and other factors. In the MGA code the correlation proposed by R. Gunnink and applied in many codes is used in the following form:

$$^{242}\text{Pu} = K \left( ^{240}\text{Pu}/^{239}\text{Pu} \right) \left( ^{241}\text{Pu}/^{239}\text{Pu} \right).$$

The disadvantage of this correlation is its dependence on the relatively short-lived $^{241}\text{Pu}$ whose content reduces with the rate of about 5% per year. So in the MGA code another polynomic correlation formula is used, less sensitive to $^{241}\text{Pu}$:


where the numbers in brackets mean the measured values of isotopic contents and the coefficients from a to g for four ranges of $^{239}\text{Pu}$ contents are experimentally determined and tabulated.

The error in $^{242}\text{Pu}$ determination by means of correlations can be significant (more than 10%, they are indicated in the MGA print-out. This fact impacts the results for other isotopes (1%) and total Pu mass (up to 2%).

Double coincidence counters measure only first two moments of counting whereas there are at least three unknown parameters: $^{240}\text{Pu}$ effective mass, multiplication factor and the ratio of $(\alpha, n)$ reaction neutrons to spontaneous fission acts. The principal solution of this problem consists in measuring the moments of the highest order (at least, the third one). A significant progress has been achieved both in developing theoretical models and in designing multiplicity counters.

In order to analyze plutonium dioxide in the end product the combined method can be used. It is based on the use of gamma-spectrometry to analyze the isotopic composition of Pu and a multiplicity counter designed in the Los-Alamos National Lab with the aim to measure the mass. It will make it possible to decrease the effect of humidity and impurities on the results of measurements.

The well diameter and depth in the counter developed in the LANL for the scrap analysis is 20 cm and 41 cm, respectively. The multiplicity counter consists of a detector unit with a high voltage supply and preamplifiers located in its upper part, an electronic package and a computer. The counter well with two graphite end plugs is surrounded with 80-130 $^3\text{He}$-tubes installed into a polyethylene moderator. The neutron registration efficiency is equal to 40-55%. For the plutonium dioxide sample with the mass of 1 kg and with insignificant amount of impurities the relative error of Pu mass measurement will be 0.3 - 2% with the confidence probability of 0.68 and with the time of measurement being equal to 1000 seconds.

The Pu content in waste is assumed to be determined by the combined method based on the use of gamma-spectrometry in order to analyze the Pu isotopic composition and the use of passive neutron coincidence counter in order to determine Pu mass. The modern commercial passive neutron coincidence counters allow to measure from 0.3 g up to several kilograms of Pu both in large and small containers. The relative error of measurements is 1%-5%.

3. MEASUREMENT CONTROL PROGRAM

The objective of the measurement control program consists in assessment of the efficiency of the measurement system being used and planned to be used, in quality assurance of measured values being used for the material accountancy and in getting the values of reproducibility and accuracy to be used in evaluation of inventory difference limits as well as error limits for evaluation of shipper-receiver data.
The measurement control program envisages the following parts:

Program of electronic scales and balances. All types of scales and balances being used for accountancy must be maintained in a good condition, be calibrated according to the time fixed and their accuracy, and scale linearity must be checked every day.

Analytical quality assurance. The routine measurement data must be statistically analyzed in order to provide accuracy and reproducibility of measurements.

Sampling conditions. The error related to the sampling uncertainties must be determined and set at the regular basis.

Physical measurement control. Reproducibility and accuracy in measuring volume, temperature, pressure, density, etc. must be definitely set and guaranteed.

Instrument calibration. All the instruments must be calibrated with the use of corresponding standards or at least the measurement values must be compared with more accurate results of measurement.

Standard samples. All calibration and working standards used in the measurement control program must meet be traceable with the national measurement system. In this case the standard sample errors must be lower than the errors of analytical methods in which they are used. Working standards must be representative with respect to the type and composition of the material under measurement when the NM matrix impacts measurement results.

Sample exchange program. A radiochemical plant likewise any other plant must participate in the programs of sample exchange with other plants or labs in order to provide independent verification of the internal quality assurance of analytical measurements.

Statistical control. For each measurement technique meant for the NM accountancy certain procedures for correcting measurement conditions must be determined and documented for the cases when the preset error limits are exceeded. These limits should be set at the level of two standard deviations (a warning signal) and three standard deviations (an alarm signal).

In the first case when the warning limit is exceeded the method must be corrected and the reasons for that must be revealed. In the second case when the alarm limit is exceeded the measurement method must be thoroughly analyzed, the reasons must be revealed and eliminated. After that the method should be demonstrated as workable within the limits of preset statistical control.

Measurement technique verification. The program of measurement technique verification must be available at any plant. The objective is to demonstrate applicability of these techniques before taking measurements for the purpose of accountancy. Both for DA and NDA methods this demonstration should be performed at least once a day before starting real measurements. When it is impossible or unreasonable, the check measurement is carried out after each five measurements.

Check measurement procedures. These procedures must be stated in the written form. The correct implementation of check measurement procedures is provided with a corresponding program.

Currently the measurement verification program is being realized at the radiochemical plant according to the sector regulatory documents (OST95.10430-90, RD95.10396-89, RD95.10398-89 and OST 95.10289-87). On the whole these documents correspond to the Measurement Verification Program with the exception of the list of required standard samples.
### TABLE 1. Summary data on MC&A methods at reprocessing plant

<table>
<thead>
<tr>
<th>Material being analyzed</th>
<th>Method</th>
<th>Δ*,%</th>
<th>Target values, %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Random</td>
<td>Systematic</td>
</tr>
<tr>
<td>Fuel Assemblies</td>
<td>Gamma spectrometry and neutron count</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Feed solution of uranium, plutonium, neptunium</td>
<td>Coulometry</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Potentiometric titration</td>
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<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Mass-spectrometry with isotopic dilution</td>
<td>0.5-0.7</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>X-ray fluorescence</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium and plutonium waste</td>
<td>Coulometry</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Neutron count</td>
<td>3-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium and plutonium solutions</td>
<td>Coulometry</td>
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<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Redox titration</td>
<td>0.3</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Mass-spectrometry with isotopic dilution</td>
<td>0.5-0.7</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>First cycle products: uranium, plutonium, neptunium</td>
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<td>0.3</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Injection Spectrophotometry</td>
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<tr>
<td></td>
<td>Gamma-Absorptiometry</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>X-ray fluorescence</td>
<td>1.0</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>0.5</td>
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<td>0.5</td>
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<tr>
<td>Liquid waste</td>
<td>Potentiostatic Voltammetry</td>
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<tr>
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<td>Extraction Chromatography/ spectrophotometry</td>
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<td>0.2</td>
<td>0.2</td>
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<tr>
<td></td>
<td>Mass-spectrometry with isotopic dilution</td>
<td>0.5-1.0</td>
<td>0.2</td>
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<tr>
<td>Plutonium and Neptunium solutions</td>
<td>Coulometry</td>
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<td>0.15</td>
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<td></td>
<td>Gamma absorptiometry</td>
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<td>Plutonium dioxide and neptunium powders</td>
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<td></td>
<td>Gamma spectrometry with neutron coincidence counting</td>
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<tr>
<td>Liquid waste</td>
<td>Potentiostatic voltammetry</td>
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<tr>
<td></td>
<td>Extraction chromatography which ends in spectrophotometry</td>
<td>0.5-1.0</td>
<td>0.2</td>
<td>0.2</td>
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<tr>
<td></td>
<td>Gamma spectrometry with isotopic dilution</td>
<td>0.5-1.0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Solid waste</td>
<td>Neutron counting</td>
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<td>Uranyl Nitrite fusion cake</td>
<td>Weighing</td>
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<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Coulometry</td>
<td>0.3</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Δ* - Relative error at the probability of 0.68.