REVIEW

On a competition to occupy academic position of Associate Professor
Professional field: 4.2. Chemical Sciences
Scientific specialty: 01.05.16 Chemical Kinetics and Catalysis
Requesting laboratory: Design and Characterization of Catalytic Materials
Thematic area: EPR spectroscopy and quality of life
Announcement: State Gazette No. 77, 1 October 2019
Reviewer: Prof. Sonia Damyanova Ivanova, DSc
Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria

Chief Assistant Professor Katerina Ivanova Aleksieva, PhD, an employee at Laboratory for Design and Characterization of Catalytic Materials of Institute of Catalysis (IC) of the Bulgarian Academy of Sciences (BAS), is a sole applicant.

Brief biographical data

Katerina Ivanova Aleksieva received her Master's Degree in 2001 from the Faculty of Chemistry at St. Kliment Ohridski University of Sofia. In 2002, she joined Institute of Catalysis as a research chemist. In 2009, she defended her dissertation on the topic: EPR spectroscopy capabilities to identify high-energy irradiated food of plant origin, and obtained an educational and scientific degree Doctor. Since 2011, Dr. Katerina Aleksieva has been Chief Assistant Professor. The candidate is a member of the Bulgarian EPR Society and the Bulgarian Catalysis Society. She possesses good skills in organizing international conferences on EPR as well as certificates for participation in various lecture courses.

Description of submitted materials

Chief Assistant Professor Dr. Katerina Aleksieva has presented all the necessary documents for participation in the announced competition: application form, copy of the announcement in State Gazette of 01.10.2019, diploma for educational and scientific degree Doctor, certificate for work experience in the specialty and for academic post of Chief Assistant Professor, reference for meeting the criteria under Article 4. The following documents are also presented: lists and reprints of scientific works for both the entire scientific period (2002–2019) and the competitive period (2007–2019); author's reference for scientific contributions of habilitation and non-habilitation works; a list of all citations; a list of citations of works submitted for participation in the competition; lists for participation in national and international scientific forums, projects, and expert activity; and certificates and popular science publications.

– Scientific publications. Throughout the scientific period, 32 publications were presented, 26 of which are in impact factor journals. The candidate participates with 27 publications including one review, of which 22 scientific papers are in impact factor journals: 6(Q1) [3, 4, 6, 12, 14, 21]; 4(Q2) [7, 17, 23, 24]; 7(Q3) [8, 9, 15, 18, 19, 22, 25], and 5(Q4) [13, 16, 20, 26, 27]. Chief Assistant Professor K. Aleksieva is the first co-author and has been mentioned as the author for correspondence in 11 of the publications. The total number of quotes noted on the works until submission of the documents is 166, and the number on the entries in the competition is 87. The candidate's Hirsch Index is 8.

According to the information provided for the fulfilment of the minimum national and additional requirements of the IC for the occupation of the academic position of Associate Professor Dr. Katerina Aleksieva has met all the requirements, even if they are significantly inflated.

– Research projects. For the period 2009–2019, Dr. K. Aleksieva participated in working groups of 10 projects, of which she is the head of three. The projects have been supported by Bulgarian National Science Fund (4); World Federation of Scientists under Operational Program Human Resources Development: Creation of highly qualified specialists in modern environmental materials: from design to innovation; BAS equivalent non-currency exchange based projects: Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, and Institute of Chemical Physics, Russian Academy of Sciences, Moscow. The applicant's involvement in these projects is evidence that she is a desirable partner, given her expertise in the field of EPR spectroscopy.

– Participation in national and international scientific forums. During the competition period, 25 of the total 29 participations in scientific forums were registered where the candidate presented poster and oral reports, which is a sign of the ability of Chief Assistant Professor K. Aleksieva to communicate and discuss her findings with the scientific community.

Main scientific and applied contributions of the applicant

According to the presented scientific works reporting the habilitation period [3, 4, 6, 8, 12, 19, 21], it can be concluded that the main scientific contributions are in the field of identification of gamma-irradiated food products and drugs by the method of EPR spectroscopy, which is one of the principal topics of EPR laboratory at IC. As is known, radiation treatment preserves the taste of the product, minimizes energy consumption, and does not pollute the environment resulting in the need to develop appropriate analytical techniques for distinguishing between irradiated and non-irradiated foods and drugs.

The purpose of the applicant's research is to improve existing standards in the European Union and this country (10 in total, three of which use EPR spectroscopy) as well as to develop new ones using EPR spectroscopy as a leading method for identifying radiation-treated foods and drugs through the presence of free radicals induced by gamma rays. Due to the detailed scientific background on Dr. Aleksieva's research and contributions, I would like to briefly introduce some of them in this area.

– New developments have been introduced that extend the scope of the European Standards EN 1787 and EN 13708 for irradiated foods. Different procedures for sample treatment (so-called sample preparation) of fresh fruits (fleshy part) before and after irradiation have been applied [3]. In order to separate water, two types of fresh fruit drying were used: washing the sample with ethyl alcohol followed by drying at room temperature and drying the sample in an oven to 40°C. For all samples after irradiation, a so-called ‘cellulose-like’ EPR spectrum has been registered due to the generation of free radicals in cellulose. This ‘cellulose-like’ spectrum is included in European Commission Standard EN 1787. The kinetic behaviour of the radiation-induced signals for a period of 50 days after irradiation was also monitored. It has been shown that in fresh fruits stored in their natural state after irradiation and dried under both procedures before EPR measurement, satellite lines can be recorded for no more than 17 days.

– The applicant has investigated irradiation treatment of commercially available juices of various fruits, nectars, and syrups, and of homemade juices to which the sampling procedures mentioned above were applied. A method for determining the fruit content of fruit juices has been developed [12]. The ‘cellulose-like’ EPR spectrum and spectra of added preservatives for juices of 25, 40, and 50% fruit content were recorded. For juices with a fruit content of 100%, only the ‘cellulose-like’ spectrum is registered, which is a consequence of missing sugars and preservatives. In concentrated syrups a typical ‘sugar-like’ EPR spectrum ascribed to saccharide-generated free radicals has been recorded, which is set out in European

Commission Standard EN 13708.

– It is established which part of the fruit should be sampled for analysis in identifying the irradiation of air-dehydrated dates, plums, and figs [19]. ‘Sugar-like’ EPR spectra were recorded in air-dehydrated dates, which is evidence of radiation treatment regardless of which part of the fruit was taken. For irradiated plums and figs ‘cellulose-like’ and ‘sugar-like’ EPR spectra are observed, respectively, and it is recommended to sample plum pits and figs from the fleshy part of the fruit. According to the protocols of the European Union, Protocol EN 13708 is applicable to irradiated dry dates and figs, and Protocol 1787 to dried prunes.

– The most commonly used drug excipients in the pharmaceutical industry were investigated using EPR spectroscopy [8], since the compatibility of the excipients (90–98% of the tablet weight) and the active substances (2–10%) is important for product stabilization. For example, after lactose, microcrystalline cellulose, and starch irradiation, EPR spectra typical of carbohydrates have been registered. While a slight symmetric signal is observed in silica (aerosil), the talc exhibits a sextet spectrum due to impurities of Mn^{2+} ions, which is the same before and after radiation treatment. With the exception of lactose, free radicals with a life span of up to 100 days after radiation treatment were detected, while in lactose the signal was stable over time.

– A link has been established between foods of plant origin and medicines by EPR analysis of herbal tablets [6]. Two groups of signals were observed with the tablets: free radicals due to saccharides used as excipients and a mixture of free radicals in the herb and inulin used as excipient. It is important to note that after irradiation the free radicals of the various saccharides are stable for more than 90 days.

According to the presented works of Dr. K. Aleksieva that are not included in the habilitation treatise it is seen that the scientific and applied contributions are grouped in three main directions.

1. Identification of gamma-irradiated foods and drugs by the EPR spectroscopy method

Chief Assistant Professor K. Aleksieva works in this direction, which is a continuation of the contribution nature of the works included in the habilitation report. The subject of the study are lyophilized products obtained after freeze-drying, which is a method of qualitative preservation of highly perishable products that retain their nutritional properties. However, some microscopic fungi and yeasts or spores of bacteria may exhibit a higher resistance to thermal and technological treatment and survive after lyophilisation. Thus, the interest is the ability to combine this technology with gamma sterilisation. Due to the detailed reference to the contribution nature of the research (total number of 12 works), I will briefly outline the main scientific and applied contributions of the applicant below.

– Lyophilised forest fruits [9] have been investigated by means of EPR, whereby only a single line whose intensity increased after irradiation was recorded. However, in the lyophilised blueberry, in addition to the central singlet line, six lines are observed due to the presence of Mn^{2+} ions. The intensity of the singlet signal was found to increase with the radiation dose, while the intensity of the manganese lines remained constant. Because the manganese spectrum is radiation-insensitive in lyophilised blueberries, it has been used as an internal standard for demonstrating radiation treatment, i.e. the Mn^{2+}/singlet line intensity ratio is taken as the standard of proof for radiation treatment. It is important to note that this approach is not laid down in the protocols of the European Commission for Standardisation, but was developed mainly by the applicant.

– Alcohol washing has been found to be the best method of preparing goji berry samples [24] to prove irradiation, which is possible within 50 days [24]. EPR analysis of goji berries shows that increasing the radiation dose to 10 kGy leads to an improvement in the antiradical (antioxidant) activity of the samples.

– The effect of different doses of gamma irradiation (10 and 25 kGy) on the lipid profile and oxidative stability of hazelnuts and peanuts [26, 27], expressed by the difference between the EPR spectra of irradiated samples for the two doses, has been investigated. It was found that the hazelnuts did not show a significant difference in the EPR spectra as well as in the kinetic behaviour of the central and satellite lines with the two doses. Radiation treatment has been shown to have no effect on the fat and fatty acid content and oxidative power of irradiated hazelnut oils. For peanuts, the results obtained are similar to those of hazelnuts.

– We compared the advantages and disadvantages of EPR spectroscopy for the identification of gamma-irradiated foods with the methods of direct epifluorescence filtering technique (DEFT) [1, 2] and DNA electrophoresis [9]. As the European Community standards EN 13783 and EN13784 for these two methods are screening, i.e. the results must be confirmed by other methods including: EPR spectroscopy. EPR spectroscopy was applied to investigate irradiated meat containing bone. The EPR method registers an asymmetric signal with two g factors attributed to irradiation-generated CO_3, CO_3^{3-} or CO_2 free radicals in calcium hydroxyapatite, which according to EN 1786 is evidence of radiation treatment. DEFT and DNA electrophoresis are methods with very low sensitivity.

– Irradiated homeopathic herbal and animal medicines were investigated using EPR spectroscopy showing a typical spectrum of sucrose used as an excipient [16]. For irradiated galantamine and cytisine, a typical spectrum of lactose used as an excipient has been reported [18]. In grandmother's teeth, the same EPR spectrum was observed before and after radiation treatment, i.e. a wide singlet line due to the presence of iron oxide clusters used to colour film coating of tablets.

2. EPR study of lignocellulosic waste materials as biosorbents of metals for water treatment [10, 15, 17, 22, 25].

In order to utilize waste hydrolysed lignin obtained from the preparation of bioethanol from plant materials, it can be used as a bioadsorbent for metal ions and organic compounds contaminating waste and natural waters. Based on the presence of different functional groups on the surface of lignin and the possibility of exchange reactions with the surface groups, using the EPR method Chief Assistant Professor K. Aleksieva was able to successfully study the adsorption of various metal ions that pollute the water:

– The adsorption of Cu^{2+} ions with samples of hydrolysed lignin and alkaline-treated hydrolysed lignin obtained from wheat straw and maize stalks was investigated [10]. The EPR spectra have been found to have parameters characterizing Cu^{2+} complexes, and in addition, a singlet line due to free radicals was also detected. It is concluded that the Cu^{2+} ions on the lignin surface are located at a considerable distance from each other.

– The adsorption of Mn^{2+} ions in hydrolysed lignocellulosic materials and alkaline-treated hydrolysed lignin was investigated [15]. The recorded EPR spectrum, consisting of six superfine lines characteristic of Mn^{2+} ions, again confirms that there is no interaction between them on the surface of the above-mentioned materials.

– The adsorption properties of silver ions (Ag^+) on lignocellulosic materialя obtained from willow, strawp and maize stems [17] as well as white poplar and white acacia [22] have been investigated. By means of EPR and X-ray photoelectron spectroscopy, the complex nature of Ag^+ ion adsorption on hydrolysed lignocellulosic materials was established, which undergoes several stages until the formation of metallic silver clusters. These findings are also confirmed by the high antibacterial properties of silver-doped lignocellulosic materials [25].

3. EPR determination of the oxidation state of paramagnetic ions in catalytic materials

By means of EPR the oxidation and coordination state of paramagnetic ions in catalytic materials have been determined, which is important for establishing the relationship between the electronic structure of catalysts and their behaviour in a number of catalytic processes. The oxidation state of palladium and cobalt in $PdCo/Al_2O_3$ catalysts for complete oxidation of methane [14], two-phase CuO-NiO samples for CO oxidation, and lanthana and ceria for decomposition of nitric oxide were determined. By calculating EPR parameters like linewidth, g factor, and resonance displacement, the active forms of the catalysts for the decomposition of various molecules that are environmental pollutants have been determined.

– Investigating the dependence of the EPR parameters for monometallic and bimetallic PdCo catalysts on temperature, it was found that the active form of the promoted Co catalyst with Pd are PdO clusters, which are sources of oxygen upon complete oxidation of methane.

– By means of EPR a wide singlet line of uniform linewidth for mixed CuO-NiO catalysts synthesized by co-precipitation of solutions of their salts, followed by mechanical treatment and treatment at different temperatures [20] that proves the formation of solid solutions from the CuO and NiO phases as confirmed by X-ray analysis.

– Using EPR alumina-supported CeO_2 or La_2O_3 have been characterized before and after the catalytic reaction of NO decomposition in the presence or absence of CO as reducing agent [23]. Comparing the EPR signals of the lanthanum-containing catalysts before and after the reaction, it was found that the intensity of the EPR singlet of the spent catalyst is higher, which is attributed to the presence of a higher concentration of La^{2+} ions of cubic or trigonal symmetry. In the case of ceria-containing catalyst, the presence of Ce^{3+} ions in trigonal environment was observed in the EPR spectrum accompanied by traces of Mn^{2+} ions, which provide the formation of oxygen vacancies, O^{2-}.

Conclusion

The scientific contributions of Chief Assistant Professor Katerina Ivanova Aleksieva have largely applied character mainly related to developing suitable methods for the study of irradiated foods and medicines by means of EPR spectroscopy. She has made an outstanding contribution to the development of EPR spectroscopy at EPR Laboratory of IC-BAS. She is also actively involved in EPR application to identify the oxidation and coordination state of a number of metal components in catalysts used for environmental catalytic reactions. The candidate has successfully applied EPR spectroscopy also in determining the adsorption of various metal ions in contaminated water using lignocellulosic waste materials as biosorbents.

Dr. Katerina Aleksieva's works are pioneering not only in Bulgaria but also at the world level as her scientific developments not only extend the scope of European standards EN1787 and EN13708 for irradiated foods, but also upgrade them. New approaches have been developed for the registration of foodstuffs subjected to radiation treatment, which are not included in the protocols of the European Commission for Standardization. For the first time, EPR analysis in food has been expanded from dry sampling to fresh sampling. For the first time, some types of foods and drugs have been investigated to identify their radiation treatment.

I know personally Chief Assistant Professor Katerina Aleksieva from her employment at the Institute of Catalysis characterized by her modesty, hard work, and thoroughness in her research work, which is a prerequisite for her excellence. She shows exceptional ability to work in a team with her own contribution and ideas. By volume and quality all science-metric indicators of Dr. Aleksieva not only meet, but also exceed significantly the recommended requirements for occupying the academic position of Associate Professor in accordance with

Rules on the Terms and Conditions for Acquisition of Academic Degrees and Occupation of Academic Positions at IC-BAS.

On the basis of aforementioned, I recommend with pleasure the honorable members of the Scientific Jury at Institute of Catalysis of the Bulgarian Academy of Sciences and the Honorable Scientific Council of the Institute of Catalysis to award to Chief Assistant Professor Katerina Ivanova Aleksieva, PhD, the academic position of Associate Professor in scientific specialty Chemical Kinetics and Catalysis, thematic area: EPR spectroscopy and quality of life, for the needs of Institute of Catalysis of the Bulgarian Academy of Sciences.

27.01.2020 Signature:
Sofia (Sonia Damyanova)