26. Lăstovička, J. (2017), A review of recent progress in trends in the upper atmosphere, J. Atmos. Sol.-Terr. Phys., 163, 2-13.

27. Bremer, J. (2005), Long-term trends in different ionospheric layers, Radio Science Bulletin, 315, 22-32.

28. Cnossen, I. (2012), Climate Change in the Upper Atmosphere, Greenhouse Gases - Emission, Measurement and Management, Dr Guoxiang Liu (Ed.), ISBN: 978-953-51-0323-3, In Tech, Available from: http://www.intechopen.com/books/greenhouse-gases-emission-measurement-and-management/climatechange-in-the-upper-atmosphere.

29. Danilov, A. D. (2012), Changes in the upper atmosphere and ionosphere over the last decades (Review, in Russian), In: http://vestnik.geospace.ru/issues/iss1/article2.pdf.

30. Danilov, A. D. and A. V. Konstantinova (2015), Comparison of trends in parameters of the F2 layer obtained by various authors, Geomagnetism and Aeronomy, 55(4), 457-466.

31. Laštovička, J., A. V. Mikhailov, T. Ulich, J. Bremer, A.G. Elias, N. Ortiz de Adler, V. Jara, R. Abarca del Rio, A. J. Foppiano, E. Ovalle, A. D. Danilov (2006), Long-term trends in foF2: a comparison of various methods, J. Atmos. Solar. Terr. Phys., 68, 1854–1870.

32. Bremer, J. (2008), Long-term trends in the ionospheric E and F1 regions, Annales Geophysicae, 26, 1189–1197, www.ann-geophys.net/26/1189/2008/.

33. Gordiyenko, G. I., V. V. Vodyannikov, A. F. Yakovets and Yu. G. Litvinov (2014), Earth Planets and Space, 66 (125), 1-6, http://www.earth-planets-space.com/content/66/1/125.

34. Wright, J.W., R.W. Knecht, K. Devies (1956), Mannual on ionospheric vertical soundings for the international geophysical year, Prepared at CRPL National Bureau of Standards Boulder, Colorado, USA, in Russian, Ed. by Mednikova N.V., and Shapiro B.S. Moscow-1957, 224 p.

35. Lauter, E. A., G. Entzian (1982), Vinter anomaly 1980/81 as an example of stratomesospheric coupling, Phys. Solariterr., 18, 83-90.

36. Kokourov, V. D. (2003), Minimum frequency of reflections as a climatic characteristic of the upper atmosphere, Geomagnetism and Aeronomy, 43(2), 274-276, in Russian.

37. Clúa de Gonzalez A. L, W. D Gonzalez, S. L. G. Dutra, B. T Tsurutani (1993), Periodic variation in the geomagnetic activity: a study based on the Ap index, J Geophys. Res., 98, 9215.

38. Echer, E., N. R. Rigozo, D. J. R. Nordemann, and L. E. A. Vieira (2004), Prediction of solar activity on the basis of spectral characteristics of sunspot number, Annales Geophysicae, 22, 2239-2243.

39. Prabhakaran Nayar, S. R. (2006), Periodicities in solar activity and their signature in the terrestrial environment, IL WS WORKSHOP, GOA, February 19-24, 9 p.

40. Henry, A. J. (1927), Brückner cycle of climatic oscillations in the united states, Annals of the Association of American Geographers, 17(2), 60-71.

41. Raspopov, O. M., O. I. Shumilov, E. A. Kasatkina, E. Turunen, M. Lindholm (2000), 35-year climatic Bruckner cycle-solar control of climate variability, Proc. 1st Solar and Space Weather Euroconference "The Solar Cycle and Terrestrial Climate", Santa Cruz de Tenerife, Tenerife, Spain, 25-29 September 2000 (ESA SP-463, December 2000).

42. Lăstovička, J. and Bremer J. (2004), An overview of long-term trends in the lower ionosphere below 120 km, Surv. Geophys., 25, 69-99.

DETERMINATION OF LANTHANIDES AND 3D METALS IN ENDOMETALLOFULLERENES WATER SOLUTIONS BY X-RAY FLUORESCENCE SPECTROMETRY

Zinovyev V. G.,.Lebedev V.T,
Mitropolsky I. A.,. Shulyak G. I,
Sushkov P. A.,. Tyukavina T. M,
Okunev I. S.,. Ershov K.V, Balin D.V.
Petersburg Nuclear Physics Institute named by B.P.Konstantinov of
NRC «Kurchatov Institute»

ABSTRACT

An XRF method was developed for determination of Fe, Co, Ni, Mn, Mo, Sc, Gd, Tb and Pr in endofullerenes. The synthesis of endofullerenes was carried out in a direct current arc in helium medium. The content of endofullerenes of 3d metals in the soot was increased by introduction of two graphite electrodes made of phthalocyanine of 3d metals and lanthanides into the arc. The extraction of endofullerenes of 3d metals and lanthanides by N,N dimethylformamide in presence of 0.2% vol. hydrazine hydrate has increased the yield of endo-fullerenes of lanthanides and 3d metals by 2–3 times. The hydroxylation of endofullerenes of 3d metals obtained from the fullerene dimethylformamide extract was carried out with concentrated H_2O_2. It was established that the yield of the water-soluble endofullerene product depends on concentration of H_2O_2 in the solution and duration of the process.

Keywords: Fullerenes, X-ray fluorescence analysis, extraction

The endofullerenes of 3d-metals and lanthanides can be used for medical purposes: for NMR tomography and for magnetically controlled delivery of drugs to the diseased organ. The endofullerenes are used in drugs for treatment of neurodegenerative diseases such as Alzheimer disease, Parkinsonism and others. Usually, endofullerenes are produced by arc or

plasma evaporation of graphite electrodes containing a metal source in an inert gas atmosphere [1], [2].

The fullerenes of Iron are produced in a plasma-chemical reactor with a high-frequency arc between graphite electrode filled with $Fe(CO)_5$ powder [3]. The Carbon condensate is extracted by benzene or toluene, and the solvent is evaporated to obtain the product. In this case, the product consists of exohedral fullerenes with trace amounts of endohedral ones. Microscopic amounts of Fe endofullerenes were obtained by ion implantation when a thin film of C_{60} was bombarded with a beam of Fe^+ ions [4]. The endohedral fullerenes $Fe@C_{60}$ are produced in helium at 50 mm Hg pressure by introducing Iron pentacarbonyl vapors $Fe(CO)_5$ into the electric arc of a graphite electrode [5]. Fullerenes are obtained by extracting for 3 hours with toluene in Soxhlet extractor. is used to purify The empty C_{60} fullerenes are removed by means of liquid column chromatography. In the electric arc evaporation, the endofullerenes are produced as insignificant impurities in the mixture of empty fullerenes C_{60} and C_{70}. The metal-carbon bonds formed in the electric arc and in plasma are weak and exist during a too short time, insufficient for formation of endofullerenes [6]. In addition, the low solubility of fullerenes in toluene, 2 mg/ml does not ensure the complete extraction of endofullerenes from the soot [7]. Therefore, it is impossible to obtain water-soluble derivatives of endofullerenes by these methods.

It is known that in pyrolysis of metal-containing compounds, such as phthalocyanine of 3d-metals and lanthanides $C_{32}H_{12}N_8Me$ (Me = Fe, Sc, Ni, Pr, Gd, Tb), the fullerenes are not formed [8]. The endofullerenes of 3d-metals were synthesized for the first time at PNPI in the process of electric arc evaporation of graphite electrodes containing an additive of phthalocyanine pyrolysate of f 3d-metal and Ln in Helium media. The methods of production of endofullerenes of 3d-metals and lanthanides have been described in three patents [9], [10], [11], [12] developed at PNPI in the laboratory for neutronic physicochemical studies. In the above methods, the content of endofullerenes of 3d metals in the soot was increased by introducing two graphite electrodes of phthalocyanine 3d metals and lanthanides into the arc of direct current. The extraction of 3d endofullerenes of metals and lanthanides with N,N-dimethylformamide (DMF) in presence of 0.2% vol. hydrazine hydrate has increased the yield of EDF lanthanides and 3d metals by 2–3 times. The hydroxylation of endofullerenes of 3d metals produced from the dimethylformamide extract of fullerenes has been performed with concentrated H_2O_2 at the rate of 20 mg of fullerenes per ml of H_2O_2 [12]. It was recognized that the yield of the water-soluble product

of lanthanide endofullerenes depends on the concentration of H_2O_2 in the solution and on the process duration. The highest yields were achieved at hydrogen peroxide concentration of 15–22% with the hydroxylation process duration of 5–20 hours. The decrease in the yield of hydroxylated endofullerenes of lanthanides at higher concentrations of H_2O_2 and with at longer duration of the procedure occurs due to the destruction of fullerenes by their oxidation. These methods were used to obtain aqueous solutions of paramagnetic endofullerenols of rare earth elements M @ C_{2n} (OH) $_{38-40}$, M = Gd, Tb, Pr, and 3d metals M = Fe, Sc, Co, Ni, Mn, Mo.

To control the concentration of 3d-metals and lanthanides in the solution, an X-ray fluorescence analysis method has been developed. The solutions were analyzed with the X-ray spectrometer consisting of the PGT1000-13 detector (GmbH) with the energy resolution of 200 eV at Kα line of Fe 6.4 eV and the Ortec spectrometric system. The X-ray source XCd9.233 based on ^{109}Cd (0.36 GBq) and the sealed gamma-source IGIA-5m-1 with ^{241}Am (8.3 10^{10} Bq) were used as the external sources of excitation of x-ray emission of the samples under study.

The method of concentration measurement of Gd, Tb, Pr, Fe, Sc, Co, Ni, Mn, Mo in aqueous solutions of $M@C_{2n}(OH)_{38-40}$. The aqueous solutions of paramagnetic endofullerenols of rare earth elements and lanthanides in the amount of 4–6 ml were evaporated in a weighting cup when heated under a mercury lamp to a volume of 100–300 µL. Then, using a microbatcher, the solution was transferred onto a polyethylene terephthalate (PET) film 10 µm thick, mounted on a ring holder. The sample solutions on the film were dried under a mercury lamp. An annular holder with the film and the dried sample on it was mounted on the X-ray spectrometer detector. The distance between the sample and the detector was 2 cm. The registration time of the spectra was 2 hours.

The standard solutions were prepared by dissolving the salts, oxides, or metal weights of the studied elements of analytical grade in distilled water or concentrated acids. The concentrations of the detected elements in the prepared standard solutions were in the range from 0.3 to 2 mg/ml. To plot the calibration graphs, the aliquots of standard solutions with volumes of 0.5–600 µL were applied to the film, dried, and then the X-ray spectra of the standard samples were recorded. The calibration plots in coordinates of the intensity of analytical X-ray radiation vs. the mass of the element in an aliquot of a standard solution taken for analysis are presented in **Figures 1** and **2**.
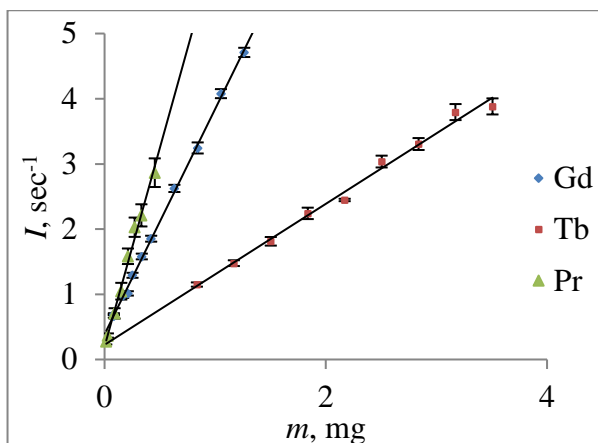
Fig. 1. Calibration plot for determination of Me = Gd, Tb, Pr in an aqueous solution of the sample Me @ $C_{2n}(OH)_{38-40}$.
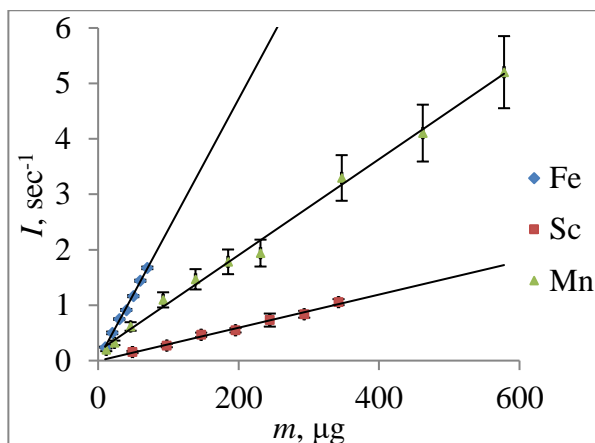

Fig. 2. Calibration plot for determination of Me = Fe, Sc, Mn in an aqueous solution of the sample Me @ $C_{2n}(OH)_{38-40}$.

The fragments of the X-ray spectra of standard solutions, registered for the calibration plot, and the spectra of the samples under study are shown in **Figures 3–6**.
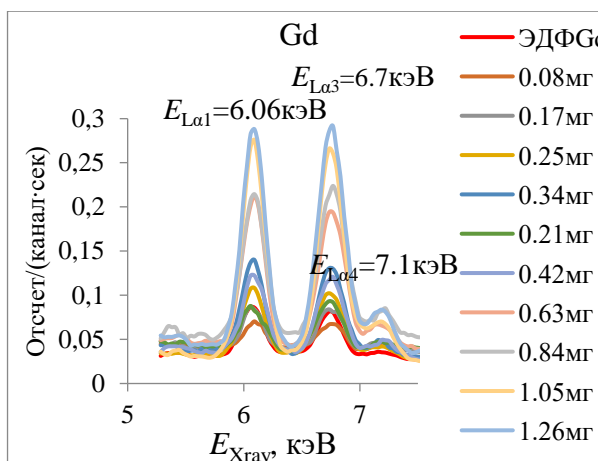

Fig. 3. Fragments of X-ray spectra of aliquots of the standard Gd solution, $C_{Gd} = 2.10$ mg/ml. The volume of the sample taken for analysis was 4 ml.
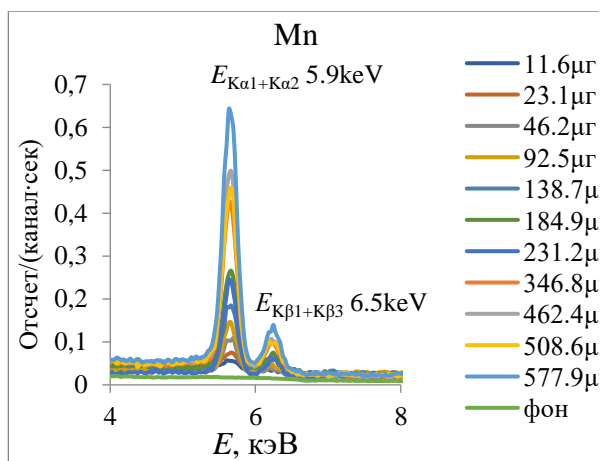

Fig. 4. Fragments of the X-ray spectra of standard solutions Mn, $C_{Mn} = 23.12$ mg/ml. The volume of the sample taken for analysis was 4 ml.
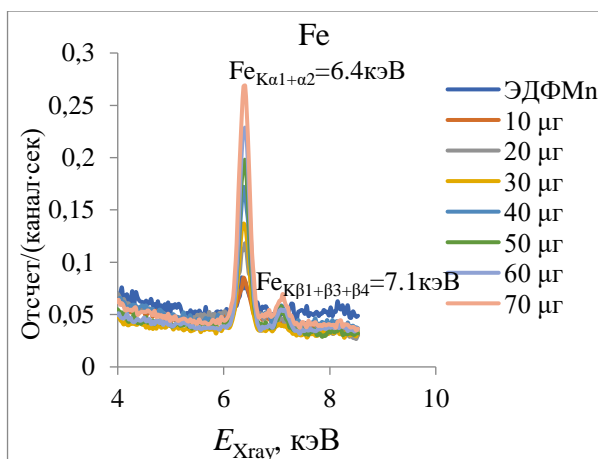

Fig. 5. Fragments of X-ray spectra of aliquots of standard Fe solution (GSO 7835-2000). The sample volume was 4 ml.
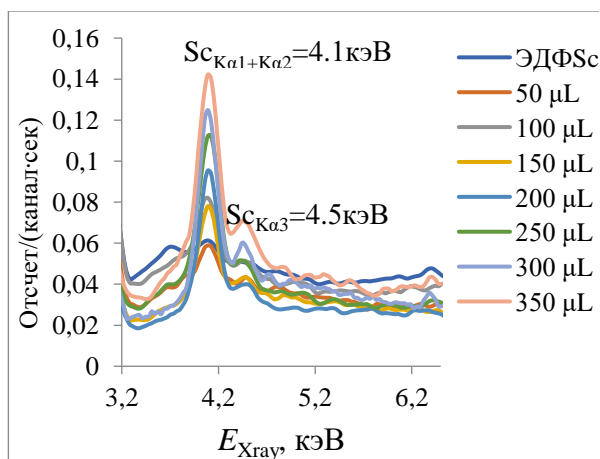

Fig. 6. Fragments of the X-ray spectra of standard solutions of Sc ($C_{Sc} = 0.98$ mg/ml) and of the sample. The sample volume was 6 ml.

The contents of Gd, Fe, Sc, Tb, Pr, Mn in aqueous solutions of endofullerenols measured with the developed technique and the detection limits are presented in **Table 1**.

Table 1

CONCENTRATIONS OF GD, FE, SC, TB, PR, MN IN AQUEOS SOLUTIONS OF ENDOFULLERENOLS.

Element	Sample	C, µg/ml	*Detection limit*, µg
Gd	$Gd@C_{2n}(OH)_{38-40}$	47.9±2	1
Fe	$Fe@C_{2n}(OH)_{38-40}$	2.6±0.1	1
Sc	$Sc@C_{2n}(OH)_{38-40}$	13.8±0.6	0.1
Tb	$Tb@C_{2n}(OH)_{38-40}$	14.7±0.6	0.1
Pr	$Pr@C_{2n}(OH)_{38-40}$		0.1
Mn	$Mn@C_{2n}(OH)_{38-40}$	1.7±0.1	0.1
Mn Gd	$Mn,Gd@C_{2n}(OH)_{38-40}$	3.6±1.4 34±14	0.1 0.1

The concentration of the element to be determined in the sample was calculated by the formula $C = \frac{I_{sam} \cdot CF_{sam}}{K}$,where I_{sam} is the counting rate in the analytical peak of the element to be determined in the X-ray spectrum of the sample under study; $K = \frac{(I_{st} - \Delta I) \cdot CF_{st}}{C_{st}}$ is the tangent of the slope of the calibration curve in the coordinates $I_{st} = f(C_{st})$; ΔI is the segment cut off by the calibration curve from the ordinate axis; $CF = \frac{-\ln\alpha}{1-\alpha}$ is the correction factor for the attenuation of radiation in the substance; $\alpha = exp\left[-\left(\frac{\mu_\gamma}{\cos\phi} + \mu_X\right)L\right]$ is the transmittance of the excitation and analytical x-ray radiation; μ_γ, μ_X — are the linear attenuation factors for the external exciting and the analytical X-ray radiation, cm^{-1}; L– the sample thickness; ϕ is the angle of incidence of the exciting radiation.

The transmittance of the excitation and secondary x-rays in the sample was used for experimental measurement of α according to the method described in [13]. In this method, the foil from the element being measured was placed behind the sample and the intensity of the secondary X-ray radiation of the element being determined was measured in presence and in absence of the sample. Then the x-ray spectrum of the sample without foil was recorded. The value of α was calculated as $\alpha = \frac{I_T - I_S}{I_0}$, where I_T is the intensity of the secondary x-ray radiation with the foil and the sample; I_S is the intensity of the secondary x-ray radiation with the sample; I_0 is the intensity of the secondary x-rays with the foil.

The dependences of the factors α and CF on thickness of the samples and the standards are shown in Figures 7 and 8. The experimentally measured values of CF for Gd(NO$_3$)$_3$ ($\square$), Fe(NO$_3$)$_3$ ($\lozenge$), ScCl$_3$·3(H$_2$O) (Δ), KMnO$_4$ ($\circ$) are shown in the **Figure 8**.

Fig. 7. Dependence of the factor α on the thicknesses of the samples and the standards.

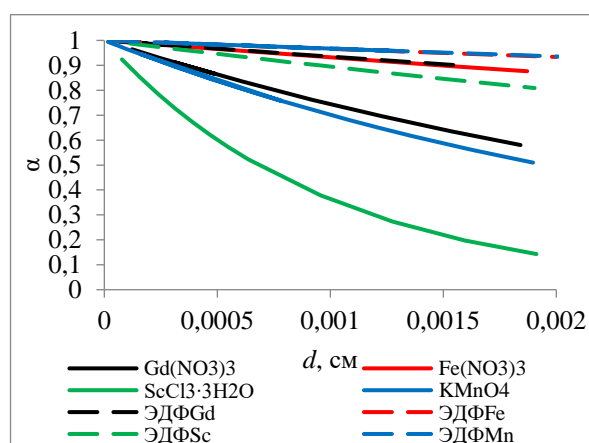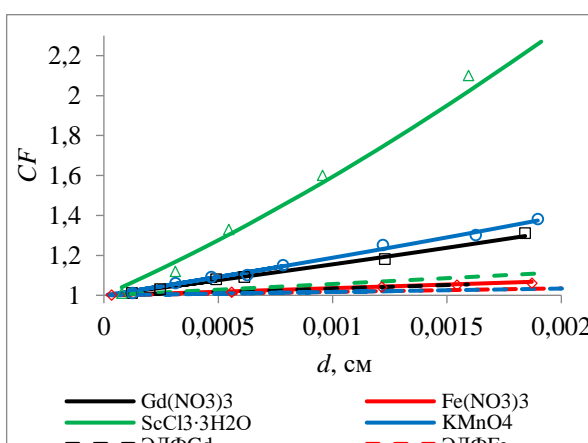*Fig. 8. Dependence of the factor CF on the thicknesses of samples and the standards.*

The detection limit DL is the lowest content at which, using this method, it is possible to detect the presence of a component at given confidence level determined by the expression $DL = \frac{2\sqrt{S_{bg}}}{K \cdot t_{bg}}$, where S_{bg} is the count in the background spectrum in the area of the analytical peak; K is the slope of the calibration curve; t is the spectrum recording time.

Bibliography

[1] Kratschmer W., Lamb L.D., Fostiropoulos K., and Huffman D. R., "Solid C60: A New Form of Carbon," // Nature, Vol. 347, No. 6291, 1990. pp. 354-358.

[2] Gerasimov V.I., "One-stage plasma-arc synthesis of metal endofullerenes," // Journal of Applied Chemistry, T. 80, No. 11, 2007. P. 1864-1869.

[3] Churilov G.H., "Obtaining and investigation of iron-containing fullerene complexes," // Journal of Technical Physics, Vol. 67, No. 8, 1997. P. 142-144.

[4] Minezaki H., Ishihara S., and Uchida T., "Synthesis of endohedral iron-fullerenes by ion implantation.," // The Review of scientific instruments, Vol. 85, No. 2, Feb 2014. P. 02A945.

[5] Pradeep, T., Kulkarni, G.U., and Kannan K.R., "A novel iron fullerene (FeC60) adduct in the solid state," // J. Am. Chem. Soc., Vol. 114, No. 6, 1992. pp. 2272-2273.

[6] Deng Q., "Self-assembly of the endohedral metallofullerenes: a decisive role of gas and carbon bonding," // Nanoscale, Vol. 8, No. 6, 2016. pp. 3796-3808.

[7] Bezmelnitsyn V.H., Eletsky A.V., Okun M.V., "Fullerenes in solutions," // Uspekhi Fizicheskikh Nauk, Vol.. 168, No. 11, 1998. p. 1195-1220.

[8] Klinke S., Kern K., "Iron nanoparticle formation in a metal-organic matrix: from ripening to gluttony," // Nanotechnology, Vol. 18, No. 21, 2007. pp. P215601 / 1-215601 / 4.

[9] Grushko Yu.S. et al., "Method for the preparation of MRI-contrasting agent," IPC C01B 31/00; A61K 49/06; C01F 17/00 2396207, Oct 27, 2010.

[10] Sedov V.P. et al, "Method for the production of water-soluble hydroxylated derivatives of endometallofullerenes lanthanides," C1 2659972, Jul 04, 2018.

[11] Sedov V.P., et al., "Method for the production of endofullerenes of 3d metals," C1 2664133, Aug 15, 2018.

[12] Grushko Yu.S. et al., "Method for obtaining an MRI-contrast agent," IPC C01B 31/00; A61K 49/06; C01F 17/00 2396207, Aug 10, 2010.

[13] D. Reilly, N. Ensslin, H. Smith, Jr. and S. Kreiner. Passive Nondestructive Assay of Nuclear Materials. (Washington, U.S. Nuclear Regulatory Commission, 1991) 700 p. (ISBN 0-16-032724-5)

КЛУМБОВЫЙ ЧЕТЫРЁХУГОЛЬНИК В РАЗЛИЧНЫХ ПРЕДСТАВЛЕНИЯХ

Малышев И.Г.
Нижегородский институт развития образования, доцент

"FLOWERBED-LIKE" QUADRILATERAL IN VARIOUS REPRESENTATIONS

Malyshev I.G.
Nizhny Novgorod Institute of the Education Development, Associate Professor

АННОТАЦИЯ

В статье рассматриваются свойства вписанного и одновременно описанного четырёхугольника, названного клумбовым. Показано, что наиболее продуктивным для их описания является использование углов четырёхугольника в качестве параметров. Это существенно упрощает многие формулы, позволяет получить новые и выводит описание четырёхугольников на новый уровень понимания.

ANNOTATION

Features of the circumscribed and at the same time inscribed quadrilateral, also known as bicentric or "flowerbed-like" quadrilateral, are analyzed in the article. It is shown that the most productive for their description is the usage of quadrangle angles as parameters. This greatly simplifies many formulas, allows to get new ones and takes the description of quadrangles at new level of understanding.

Ключевые слова: четырёхугольник, вписанная окружность, описанная окружность, вневписанная окружность, отрезки Брианшона

Keywords: Quadrilateral, incircle, circumcircle, excircle, Brianchon's segments

Среди различных видов четырёхугольников встречается четырёхугольник, который вписан в окружность и в который вписана окружность. На рис. 1 представлен такой четырёхугольник.

Судя по Википедии, у этого четырёхугольника оказалось много названий. Например, вписано-описанные четырёхугольники, бицентрические четырёхугольники (Bicentric quadrilateral), хордо-касающиеся четырёхугольники (chord-tangent quadrilateral), двух-окружностные четырёхугольники (double circle quadrilateral). В российской литературе по элементарной геометрии он нигде серьёзно не представлен, поэтому и названия не получил.