Journal of Communicable Diseases
Special Issue - COVID-19 & Other Communicable Diseases, Pg. No. 75-81
Peer Reviewed & Open Access Journal

Research Article

Determination of Zinc Level in Serum and Urine of COVID-19 Patients by New Metal Oxide Nanoparticles Carbon Paste Electrode

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DOI: https://doi.org/10.24321/0019.5138.202212

I N F O

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How to cite this article:
Abood ES, Abed AS, Judi HK. Determination of Zinc Level in Serum and Urine of COVID-19 Patients by New Metal Oxide Nanoparticles Carbon Paste Electrode. Special Issue - COVID-19 & Other Communicable Disease. 2022;75-81.

Date of Submission: 2021-10-27
Date of Acceptance: 2021-12-18

A B S T R A C T

Introduction: Zinc is one of the most essential bio-elements, especially when it comes to the human body's defence against viral or bacterial invaders, for individuals infected with Coronavirus, many experts recommend taking zinc supplements.

Method: To assess the amount of zinc in the blood and urine of the wounded patients, a novel analytical technique with high purity and sensitivity is needed. It must also be affordable, short-time and waste less and not take a long time to analyse.

Results: Zinc oxide nanoparticles are used to fabricate an electrode with excellent sensitivity and selectivity for zinc ions.

Conclusion: Finally, after testing, it was shown that utilising the cyclic voltammetry technique, zinc oxide nanoparticles carbon past electrode were very sensitive and selective in detecting minute changes in current caused by both the reduction and oxidation processes in COVID patients. Variations in the surrounding environment were also examined for optimum results.

Keywords: CoVID-19, ZnO Nanoparticles, Cyclic Voltammetry, Electrode

Introduction

Coronaviruses are significant organisms and present for many years to animals and people. More infectious and deadlier strains of SARS-CoV-2 are of considerable worry because effective treatment is unavailable and the coverage rates for vaccines are lower than expected. In addition, vaccine protection may only endure for one or two seasons. One of the life-saving techniques is to identify and implement actions to address groups that are at risk of severe COVID-19 diseases. The most common mortality toll in the COVID-19 was the old, men, obese, chronic diseases patients, malignant patients, immune-compromised, obscure skin patients, socioeconomic poor and cigarette users.[1] A large dose of supplemented vitamins and trace elements (micronutrients) is part of a strategy to reduce serious COVID-19 symptoms. Vitamin D, zinc and selenium are especially significant in coping with viral respiratory illnesses such as COVID-19 as micronutrients that are necessary to optimal immune function.[2] Not only is the adequate status of these micronutrients matter for immune function and viral clearance, but also could alleviate life-threatening SARS-CoV-2 infection sequelae, including thrombosis and uncontrolled inflammation leading to cytokine storm. Zinc acts as a cofactor for hundreds of proteins crucial for immune function and regulation as well as antioxidant defence. It has a direct anti-viral effect.[3] The second largest abundance of iron trace metal in the human body, and essential component of the protein structure and function, according to Read SA et al., is a biologically essential component of cellular processes, including growth and development as well as DNA synthesis and transcription of RNA. Importantly, zinc is a structurally constituted component of a total of roughly 2,000 enzymes (hydrolase, transfers, oxidoreductase, ligase, lyase and isomerase) of zinc-finger transcription factor - which permits gene transcription and includes all 6 different classes.[4] Zinc insufficiency has been clearly shown to lead to a damaged immune system. Zinc-induced activity in T cell divide, maturation and distinction, mitogens lymphocyte response, lymphoid and myeloid cell death program, gene transcription and biomembrane function may be improved. In many of the activities, including transcribed DNA and gene expression, signal transduction pathways and endocrine function, zinc is an important trace element that works as a catalyst, a structural element or a regulatory ion.[5] Zinc is therefore essential for immunological function, reproductive health, child development and growth. In view of the established structure, zinc additionally plays an important catalytic role in a broad range of enzymes and is a crucial component in the antioxidant activity of an immune system. It also has an important function in the prevention and control of infections. Zinc hinders its replication by blocking the rhino viral protease enzyme. Zinc supplementation lowers pneumonia prevalence considerably in youngsters. Zinc can block viral attachment while lowering inflammatory effects. It is uncertain as zinc achieves its antiviral actions. In addition, zinc affects leucocytes and lymphocytes proliferation, difference, maturity and function.[6] On the other hand, electrochemical analysis is a set of procedures for determining the chemical reactivity of a sample surface or a solution using electrical stimulation. A potentiostat linked to electrodes submerged in an electrolyte control measures the rates of oxidation and reduction reactions.[7-9] It is one of the most effective ways of investigating a strong electrochemical method used to study molecular species reduction and oxidation processes, cyclic voltammetry (CV) is widely used.[10] In addition, CV may be used to examine chemical processes that are triggered by electron transfer, including catalysis.[11-13] In this study, zinc is an electroactive metal.[14-17]

Materials and Method

Hydrothermal Method for Preparation of ZnO Nanoparticle

The hydrothermal technique was used to manufacture ZnO nanoparticles. A typical procedure involves dissolving 10 g of $ZnCl_2$ in 150 mL of distilled water, and then slowly adding a 4 g NaOH solution while stirring. A white precipitate formed after 3 hours. In order to obtain a homogenous solution, the resultant precipitate was washed with distilled water and dissolved again in water to obtain a solution, which was then combined with 20 mL of polyvinylpyrrolidone (PVP), the homogenous solution was heated at 160°C in an autoclave overnight. It was then dried at 100°C using ZnO powder that had been rinsed in distilled water. In order to assess the shape of the produced ZnO sample, we employed the TEM INSPECT S50. SEM imaging was used to determine how the ZnO produced had changed in morphology (Figure 1). Particles were found to be about 200 nanometers in size in the TEM picture of the agglomerated ZnO particles.[18]

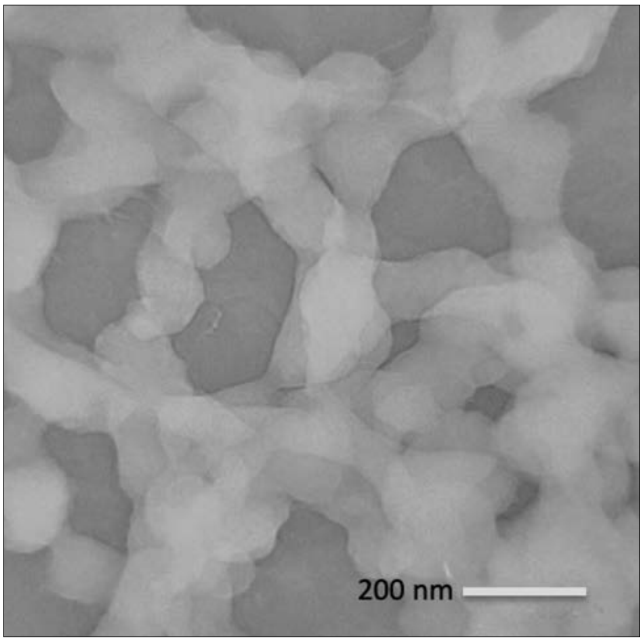

Figure 1.TEM for ZnO Nanoparticles

Preparation of Body Electrode

Prepared using a mortar and pestle, the ZnO modified graphite paste electrodes were made by combining ZnO nanoparticles (0.5 g) with graphite powder and paraffin oil (0.9 mL). In a glass tube, the paste was placed at the end (cross-section area 0.22 mm^2 and length 5 cm). A gold wire was inserted into the carbon paste to establish electrical contact. In order to prepare for this experiment, a fine paper was used to smooth up the carbon paste's surface. No nanoparticles of ZnO were added to the unmodified carbon paste electrode. Figure 2 show the diagram of ZnO-NPs carbon past electrode.

Cyclic Voltammetry Cell

Involves linearly changing a voltage value between a set of starting and final potential values and then sweeping back to the initial value at a constant pace. This was done by utilising three-electrode cells (calomel, Platine wire and

ISSN: 0019-5138
DOI: https://doi.org/10.24321/0019.5138.202212

ZnO-NPs carbon past electrode it was references electrode, axillary electrode and working electrode) reactively; with a regulated potential (Figure 3).

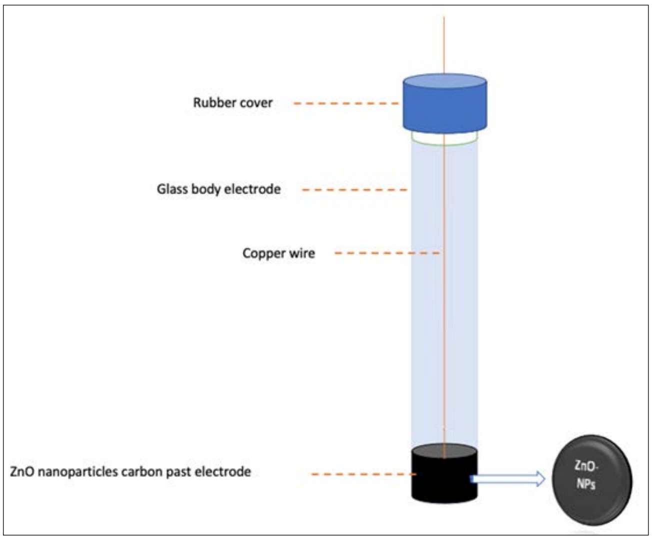

Figure 2.Body of Electrode

Rather than plotting the current response as a function of time, this plots it as a function of voltage. Reversible reactions were used to decrease and oxidise the species. It was utilised as a supporting electrolyte in all measurements

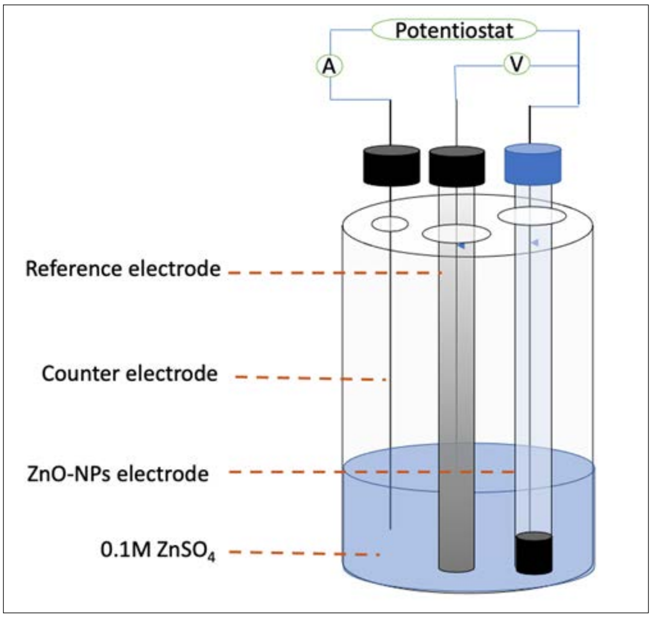

Figure 3.Cyclic Voltammetry Cell

Colorimetric Determination of Zinc in Serum and Urine

Zinc reacts with the chromogen present in the reagent forming a colored compound whose color intensity is proportional to the zinc concentration present in the sample.[19] Zinc kit: (REF CC02750, LOT: E239.20A) containing Reagent A (Borate buffer Saliciadoxim dimetilgioxim and preservatives. 0.37M and pH 8.2) and Reagent B (NITRO-PAPS: 0.4 mM preservatives) finally; Zinc ion 200 ug/dl. Zinc kit: LTA S.r.l – viaMilano, 15/F-Bussero (MI)-Italy.

Sample Collection

Fifty patients (suffering from COVID-19) were recruited as the subject of this study and all of them visited the Alburaq medical laboratory from January to June 2021. They were asked about their medical history and undertook a physical examination of the genital system. The age of all the patients in our study ranged between 25 and 60 years.

Serum: All patient samples have been taken 5ml whole blood and let for 15 min for clotting and isolated serum by using a centrifuge (deLAB1113) 4000 rpm for 10 min. Keep in sample tube and storage in -20°C.

Urine: Sterilised cup sample collected was used for urine collection, 5ml urine sample storage after clarified by centrifuge.

Results

ZnO-NPs Carbon Pate Electrode

The hydrothermal technique was successful in producing zinc oxide nanoparticles, whose diameters were smaller than 150 nanometers on TEM images. Since the nanoparticles are more sensitive to small changes in current during oxidation and reduction, the electrode can measure concentrations with greater precision because of the increased surface area. The conductivity of carbon paste electrodes modified with ZnO nanoparticles was studied by measuring the conductivity of a standard quality control solution (0.2M) of $ZnCl_2$ (10^{-2}-10^{-3} S/cm), and distilled water (0.51 S/cm) when ZnO nanoparticles were combined with carbon paste and paraffin oil of varied weights. As a result, the 0.2 g ZnO nanoparticles with 0.5 grams of carbon and 0.3 mL of paraffin oil have a high signal conductivity from each other, because ZnO is one of the potential semi-conducting materials in solar energy conversion due to its stability against photo corrosion and photochemical properties, as well as the beast disruption distance between the particles. ZnO nanoparticle electrodes with selected signals and interference investigation, this study used various solutions and put in the cell for motion the sensitivity of electrodes.

Physical and Chemical Properties Study

CV was utilised to examine the electro-oxidation of electrodes in the temperature range of 20 °C to 30°C using calomel electrodes; the optimal temperature range was 18-25 °C.[19] Due to variations in the curves, it was possible to determine the activation energy over a wide range of potentials where the typical peak of oxidation emerged. It was possible to determine the activation energy under pure kinetic area circumstances using measurements of the current intensity at a fixed point in time.

ISSN: 0019-5138
DOI: https://doi.org/10.24321/0019.5138.202212

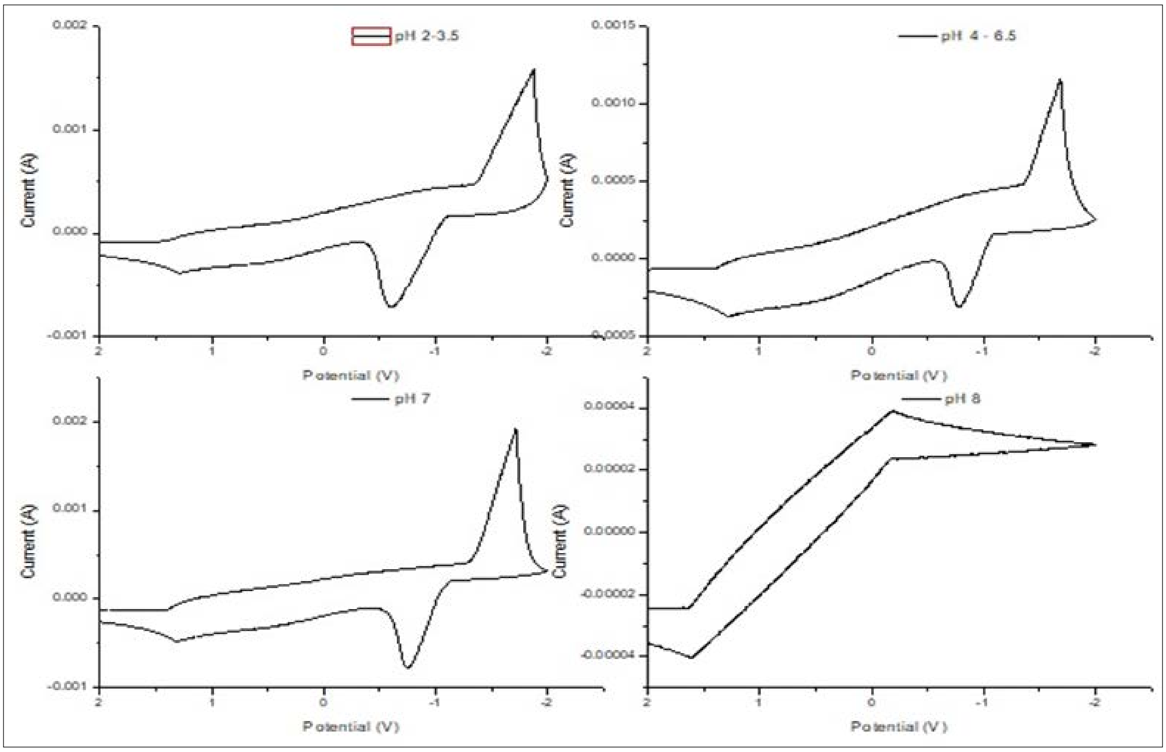

Figure 4.Cyclic Voltammograms Response for ZnO-NPs Carbon Paste Electrode

$\ln D = \ln D_o^{(Ea/RT)}$ ... (1)

Where D is the diffusion coefficient, T is the temperature, and K is the kelvin temperature.

All physical parameter was calculated. Table 1 refers to the result of kinetic and thermodynamic parameters.

Calibration Curve

The method's analytical characteristics, such as linear ranges of the calibration plots and detection of Zn^{2+} limits, were obtained using cyclic voltammetry.[21] The ability of a ZnO nanoparticle-modified electrode to separate the electrochemical response of Zn^{2+} was investigated. As a result of its improved removal of capacitive background current, CV was utilized for simultaneous species determination. Using a ZnO nanoparticle electrode, analytical tests were carried out on various quantities of $ZnSO_4$ pure stock solution with pH 7.0. The calibration curve produced by CV at 20-200 ug/dl is shown in Figure 5, clearly demonstrating the reaction of the ZnO nanoparticle to Zn.

Table 1.Kinetic Parameters of ZnO NPs Electrode Carbon Paste Electrode

Type of Electrode	ΔE KJ/mol	ΔH KJ/mol	ΔG KJ/mol	ΔS KJ/mol	K $S^1 10^{-5}$	$D^o \times 10^{-7}$	A	K_0
ZnO NPs Carbone past electrode	-48.92	-5.79	-75.3	0.19	4.90	1.00	0.1	0.11

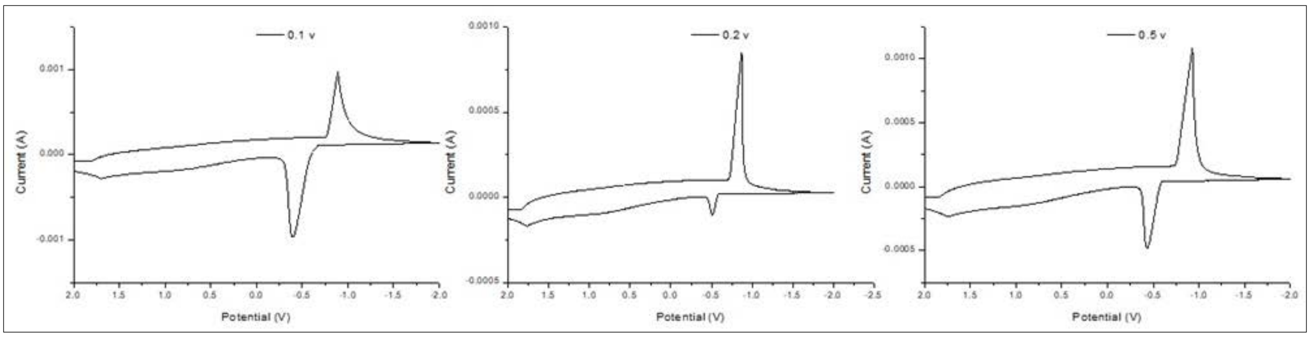

Figure 5.Cyclic Voltammograms for Calibration Plot to ZnO-NPs Carbon Paste Electrode

ISSN: 0019-5138
DOI: https://doi.org/10.24321/0019.5138.202212

Serum and Urine of Zinc Level Determination

Colorimetric

Reagents/ serum	Blank	Standard	Sample
Working reagent	1 mL	1 m	1ml
Distilled water	50 ul	-	-
Standard	-	50 ul	-
Sample	-	-	50 ul
Mix and read the absorption against blank at 578 nm colour is stable for 30 min			
Calculation	**Serum**	**Calculation**	**Urine**
Zn ug/dl = [A sample/A standard] x 200		Zn ug/24h = [A sample/A standard] x 200 x dl urine	
Expected values for serum 70 – 150 ug/dl		Expected values for urine 100 – 1000 pg/24h	

Electrochemistry

Add 100 ul from the sample (serum/ urine) in the electrochemistry cell attach with the surface of the electrodes and applied 0.1 V/s^{-1} and the cyclic voltammograms peak show result after selecting the head peak current and using the calibration plot to determine the zinc concentration. Figure 6 refers to the real cyclic voltammograms test and Table 2 refers to the comparison result for the patients that are determined by colorimetric and cyclic voltammetry at the same time.

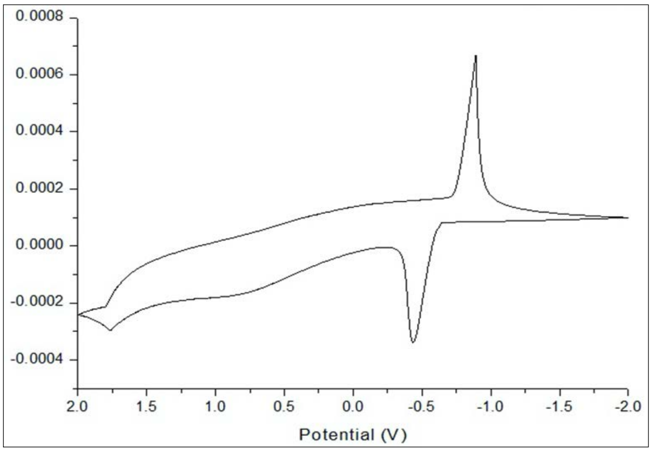

Figure 6.Cyclic Voltammograms for Patient Sample Response

Table 2.Result of Comparison between Colorimetric and ZnO-NPs Electrode

No. of Patients	Colorimetric		ZnO-NPs Electrode	
	Serum	Urine	Serum	Urine
1	102	620	96	520
2	87	112	81	98
3	98	871	87	710
4	123	791	110	678
5	114	432	98	382
6	98	404	81	354
7	112	278	98	196
8	125	756	105	676
9	76	598	69	472
10	69	700	60	610
11	141	690	121	560
12	113	789	93	679
13	126	436	102	375
14	88	543	76	493
15	71	232	61	182
16	178	891	148	699
17	117	689	97	574
18	102	514	89	443
19	98	345	90	395
20	78	119	69	88
21	79	345	68	254
22	102	499	87	379
23	99	278	85	158
24	189	980	169	698
25	60	119	-	87
26	143	786	114	641
27	78	345	70	275
28	187	984	148	798
29	113	434	97	332
30	154	877	124	715
31	167	950	137	796
32	141	820	112	680
33	99	414	87	333
34	80	220	71	180

ISSN: 0019-5138
DOI: https://doi.org/10.24321/0019.5138.202212

35	84	212	69	182
36	111	189	91	139
37	139	564	110	476
38	171	809	143	641
39	108	457	86	334
40	117	517	87	389
41	125	423	102	301
42	123	254	98	174
43	87	189	79	121
44	156	786	121	593
45	180	920	167	789
46	187	910	162	770
47	102	324	88	276
48	116	403	95	312
49	89	476	76	361
50	71	217	63	177

Discussion

The electrode was worked ion-selective electrode for specific ions by experimental, in other hands, a solution with free zinc ion tack no signal response.

The cyclic voltammetric response of 0.1 mol $ZnSO_4$ electrochemical oxidation-reduction at a ZnO nanoparticle carbon paste electrode is shown in Figure 4. The oxidation and reduction anodic peak potentials for Zn^{+2} oxidation and reduction, respectively, were approximately -1.061 V and -0.810 V on the carbon paste electrode.

While electro oxidation was occurring, the charge-transfer resistance and rate were always influenced by surface covered by a diffusion intermediate. This was analysed and discussed, implying that an electro-oxidation pathway devoid of significant contacts with the ZnO nanoparticle electrode surface took occurred.[20] At 15-30°C[21], the working electrode tacked the clear signal with Nernst equation (Eq. 1).

Conclusion

We were able to produce nanoparticles of zinc oxide using the hydrothermal technique. Carbon, paraffin, and zinc oxide nanoparticles may be mixed to form a paste with great sensitivity and purity to tiny variations in current throughout the oxidation and reduction process, according to the study. Also, compared to spectroscopic methods for evaluating 100 samples of corona patients in different serum and urine samples, the zinc oxide nanoparticle showed a wider natural ratio, indicating the feasibility of employing a zinc oxide nanoelectrode in place of spectroscopic methods. To measure zinc levels in patients quickly and affordably, it relies on a spectrophotometric approach that doesn't require solutions to be used. The result was a significant reduction in time and effort.

Source of Funding: Not Applicable

Conflict of Interest: None

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ISSN: 0019-5138
DOI: https://doi.org/10.24321/0019.5138.202212