Precise determination of plutonium in nuclear fuel process samples

K. Dhamodharan · Satya Narayan Das · D. Sivakumar · K. Ananthasivan

Abstract
A REDOX-based analytical method was developed for determining the plutonium concentration. In this method, plutonium was oxidized to the +6-oxidation state using ceric ammonium nitrate solution. The interference from ceric(IV) nitrate was suppressed by reducing its oxidation state from +4 to +3 with sodium nitrite. Hexavalent plutonium in this sample was then reduced to be tetravalent by adding a known volume of excess standard ferrous ammonium sulphate. The dichromate equivalence required for unreacted ferrous ammonium sulphate was determined to obtain the concentration of plutonium. Interference studies from chemicals envisaged to be present in the PUREX process stream, such as dissolved tri-n-butyl phosphate, uranium, and various reagents employed during analysis, were performed for the determination of plutonium concentration. The relative standard deviation was found and it is within ± 1.0% for an aliquot containing plutonium in a range of 0.7–2.5 mg.

Keywords Redox titration · Plutonium determination · Fast reactor · High burn up · Ceric nitrate

Introduction
Mixed carbide fuel containing 70% plutonium and 30% uranium is being used as a driver fuel in the Fast Breeder Test Reactor (FBTR) at Kalpakkam, India. The spent fuels discharged after irradiation up to 155 GWD/T is being reprocessed in the Compact Reprocessing facility for an Advanced fuel in a Lead shielded cell (CORAL) using the PUREX process [1–5]. In this process, an irradiated fuel pin is chopped into small pieces, and this fuel matrix is dissolved in 11 M nitric acid under a reflux condition. A dissolved fuel solution contains nitrate complexes of uranium (U), plutonium (Pu), minor actinides (MA) and fission products (FPs) in addition to small quantities of undissolved residues. These residues are intermetallic alloys consisting mainly FPs of palladium, ruthenium, and molybdenum and tiny debris of the clad material. These insoluble residues are removed from the fuel’s solution prior to solvent extraction either by filtering or centrifuging the solution. Then, U and Pu in this solution are selectively extracted into an organic phase leaving FPs, MA in high-level waste (HLW) by liquid–liquid extraction.

Because of a need for the analysis of Pu with high precision and accuracy, several instrumental techniques were employed for analyzing the Pu concentration which are inductively coupled plasma mass spectrometry (ICP-MS) [6, 7], alpha spectrometry [9], energy-dispersive X-ray fluorescence [9] and a coulometry method [10]. These techniques require expensive instrumentation and skilled operators, and these methods generate a large volume of wastes. For determining the Pu concentration by a potentiometric method, several oxidants such as silver oxide and fuming perchloric acid were employed for the oxidation of Pu(IV) to PuO2+. In the presence of fuming perchloric acid, as an oxidant for Pu, the formation of an explosive metal perchlorate due to the reaction of its vapor with the metal surface of exhaust duct cannot be ruled out [11]. However, in the case of silver(II) oxide, there is a potential for the reduction of Ag+ into metallic Ag by Fe2+ due to a lower reduction potential of the Fe3+/Fe2+ (0.76 V) system than Ag+/Ag (0.80 V). During titration, orthophosphoric acid is added to improve endpoint detection. This is because, reduction potential of the Fe3+/Fe2+ system is further lowered in the presence of ortho...
phosphoric acid due to the formation of an iron-phosphate complex [12], which enhances the reduction of Ag⁺ into metallic Ag by Fe²⁺ contributing a positive bias in the Pu concentration value. Hence, a stringent concentration control of AgO and FAS is required to improve the precision of the titration. The sluggish kinetics accompanying with the oxidation of Pu⁴⁺ to PuO₂²⁺ using fuming perchloric acid results in a more radiation exposure to analysts. Owing to the above difficulties with the existing methods, we need to develop a simple, rapid and reliable method for determining the concentration of Pu.

**Experimental**

**Chemicals and reagents**

The chemicals employed for the preparation of reagents and a standard solution were of analytical reagent grade (AR). Exactly, 4 g of sodium hydroxide (Merck, AR) was dissolved in distilled water, made up to 1000 mL. and this solution was standardized by titrating against crystalline potassium hydrogen phthalate (Merck, AR) using phenolphthalein as an indicator. A uranyl nitrate solution was prepared by dissolving uranium oxide powder obtained from Nuclear Fuel Complex (NFC), Hyderabad, in 10 M nitric acid and uranium content in the stock solution was estimated by the redox titrimetric or spectrophotometric method [13, 14]. Sulphamic acid (Loba, AR), sodium nitrite (Merck, AR), ortho phosphoric acid (Merck, AR), ferrous ammonium sulphate (Merck, AR) and potassium dichromate (Merck, AR) were used for preparing required reagents.

**Preparation of plutonium nitrate solution**

The plutonium oxide powder (PuO₂) employed for preparing the stock solution was obtained by the calcination of dried plutonium(IV) oxalate precipitate at 500 °C in a muffle furnace. Extreme care was adhered while handling PuO₂ owing to its high radio toxicity. Hence, a glove box with a negative pressure with a leak rate < 0.1% box vol/h was used for handling solid PuO₂. And weighed quantity of PuO₂ was dissolved in a mixture of 11 M nitric acid and 0.1 M hydrogen fluoride at 85–90 °C in a 100 mL Teflon beaker. A plutonium nitrate solution thus obtained was separated from americium by employing an anion-exchange separation procedure using DOWEX 1 × 8 in a nitric acid medium [15]. The plutonium content in the purified stock solution was determined by a redox titrimetric or direct spectrophotometric method [16], and the initial acidity of a dissolved sample was determined by potentiometric titration without employing complexing agents. [17].

**Instrumental analysis**

Acid–base titration was carried out using a high-resolution and precise Syntronics pH system 361. A pH electrode with a glass membrane and a Ag/AgCl reference electrode were employed. Furthermore, this pH glass electrode system was calibrated with buffer solutions of different pH, i.e., potassium hydrogen phthalate (pH at 4.2), potassium phosphate (pH at 7.0), and a sodium borax solution (pH at 9.0). High-resolution UV–visible spectrophotometer (Ocean Optics USB 4000 model) and an alpha scintillation counter with a ZnS(Ag) detector, supplied by Nucleonix, Hyderabad, were employed for all spectrophotometric and radiometric determinations of Pu, respectively.

**Optimization of quantity of sulphamic acid addition**

Exactly, an aliquot containing a known quantity of Pu was added into a series of titration flasks containing 0.5 mL of HNO₃. Pu in the sample was oxidized to Pu(VI) by adding ceric ammonium nitrate, 1 M (CAN) until the solution mixture became brown in color. A few drops of sodium nitrite (0.01–0.02 M) were added slowly to the solution mixture until the disappearance of the brown color so as to reduce excess ceric(IV) nitrate to cerous(III) nitrate. Different quantities of sulphamic acid (SA) from 0.1–0.6 mmol were added to destroy HNO₃ present in the solution mixture. This solution mixture was then added with 10 mL of sulphuric acid (1 M) containing 0.5 mL orthophosphoric acid (H₃PO₄) followed by the addition of excess FAS consisting fixed milli moles. Unreacted ferrous in the solution mixture was determined by titration with the standard potassium dichromate solution (0.0251 N) using barium diphenyl amine sulphonate (BDS) as an indicator or measuring end-point potential. In blank titration, FAS was titrated against standard potassium dichromate without Pu following the same conditions as described above. Equations (1) and (2) were employed for determining the weight of potassium dichromate required to react with Pu, and its quantity in mg present in the given aliquot, respectively

\[
	ext{Weight of } K_2Cr_2O_7 = \left( W_B - W_T \right)
\]

(1)

\[
\text{Quantity of Pu in aliquot (mg)} = \text{Weight of } K_2Cr_2O_7 \times \text{Normality} \times 119.5
\]

(2)

\( W_B \): weight of \( K_2Cr_2O_7 \) required to react with FAS during blank titration, \( W_T \): weight of \( K_2Cr_2O_7 \) required to react with excess FAS during titration in presence of Pu, and 119.5: Equivalent weight of Pu.
Proposed procedure for determining the concentration of plutonium in the standard solution

Exactly, an aliquot of stock solution consisting Pu in the range of 0.7–2.0 mg was transferred into a series of titration flasks containing 0.5 mL of nitric acid (1 M). To this, a few drops (0.1 mL) of ammonium ceric nitrate at a concentration of 1.0 mol/L were added until the solution mixture became brown, and were stirred well using a magnetic stirrer. With this solution mixture, a few drops of a sodium nitrite solution (0.01 M) were added until de-colorization occurred. Then, this solution mixture was added with 0.5 mL of SA and 10 mL of sulphuric acid (1 M) containing 0.5 mL ortho phosphoric acid (H₃PO₄). It was then followed by the addition of a known volume of a standard solution of excess FAS. The potassium dichromate equivalence requirement for unreacted ferrous in the solution mixture was determined by titration with the standard dichromate solution.

Interference studies from dissolved TBP and uranium

In another set of titrations, nitric acid (4 M) was equilibrated for 10 min with 30% tri-n butyl phosphate to attain saturation in the solubility [18] as well as the equilibrium condition. The concentration of dissolved TBP in pre-equilibrated nitric acid was determined by a spectrophotometric method after converting all organic phosphate to inorganic phosphate by evaporation with per chloric acid [19]. Then, an aliquot containing a known weight of Pu was added into a titration flask containing 0.5 mL nitric acid (1 M). To this, pre-equilibrated nitric acid of various volumes (0.1–0.5 mL) was added and concentration of Pu in this sample was determined as the procedure described above. In another set of experiments, interference studies were performed in the presence of uranyl nitrate in the expected concentration range as found in the nuclear fuel of a fast reactor.

Spectrophotometric determination of stability Pu (VI)

A known volume of aliquot from a Pu(NO₃)₄ stock solution was transferred into a titration flask containing nitric acid (1 M) and mixed with few drops of ceric ammonium nitrate (1 M) until the solution mixture became brown and made up to 5 mL. A portion of this solution was transferred into a cuvette and spectrum was recorded from 400–900 nm with a scan speed of 100 nm/s against a reference solution. In another titration flask containing nitric acid (1 M), a known volume of aliquot from a Pu(NO₃)₄ stock solution was transferred. It was then oxidized to Pu(VI) by adding ceric ammonium nitrate until the solution mixture became brown. This solution mixture was then treated with a few drops of sodium nitrite until decolonization took place, and made up to 5 mL using nitric acid. The UV–visible spectrum was obtained for this solution after the destruction of Ce (IV) using sodium nitrite at a time intervals of 5 and 10 min.

Determination of plutonium concentration in plant samples

A known volume of aliquot containing Pu in the range of 1.0–2.0 mg from the samples received from different process tanks was transferred into a titration flask containing 0.5 mL of 1 M HNO₃. To this, CAN was added slowly with constant stirring until color of solution mixture became brown followed by reducing excess Ce(IV) to Ce(III) using sodium nitrite. The concentration of Pu in this sample was then determined by a procedure described above.

Results and discussion

The term “disproportionation” is defined as the phenomenon of undergoing self-oxidation and self-reduction by the same metal ion having different oxidation states. Since the difference in the reduction potential value of Pu between any two oxidation states from +3 to +6 (+3, +4, +5 and +6) is marginally small, Pu exists in various oxidation states, which are susceptible to undergo disproportionation. Hence, Pu in the PUREX process stream is found to exist in different oxidation states. Therefore, it is necessary to convert the oxidation state of Pu to a single oxidation state before determining its concentration by redox titration. Hence, strong oxidizing agents, such as fuming per chloric acid and silver(II) oxide (AgO), were employed to oxidize all Pu to PuO₂²⁺ [20, 21]. In the present studies, ceric ammonium nitrate was employed for the quantitative oxidation of Pu from its lower oxidation state to PuO₂²⁺. The efficacious management and control of it also depends on the amenability of the resulting analytical wastes with respect to waste management. Cerium is part of the fission product, and its oxide, are being employed for making colored glass [22]. Hence, Cerium(IV) compounds are promising agents for the oxidation of Pu based on the reduction potential of Ce(IV)/Ce(III) couple (1.44 V) [23]. Presence of cerium in analytical alpha bearing wastes does not pose any compatibility issues in the formation of a glass matrix during the radioactive waste management. Hence, radioactivity is highly contained without breaching to the environment from resultant glass matrix obtained after fixing the concentrated analytical wastes.

When a test sample containing Pu was treated with CAN, the oxidation of lower valences of Pu (+3, +4 and +5)
proceeded efficiently and formation of a red–orange color of CAN indicated completion of the oxidation of Pu from a lower oxidation state into Pu(VI). The fading of red orange color upon the addition of sodium nitrite shows that the destruction of excess reagent is completed. As SA is an excellent scavenger of HNO₂, as reaction described by a chemical Eq. (3), SA is employed to destroy the presence of HNO₂ [24] if any exist in the titration mixture.

\[
\text{NH}_2\text{SO}_3\text{H} + \text{HNO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}.
\] (3)

Hence, the effect of the presence of SA on determination of the Pu concentration was studied. The results from Table 1 indicate that SA < 0.3 mmol rendered a positive bias. This reason may be due to an incomplete destruction of NO₂⁻, which oxidizes unreacted excess Fe²⁺ present in the system. And SA of 0.5–0.6 mmol of was optimized, and it was sufficient to destroy HNO₂ or NO₂⁻ present in the reaction mixture.

Since Pu is a nuclear material, choosing analytical methods for determining the Pu concentration in an aliquot containing minimal Pu is preferred (i.e., < 2 mg). Hence, this method was assessed with Pu in the range of 0.7–2.0 mg per aliquot. The results from Table 2 show that the calculated coefficient variation was found to be < 1.0% during the determination of Pu in the above concentration range.

To test the effect of diverse ions, consideration has been given to ions that are likely to be present in the process solutions. Amongst species, dissolved tri-n-butyl phosphate (TBP) and uranium are present in the process solutions resulting from the PUREX process. Hence, the effect of the presence of these species in determining the Pu concentration was investigated on envisaged concentration range. The results are present in Tables 3 and 4 which indicates that presence of dissolved TBP, and U in the concentration range investigated do not interfere upon determining the concentration of Pu.

The reduction potential of the NO₃⁻/NO₂⁻ couple is about 0.92 V, and that of PuO₂²⁺/Pu⁴⁺ is 1.09 V. Based on the value of the potential of NO₃⁻/NO₂⁻, the reduction of PuO₂²⁺ to Pu⁴⁺ by NaNO₂ is thermodynamically feasible, but it is kinetically hindered due to bond cleavage involved during reduction of PuO₂²⁺ to Pu⁴⁺. The reduction of PuO₂²⁺ to Pu⁴⁺ depends on various parameter such as the temperature, time, and the concentration of NO₃⁻, H⁺ and the ferric ion [25]. Because of above-mentioned reasons, the reduction of PuO₂²⁺ to Pu⁴⁺ in the presence of sodium nitrite is insignificant under the titration conditions studied. Hence, NaNO₂ was found to be an appropriate reagent for reducing excess Ce⁴⁺ to Ce³⁺ without affecting [PuO₂²⁺]. To test the effect of the presence of sodium nitrite on the stability of PuO₂²⁺, an experiment was performed to monitor the stability of PuO₂²⁺ at different intervals of time in the presence of sodium nitrite. For this, a sample solution containing a known quantity of Pu was oxidized to PuO₂²⁺ using a CAN solution followed by the destruction of excess Ce(IV) with a sodium nitrite solution. Also, a UV–visible spectrum was recorded for the above solution from 400 to 900 nm against a reference solution containing 0.5 M HNO₃.

The absorbance spectra obtained at different intervals for a solution containing PuO₂²⁺ in the presence of sodium nitrite

| Sl. no | Aliquot weight (g) | Weight of dichromate (g) | Plutonium obtained (mg) | [Pu] × 10⁻² (mol/L) | % Error (±) |
|-------|------------------|--------------------------|------------------------|---------------------|-------------|
| 1     | 0.202            | 0.257                    | 0.771                  | 1.597               | 0.08        |
| 2     | 0.201            | 0.254                    | 0.762                  | 1.586               | 0.77        |
| 3     | 0.201            | 0.255                    | 0.765                  | 1.592               | 0.37        |
| 4     | 0.203            | 0.256                    | 0.768                  | 1.583               | 0.95        |
| 5     | 0.201            | 0.258                    | 0.774                  | 1.611               | 0.81        |
| 6     | 0.500            | 0.632                    | 1.896                  | 1.586               | 0.74        |
| 7     | 0.500            | 0.641                    | 1.923                  | 1.609               | 0.68        |
| 8     | 0.501            | 0.640                    | 1.920                  | 1.603               | 0.34        |
| 9     | 0.501            | 0.641                    | 1.923                  | 1.606               | 0.49        |
| 10    | 0.502            | 0.637                    | 1.911                  | 1.592               | 0.35        |

Σ = 1.597 × 10⁻² ± 0.0001

[Pu] = 1.598 × 10⁻² mol/L (by conventional method)

[Pu] = 1.597 × 10⁻² mol/L (by developed procedure)

Coefficient of variation (CV) = 0.63%
Precise determination of plutonium in nuclear fuel process samples

Table 3 Interference of dissolved TBP on the determination of the concentration of Pu

| Sl. no | Weight of Pu taken (mg) | Amount of dissolved TBP (mg) | Weight of dichromate (g) | Plutonium obtained (mg) | % Difference (±) |
|--------|------------------------|----------------------------|-------------------------|------------------------|-----------------|
| 1      | 1.910                  | 35                        | 0.642                   | 1.892                  | 0.94            |
| 2      | 1.911                  | 70                        | 0.641                   | 1.924                  | 0.68            |
| 3      | 1.910                  | 105                       | 0.640                   | 1.920                  | 0.52            |
| 4      | 1.912                  | 140                       | 0.641                   | 1.922                  | 0.52            |
| 5      | 1.900                  | 175                       | 0.639                   | 1.890                  | 0.53            |

Nitric acid containing dissolved TBP is employed for this study

Table 4 Interference studies with (UO₂)(NO₃)₂ on the determination of the concentration of Pu

| Sl. no | Weight of Pu taken (mg) | U added (mg) | Weight of dichromate (g) | Plutonium obtained (mg) | % Difference |
|--------|------------------------|--------------|-------------------------|------------------------|--------------|
| 1      | 2.000                  | 0.0          | 0.669                   | 2.005                  | 0.25         |
| 2      | 2.003                  | 1.5          | 0.665                   | 1.995                  | 0.40         |
| 3      | 2.001                  | 3.0          | 0.671                   | 2.012                  | 0.55         |
| 4      | 2.002                  | 4.5          | 0.662                   | 1.986                  | 0.80         |
| 5      | 2.001                  | 6.0          | 0.672                   | 2.016                  | 0.75         |

Envisaged ratio of U and Pu in nuclear fuel of FBR composition is 0.75–3.0

solution are given in Fig. 1. It is revealed from Fig. 1 that the presence of excess NaNO₂ employed for the destruction of Ce(IV) has no significant impact on the stability of PuO₂²⁺. When this Pu in PuO₂²⁺ was treated with 20 mL of 1 M H₂SO₄ followed by the addition of known volume of excess FAS, FAS reduced all the PuO₂²⁺ to Pu⁴⁺ as the chemical reaction described in Eq. (4):

\[
\text{PuO}_2^{2+} + 2 \text{Fe}^{2+} + 4 \text{H}^+ \rightarrow \text{Pu}^{4+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O}. \quad (4)
\]

A sulphuric acid medium is preferred during titration. This is because, the presence of sulphuric acid in the titration mixture aids to retain all Pu in the +4-oxidation state which preventing a further reduction of Pu⁴⁺ into Pu³⁺. The potassium dichromate equivalence required for unreacted FAS was obtained by the titration of a reaction mixture against the standard potassium dichromate solution. To validate and address the efficacy of the proposed method, it was applied to determine the concentration of Pu present in real plant samples collected during the reprocessing of spent nuclear fuels. The results of these studies are shown in Table 5, which demonstrates that the proposed method works satisfactorily and the results obtained are in close agreement with standard method.

\[\text{PuO}_2^{2+} + 2 \text{Fe}^{2+} + 4 \text{H}^+ \rightarrow \text{Pu}^{4+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O}. \quad (4)\]

Fig. 1 UV–visible absorbance spectra of PuO₂²⁺ at different intervals of time after reducing excess Ce⁴⁺ by NaNO₂ addition

Conclusion

The redox titration method developed for analysis of the Pu concentration in the present form using CAN as an oxidizing agent provides not only a simple but rapid and accurate method. The interferences from associated species anticipated in the PUREX process stream, such as uranium and dissolved tributyl phosphate, are found to be insignificant. This method can be employed for estimating at as low as 0.7 mg of Pu in the sample aliquot. The method has been applied to nuclear fuel process solutions, and the obtained results have been found to have good precision and accuracy as per the plant specification; these results are in close agreement with values obtained with the conventional Redox titration method.
Acknowledgements The authors are thankful to Smt C.S. Suganya-devi, Smt V. Rekha, Smt C. Shibina, Smt V. Ramya, Smt T. Selvi, and Shri Suresh Borado for their valuable contributions in carrying out the experimental work. The valuable suggestions and guidance of Dr. R.V. Subba Rao, Head, Process & Radio Chemistry Division, Reprocessing Group during preparation of this manuscript are greatly acknowledged.

References

1. R. Natarajan, IANCAS Bull. 14(2), 27 (1998)
2. R. Natarajan, B. Raj, J. Nucl. Sci. Technol. 44(3), 393 (2007)
3. Lanham WB, Runion TC, Purex process for plutonium and uranium recovery. Oak Ridge National Laboratory, Oak Ridge, ORNL 479, (1949)
4. R. Natarajan, V. Vijayakumar, R.V. Subba Rao, N.K. Pandey, J. Radioanal. Nucl. Chem. 304(1), 401 (2015)
5. R. Natarajan, K. Damodaran, P.K. Sharma, S. Pugazhendi, V. Vijayakumar, R.V. Subba Rao, Sep. Sci. Technol. 48, 2494 (2013)
6. R. Balasubramanian, D. Darvin Abert Raj, S. Nalini, M. Sai Baba, Int. J. Nucl. Energy. Sci. Technol. 1, 197 (2005)
7. S. Bera, R. Balasubramanian, A. Datta, R. Saikumar, S. Nalini, T.S. Lakshmi Narasimhan, M.P. Antony, N. Saiyaraman, K. Nagarajan, P.R. Vasudeva Rao, Int. J. Anal. Mass. Spectro. Chromatogr. 1, 55 (2013)
8. S.K. Aggarwal, S.A. Chitambar, V.D. Kavimandan, A.I. Almaula, P.M. Shah, A.R. Parab, V.L. Sant, H.C. Jain, M.V. Ramaniah, Radiochim. Acta. 27, 1 (1980)
9. J. Py, J.E. Groetz, J.C. Hubiniois, D. Cardona, Nucl. Instrum. Methods Phys. Res. Sec A: Accel. Spectrom. Detect. Assoc. Equip. 780, 131 (2015)
10. Sharma MK, Kamat JV, Ambolikar AS, Pillai JS and Aggarwal SK, BARC: /E/001, 2012.
11. Chandra Prakash Singh, Abhishek Singh, Indian J. Mater Sci. 2014, 787306 (2014).
12. O.E. Lanford, S.J. Kiehl A, Am. Chem. Soc. 64(2), 291 (1942)
13. W. Davies, W. Gray, Talanta 11, 1203 (1964)
14. R.V. Subba Rao, K. Dhamodaran, G. Santosh Kumar, T.N. Ravi, J. Radioanal. Nucl. Chem. 246, 433 (2000)
15. K. Akira, K. Hisao, S. Junji, Susumu, J. Nucl. Sci. Technol. 4, 289 (1967)
16. K. Dhamodharan, A. Pius, Determination of plutonium present in highly radioactive irradiated fuel solution by spectrophotometric method. Nucl. Eng. Technol. 48, 727–732 (2016)
17. K. Dhamodharan, P. Anitha, Anal. Sci. 32, 401 (2016)
18. S. Mishra, S. Ganesh, P. Velavendan, N.K. Pandey, C. Mallika, U.K. Mudali, R. Natarajan, Adv. Chem. Eng. Res. 2, 55 (2013)
19. P. Velavendan, S. Ganesh, N.K. Pandey, R. Geetha, M.K. Ahmed, U. Kamachi Mudali, R. Natarajan, J. Radioanal. Nucl. Chem. 295, 1113 (2013)
20. G.R. Waterbury, C.F. Metz, Anal. Chem. 31(7), 1144 (1959)
21. J.L. Drummond, R.A. Grant, Talanta 13, 477 (1966)
22. E.E. Trusova, N.M. Bobkova, V.S. Gurin, N.I. Gorbachuk, Glass Ceram. 64, 9 (2007)
23. A.H. Kunz, J. Am. Chem. Soc. 53(1), 98 (1931)
24. J. Fitzpatrick, T.A. Meyer, M.E. NeillO, D.H. Lyn, Williams J. Chem. Soc, Perkin. Trans. 2, 927 (1984)
25. C.A. Colvin. United States: N 1963. https://doi.org/10.2172/408440