5 (2026) 100205

Contents lists available at ScienceDirect

Nuclear Analysis

journal homepage: www.keaipublishing.com/en/journals/nuclear-analysis

Determination of gadolinium in leachate by PGNAA☆

O.V. Chakilev*, S.V. Kolesnikov, S.G. Rudakov

National Research Nuclear University «MEPhI», Kashirskoye Shosse 31, Moscow, 115409, Russian Federation

HIGHLIGHTS

- Prompt gamma neutron activation analysis (PGNAA) with a neutron generator can be used as an acceptable method to detect REE in the filtrate.
- The method of accounting for the effect of neutron self-shielding is analyzed.
- The minimum detection concentration (MDC) of gadolinium determined from aqueous samples was 11 ppm.

ARTICLE INFO

Keywords:
Prompt gamma neutron activation analysis
Thermal neutron capture reactions
MDC of gadolinium

ABSTRACT

The determination of gadolinium in aqueous solution was carried out using a DT portable pulsed neutron generator and a ∅7.6 ×7.6 cm $LaBr_3$ detector. The pulse mode of the acquisition process allows the separation of the registration of radiation capture, inelastic scattering and induced activity. The technique is based on the registration of secondary gamma radiation of the sample from the thermal neutron capture reaction. After correction of the neutron self-absorption effect, the nonlinear response between peak areas and Gd concentrations was converted to a linear response, and calibration curves were used to determine the minimum detection concentration (MDC). Significant improvements in gadolinium detection are achieved, and the MDC of Gd in 300 ml of aqueous solution was 11 ppm.

1. Introduction

The control of the rare-earth element (REE) content in leachate is important in manufacturing processes, such as metallurgy or refining, because the REE content in leachate can affect the quality of the final product. The excess or deficiency of these elements can lead to the deterioration of material properties. REEs have a high economic value, and their utilization or recycling of leachates can be an important aspect of resource management. Control of the content can optimize extraction and recycling processes.

In work [1], REE in aqueous solutions were successfully determined using prompt gamma neutron activation analysis (PGNAA). The PGNAA facility, consisting of a neutron source $^{241}Am-Be$ and an HPGe detector, was proposed for the determination of rare earth elements in samples containing gadolinium, samarium and neodymium. Gadolinium, samarium and neodymium were dissolved in 50 liters of deionized water. The measurement time was 3600 s. The results showed that the minimum detectable concentrations were 27.94 mg/L (Gd), 4.77 mg/L (Sm) and 1077 mg/L (Nd), respectively. Neutron sources in PGNAA are typically reactors and radioisotope sources. Most research facilities are located in research reactors because they can provide high thermal neutron fluxes. However, the costs and inconveniences associated with reactors limit their use. Radioisotope neutron sources such as $^{241}Am-Be$, $^{239}Pu-Be$, and ^{252}Cf have also been widely used in PGNAA. To use a radioisotope as a means of irradiation, a suitable facility must be designed to localize the source and reduce radiation doses. Neutron generators have been widely used as neutron sources during the last four decades. Conventional neutron generators based on the D-T and D-D reactions can produce monoenergetic neutrons with approximate energies of 14 MeV and 2.5 MeV, respectively. The neutron generators can provide reliable neutron fluxes. With some electronic control systems, neutron generators can also provide pulsed neutron beams.

☆ Peer review under the responsibility of Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics.

* Corresponding author.
Email address: OVChakilev@mephi.ru (O.V. Chakilev).

https://doi.org/10.1016/j.nucana.2025.100205
Received 30 May 2025; Received in revised form 2 December 2025; Accepted 5 December 2025
Available online 11 December 2025

2. Materials and methods

The technique is based on the detection of the gamma-ray spectrum induced by thermal neutron capture (TNC) reactions in the sample. Fig. 1 shows the experimental setup. The source of DT neutrons is the generator ING-07 T [2]. The yield of neutrons with 14 MeV energy was 10^8 n/s. To slow down the fast neutrons, a 6 cm thick polyethylene disk and a bismuth cone were placed between the generator and the sample.

The scintillation crystal $LaBr_3$ with dimensions ∅ 76x76 mm is used as a gamma detector. As shown in Fig. 1, the neutron source, detector, and sample are vertically arranged along one axis. The distance between the generator and the detector is 12 cm.

The spectra were obtained using a CAEN DT5740D analyzer, and the measurement time was set equal to 1800 s. The data acquisition process is performed in pulse mode. Neutron pulse parameters: pulse duration 27 μs, period 128 μs, number of pulses in one cycle - 48, pause after each cycle - 2048 μs. This division allows for the separate registration of radiation capture, inelastic scattering, and induced activity. The hardware data processing program generates energy spectra of thermal neutron capture after subtracting the induced activity. A detailed description of the experimental setup parameters and data processing is provided in the previous paper [3].

2.1. Measurements of standard samples

Eight samples of aqueous solutions containing Gd of different concentrations according to Table 1 were prepared. Boric acid was added to the samples to create an internal standard. The concentration of boron in the solution was 5 g/L. In each sample, gadolinium nitrate was dissolved in 300 ml of deionized water. The characteristic thermal neutron capture gamma-ray energies of Gd and their cross sections are given in Table 2. Lines with close energies were converted to the average value taking into account their cross sections.

In accordance with the measurement process described above, the resulting spectra of the aqueous solution containing different concentrations of Gd obtained with the $LaBr_3$ detector from the experiments are shown in Fig. 2. The gamma radiation resulting from the interaction between neutrons and the structural materials of the setup and room leads to a complex and high background in the spectra. Therefore, peak identification was performed on the spectra after background subtraction.

Background subtraction was carried out using a baseline with asymmetric least squares (ALS) smoothing [5]. The baselines for the background spectrum of water and the spectrum of the samples containing gadolinium are shown in Fig. 3. The final result is the difference between the sample and background spectra after subtraction of the baseline. Subsequently, the obtained peaks were fitted using a Gaussian curve

Table 1
Concentrations of Gd in standard aqueous solutions.

Sample	Concentration of Gd, mg/L
1	2,32
2	17
3	68
4	137
5	293
6	450
7	613
8	941

Table 2
Characteristic thermal neutron capture lines of Gd [4].

Isotope	Energy, keV	Cross-section, barn
^{157}Gd	780	1010
	897	2290
	957	6580
	1112	3010
	1186	3978
	1263	641

Fig. 1. Experimental PGNAA setup.

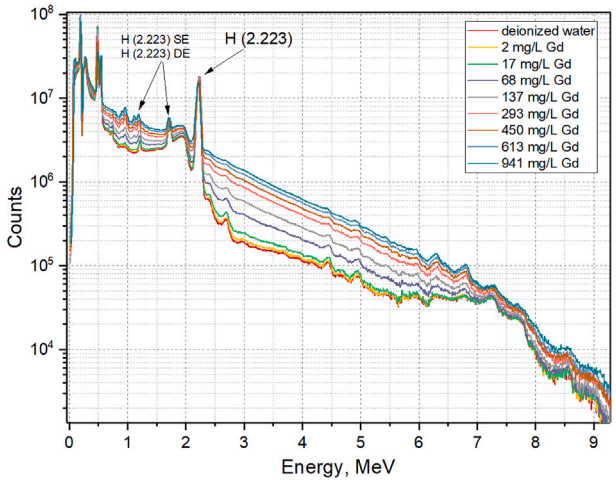

Fig. 2. Prompt gamma-ray spectra with different concentrations of gadolinium in the sample.

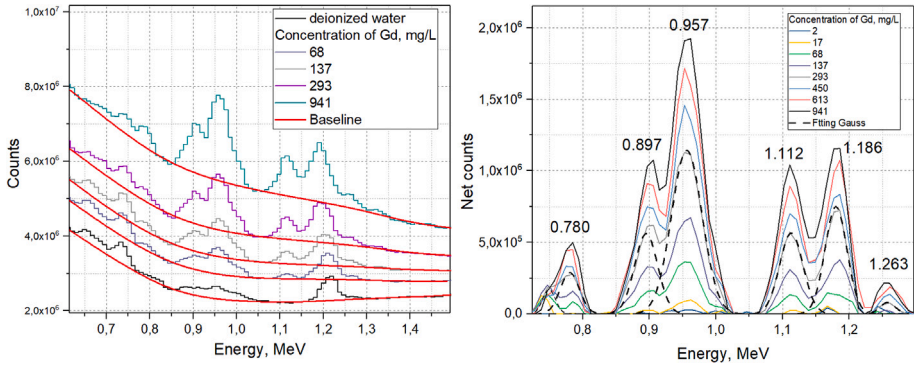

Fig. 3. Baseline asymmetric least squares (ALS) (Left). Net counts in signature gamma-ray peaks of Gd in standard samples (Right).

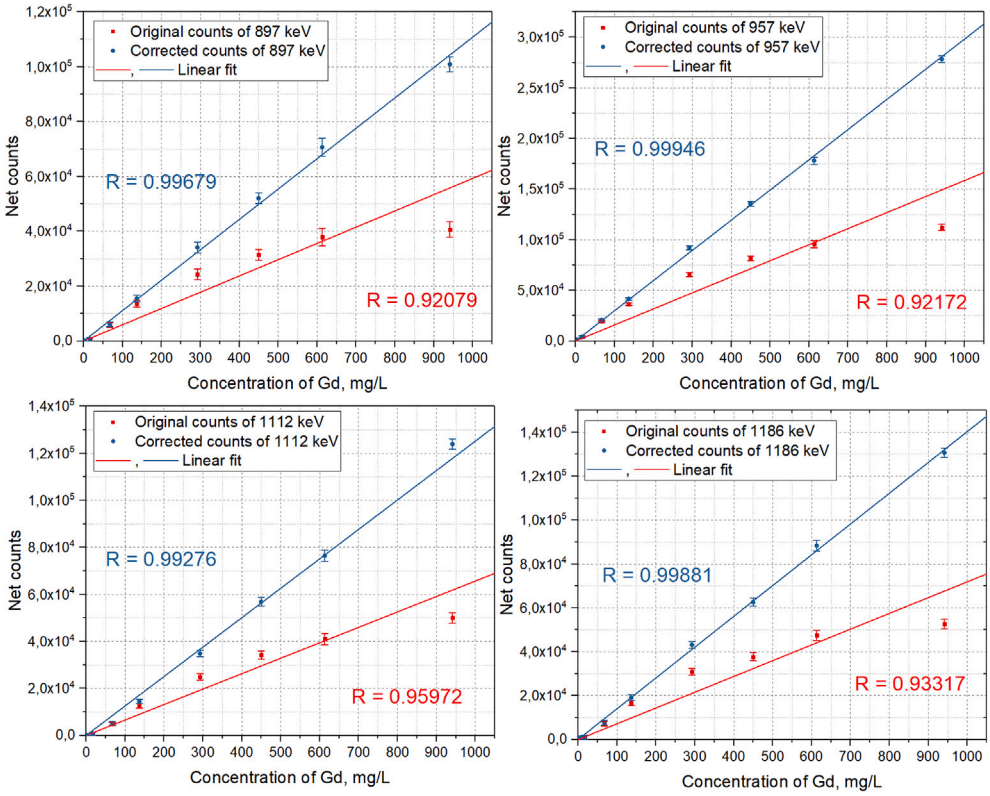

Fig. 4. The net counts vs. concentration of Gd for 897, 957, 1112, 1186 keV.

to determine the area. Due to the presence of water, the background hydrogen peak with single and double escape peaks (SE, DE) is shown in Fig. 2. The DE peak is located in the region of the Gd peak with an energy of 1263 keV. Due to the subtraction between the sample and the background spectra after the difference of the baseline, the DE hydrogen peak is missing and the Gd peak at 1263 keV is identified in Fig. 3. However, because of its relatively low cross section, it was not used for quantitative analysis.

The concentrations of Gd in the unknown sample were determined using the calibration curves. For this purpose, it is necessary to perform experiments involving the irradiation of samples with different concentrations of the element under identical conditions. Next, the area under the peak of the element is measured and the calibration curve is plotted. Fig. 3 shows the spectra of samples containing different concentrations of Gd obtained after the subtraction of the background. The characteristic Gd peaks at 897, 957, 1112, and 1186 keV can be clearly identified. The relationship between the area of the characteristic peaks and the concentration of Gd is shown in Fig. 4.

2.2. Neutron self-shielding correction

Based on Fig. 4, due to the large Gd absorption cross sections shown in Table 2, there is no obvious linearity between the concentration and the original peak area. As the concentration of gadolinium increases, the peak area does not gradually increase, i.e., the original linear fitting coefficient R is 0.92 (at 897 keV). To take into account this effect, an internal standard method was used in this work. The internal standard method is a relative method and is used to estimate the neutron self-absorption of the sample.

In works [1,6] an element with large and constant mass was chosen as the standard element. The change in neutron density inside the sample can be calculated from the change in gamma ray emission of the standard element. Hydrogen with constant mass and large volume was chosen as the standard element.

$$f_1 = \frac{A_s - A_b}{A_d - A_b} \tag{1}$$

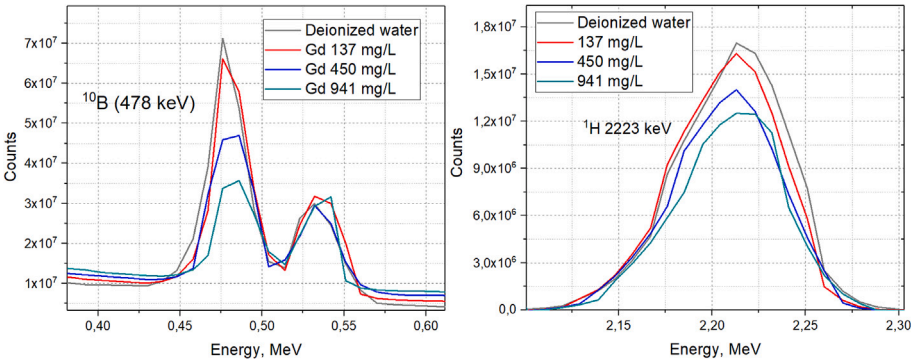

Fig. 5. Reduction of ^{10}B and ^{1}H peaks due to the neutron self-shielding effect.

Table 3
Neutron self-shielding factors and their linear fitting coefficients R.

Concentration of Gd, mg/L	f_{H1}	f_{B1}	f_{H2}	f_{B2}
2,32	1,00	1,00	1,00	1,00
17	1,00	0,99	1,00	0,99
68	0,96	0,94	0,99	0,94
137	0,84	0,87	0,96	0,87
293	0,55	0,75	0,89	0,71
450	0,35	0,68	0,83	0,60
613	0,24	0,65	0,81	0,537
941	−0,02	0,59	0,74	0,40
$R_{original}$	0,92,172			
$R_{corrected}$	0,37,605	0,97,568	0,96,298	0,99,946

Table 4
Elemental analysis of the test sample.

Energy, keV	Concentration Gd, mg/L	True concentration of Gd, mg/L
897	26±4	37
957	36±2	
1112	20±4	
1186	26±3	

Table 5
MDC values for different peaks.

Energy, keV	MDC of Gd, mg/L
897	23 ± 7
957	11 ± 3
1112	19 ± 6
1186	24 ± 7

where A_d, A_b and A_s are the net areas of the 2223 keV hydrogen peak for the water sample without impurities, empty container and sample with different Gd content, respectively. The areas of the elements should be divided by the correction factor f_1 to obtain the corrected calibration curves.

In works [7,8], the correction factor is calculated as a ratio:

$$f_2 = \frac{A_s}{A_d} \tag{2}$$

where A_s and A_d are the net areas of standard peaks (in some works the hydrogen peak 2223 keV or the boron peak 478 keV) for a water sample without impurities and a sample with different Gd content, respectively. The relative change in the number of captured neutrons can be calculated through the counts of characteristic peak of the standard element. The measured counts of the characteristic peak, which are emitted from the element with large neutron absorption cross-section in the sample, can then be corrected with the correction factor f by using the following equation:

$$A_c = \frac{A_o}{f} \tag{3}$$

where A_o and A_c are the original measured counts and the corrected counts of the Gd peaks, respectively.

Both boron with a peak of 478 keV and hydrogen with a peak of 2223 keV can be chosen as the standard element. Fig. 5 shows a comparison of the standard peaks of boron and hydrogen, from which the decrease in area due to the self-absorption effect is noticeable. To select a suitable correction factor, the coefficients calculated using the formulas 1 and 2 were compared, where the peaks ^{1}H 2223 keV and ^{10}B 478 keV were used as the standard peaks. The results of the comparison of the coefficients for the peak with energy 957 keV are summarized in Table 3. Based on Table 3, the coefficient determined by formula 2 using the standard boron peak has the best correlation coefficient. Further this correction factor f_{B2} is used to take into account self-absorption. A sample of aqueous solution containing 37 mg/L of Gd was selected as a test sample for elemental analysis. Table 4 summarizes the results of concentration determination according to the calibration curves for different peaks of Gd.

As shown in Table 4, the determined concentration coincides with the true concentration only for the 957 keV peak. The calibration curve method is not effective in the lower concentration range for the peaks 897, 1112, and 1186 keV. In this area, the calibration curves for these peaks exhibit some divergence, which becomes less significant as the concentration increases. As a result, there is a discrepancy between the test and the calculated concentrations presented in Table 4. This could be attributed to the fact that the test value of 37 mg/L is close to the minimum detectable concentration (MDC) for these peaks, shown in Table 5. Therefore, the peak with the lowest MDC (957 keV) can provide a reasonably reliable result.

3. Results and discussion

In order to quantify the detection limits for Gd in aqueous samples, the minimum detection concentrations (MDC) were calculated. The MDC and its standard deviation error (σ_{MDC}) were determined using the following equations [9]:

$$MDC = \frac{4.65 \times \sqrt{N_b} + 2.71}{k} \tag{4}$$

$$\sigma_{MDC} = \frac{\sqrt{N_b}}{k} \tag{5}$$

where k is the slope of the calibration curve of the corrected data, N_b is the integral of the background under the peak. The results are presented in Table 5.

Table 6
MDC values based on PGNAA setups.

Neutron source	Neutron emission, n/s	Detector	Sample	Measurement time, s.	MDC, ppm	Ref.
$^{241}Am-Be$	1.0×10^{7}	Large liquid scintillation detector	$35\times35\times8$ cm of water	150	0.426	[10]
$^{241}Am-Be$	6.6×10^{5}	HPGe	50 L of water	3600	27.49	[1]
DT	10^{8}	$LaBr_3$	0.3 L of water	1800	11 ± 3	Current work

Table 7
Detection limit (DL) based on PGNAA setups.

Neutron source	Neutron emission, n/s	Detector	Sample	Measurement time, s.	MDC, ppm	Ref.
Reactor IRT MEPhI	Thermal neutron flux 2.7×10^{6} n/$cm^2\times$ s	HPGe	1.5 mL of water	54,000	1.33	[11]
DT	Neutron emission 10^{8} n/s	$LaBr_3$	0.3 L of water	1800	6.93	Current work

Thus, the lowest MDC of Gd in a 300 mL aqueous solution sample, with a neuron emission of 10^{8} n/s and a measurement time of 1800 s, was found to be 11 ± 3 mg/L or 11 ppm for the 957 keV peak. This result may be related to the largest cross section for this line relative to the others.

The comparison of results in Table 6 shows that our PGNAA setup can detect Gd with a concentration not lower than 11 ± 3 ppm, which is more precise than the 27.49 ppm reported in [1]. This is because in the study mentioned the neutron emission from the $^{241}Am-Be$ source was smaller. The better result 0.426 ppm obtained in work [10] is due to the large size of the liquid scintillation detector.

In many works also used a different definition of detection limit:

$$DL=\frac{3\times\sqrt{N_b}}{k} \tag{6}$$

The detection limit is shown in Table 7. The better result of 1.33 ppm obtained in work [11] is due to a longer measurement time and a higher portion of the thermal neutron component in the incident neutron spectrum of the reactor. The findings of our research suggest promising potential for the application of our PGNAA setup, which could be expanded to analyze other rare earth elements. This is a promising premise for future research.

4. Conclusions

In this paper, the gamma-ray energy spectra of the radiation capture of aqueous solutions containing Gd were obtained. After correction of the neutron self-absorption effect, the nonlinear response between peak areas and element concentrations was converted to a linear response, and calibration curves were used to determine the composition of the test sample. The minimum detection concentration (MDC) of gadolinium in aqueous samples was determined through thermal neutron capture reactions. The extracted MDC value for Gd in 300 ml of water is 11 ppm. The results show that better improvements in gadolinium detection compared to previous studies are achieved. As a result of this work, a technique based on neutron-radiation analysis was developed to be able to detect REEs in aqueous leachate. Finally, the results obtained indicate that PGNAA with a neutron generator can be used as an acceptable method for the detection of REE in leachate generated from an industrial process.

CRediT authorship contribution statement

O.V. Chakilev: Writing – original draft, Software, Methodology, Conceptualization. **S.V. Kolesnikov:** Writing – original draft, Data curation. **S.G. Rudakov:** Writing – original draft, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors extend their gratitude to the Federal State Unitary Enterprise Dukhov Automatics Research Institute (FSUE VNIIA) for providing the opportunity to carry out experiments with the ING-07 T neutron generator.

References

[1] Y. Ling, J. Chen, P. Cai, W. Jia, D. Hei, J. Li, C. Cheng, Q. Shan, Determining rare-earth elements in aqueous solutions using PGNAA technology, J. Radioanal. Nucl. Chem. 331 (2) (jan 13 2022) 1101–1108.
[2] N. Marchese, A. Cannuli, M.T. Caccamo, C. Pace, New generation non-stationary portable neutron generators for biophysical applications of neutron activation analysis, Biochim. Biophys. Acta Gen. Subj. 1861 (1) (Jan 2017) 3661–3670.
[3] O.V. Chakilev, S.V. Kolesnikov, S.G. Rudakov, P.S. Dzhumaev, Elemental analysis of nickel ORE by PGNAA, J. Radioanal. Nucl. Chem., nov 8 2024).
[4] Agency, International Atomic Energy, Database of Prompt Gamma Rays from Slow Neutron Capture for Elemental Analysis, IAEA, 2007.
[5] P.H. Eilers, H.F. Boelens, Baseline Correction with Asymmetric Least Squares Smoothing, Leiden University Medical Centre Report, 2005.
[6] C. Cheng, Z. Wei, D. Hei, W. Jia, J. Li, P. Cai, Y. Gao, Q. Shan, Y. Ling, MCNP benchmark of a 252cf source-based PGNAA system for bulk sample analysis, Appl. Radiat. Isot. 158 (Apr 2020) 109045.
[7] W. Jia, C. Cheng, D. Hei, Y. Ling, H. Wang, D. Chen, Method for correcting thermal neutron self-shielding effect for aqueous bulk sample analysis by PGNAA technique, J. Radioanal. Nucl. Chem. 304 (3) (feb 14 2015) 1133–1137.
[8] D. Hei, Z. Jiang, W. Jia, C. Cheng, H. Wang, J. Li, D. Chen, The background influence of cadmium detection in saline water using PGNAA technique, J. Radioanal. Nucl. Chem. 310 (1) (mar 25 2016) 27–31.
[9] A. Lloyd Currie, Limits for qualitative detection and quantitative determination. Application to radiochemistry, Anal. Chem. 40 (3) (1968) 568–593.
[10] Y. Xie, C. Cheng, W. Zhang, X. Wang, W. Qin, W. Liu, S. Lin, P. Xiao, Z. Wu, W. Jia, Feasibility study of on-line monitoring gadolinium based on neutron induced gamma activation, Appl. Radiat. Isot. 197 (Jul 2023) 110817.
[11] V.F. Khokhlov, K.N. Zaitsev, V.N. Beliayev, V.N. Kulakov, A.A. Lipengolts, A.A. Portnov, Prompt gamma neutron activation analysis of 10b and GD in biological samples at the Mephi reactor, Appl. Radiat. Isot. 67 (7–8) (Jul 2009) S251–S253.