

# Theoretical Description for Adamsite and Lewisite VO(OH)-Assisted Electrochemical Removal from Wastewater

Volodymyr V. Tkach <sup>1,\*</sup> , Tetiana V. Morozova <sup>2</sup> , Marta V. Kushnir <sup>1</sup> , Sílvia C. de Oliveira <sup>3</sup> , Viktor V. Kryvetskyi <sup>4</sup> , Inna I. Kryvetska <sup>4</sup> , Igor V. Kryvetskyi <sup>4</sup> , Igor G. Biryuk <sup>4</sup> , Tetiana B. Sykyrytska <sup>4</sup> , Yana G. Ivanushko <sup>4</sup> , Alla V. Velyka <sup>4</sup> , Petro I. Yagodynets <sup>1,\*</sup> , Adriano O. da Silva <sup>5</sup> , Jarem R. Garcia <sup>6</sup> , José Inácio Ferrão da Paiva Martins <sup>7</sup> , Gennadii F. Tkach <sup>8</sup> , Oleg P. Melnyk <sup>8</sup> , Oleksii O. Melnyk <sup>8</sup> , Maria V. Melnyk <sup>8</sup> , Maria João Monteiro <sup>9</sup> , Viktoriia O. Khrutba <sup>2</sup> 

<sup>1</sup> Chernivtsi National University, 58001, Kotsyubynsky Str. 2, Chernivtsi, Ukraine

<sup>2</sup> National Transport University, 02000, Omelianovych-Pavlenko Str. 1, Kyiv, Ukraine

<sup>3</sup> Institute of Chemistry. Federal University of Mato Grosso do Sul, 79074 – 460, Av. Sen. Felinto Müller, 1555, Vila Ipiranga, Campo Grande, MS, Brazil

<sup>4</sup> Bukovinian State Medical University, 58001, Teatralna Sq. 9, Chernivtsi, Ukraine

<sup>5</sup> Federal University of the West of Pará, Juruti Campus, 68170 – 000, Rua Veríssimo de Souza Andrade, s/n, Juruti, PA, Brazil

<sup>6</sup> State University of Ponta Grossa, Uvaranas Campus, Av. Gal. Carlos Cavalcanti, 4748, 84030-900, Ponta Grossa, PR, Brazil

<sup>7</sup> Engineering Faculty of the University of Porto, 4200-465, Rua Dr. Roberto Frias, s/n, Porto, Portugal

<sup>8</sup> National University of Life and Environmental Science of Ukraine, 03041, Heroiv Oborony Str, 15, Kyiv, Ukraine

<sup>9</sup> University of Trás-os-Montes and Alto Douro, Quinta de Prados, 5001-801, Folhadela, Vila Real, Portugal

\* Correspondence: nightwatcher2401@gmail.com (V.V.T.), ved1988mid@rambler.ru (P. I.Y.);

Scopus Author ID 55758299100

Received: 23.08.2023; Accepted: 12.05.2024; Published: 22.09.2024

**Abstract:** An electrochemical process for adamsite and lewisite chemical warfare agents has been proposed for the first time. The process is given by single or double membrane electrolysis and is carried out to remove the warfare agents from the wastewater. From the theoretical analysis of this system, it has been possible to conclude that vanadium oxyhydroxide can remove both warfare agents from the treated wastewater. Although the oscillatory behavior becomes more probable due to the hybrid scenario, the process may be widely used for electroanalytical and removal purposes.

**Keywords:** adamsite; lewisite; wastewater treatment; chemically modified electrodes; Vanadium (III) oxyhydroxide; stable steady-state.

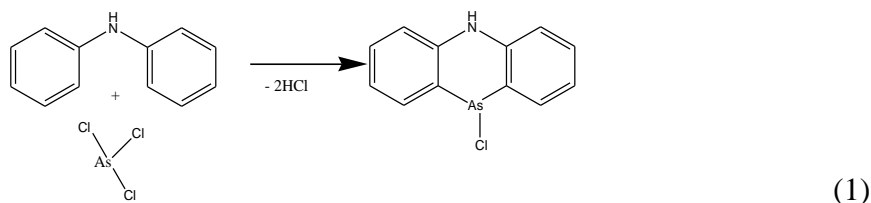
© 2024 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

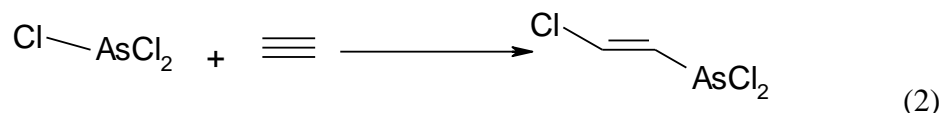
World War I was an important event for the development of chemical warfare agents (CWA) [1–4], the reason why it is often called “The War of Chemists”. Iprite, sarin, adamsite, and lewisite are compounds synthesized and used by both combating alliances.

Adamsite was first synthesized parallelly by the groups of G. Wieland (Germany) and R. Adams (USA) from Illinois University, which is why it is named adamsite. It is a slow-acting irritant and lachrymatory substance, actively used in both World Wars but forbidden by the UNO. Nevertheless, it is still used by the armies of Venezuela, North Korea, and some of

the African countries [5–8]. It is obtained by Friedel-Crafts reaction of arsenic trichloride with diphenylamine (1).



As for lewisite, it is one more arsenic-based CWA [9–12], acting as a vesicant and lung irritant. It was used by the US, Germany, Japan, the Soviet Union, and furtherly Russia [9 – 12]. It is obtained by arsenic trichloride reaction with acetylene (2):



Considering the ecotoxicity of both compounds [13–15], the development of efficient means of removal of arsenoorganic chemical warfare is actual, including the postwar reconstruction of Ukraine. Since both compounds are redox-active, both cathodic and anodic processes may be used for electrochemical quantification and removing lewisite and adamsite.

Considering the presence of chlorine and arsenic in the compounds, the oxidative methods may not be viable, leading to toxic chlorine and arsenic compounds. It is recommended that cathodic methods be used instead. By this, the chlorine will be reduced in an acidic medium to the organic chloride and arsenic to elementary arsenic or arsine, leaving the reaction cell. A single or double membrane set is used to impede the diffusion of chlorine and arsenic compounds towards the anodic electrolyte [16–21]. Using  $\text{VO}(\text{OH})$  as a proton and electron transfer mediator lets us avoid a strongly acidic medium in this reaction and stabilizes the system.

In this work, we describe from the theoretical point of view the possibility of the electrochemical reduction of adamsite and lewisite on  $\text{VO}(\text{OH})$ -modified cathode in a neutral and mildly acidic and neutral medium. This investigation includes the mechanistic stability analysis and comparison of the behavior of this system with that of similar ones [16–21].

## 2. Materials and Methods

Depending on the concentration and the solution pH, two variants for adamsite and lewisite reduction are possible, either the elementary arsenic or arsine, the products of the reaction. Vanadium is, in turn, oxidized to a tetravalent state.

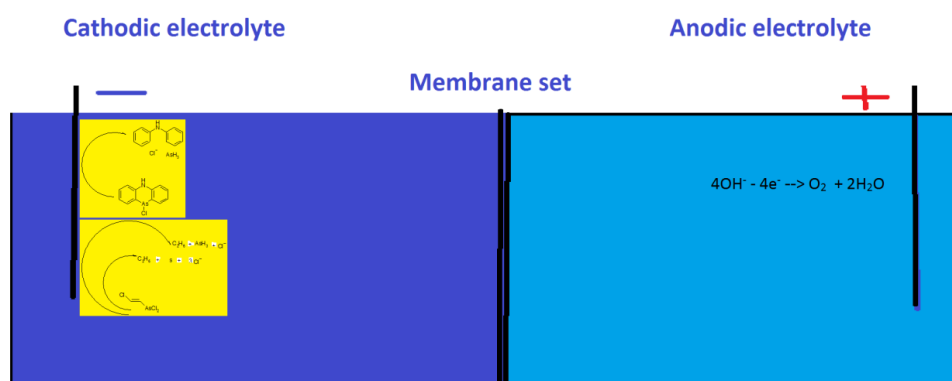
As in the similar systems,  $\text{VO}(\text{OH})$  becomes thereby regenerated by (3):



A membrane set splits the cell into two parts, separating the cathodic and anodic electrolytes. It doesn't let the arsenic compounds and the chlorine atoms penetrate the anodic electrolyte (and prevents them from oxidizing, yielding the toxic compounds). As the anodic compartment does not contain the elementary anions, the water electrolysis or hydroxyl oxidation will be the anodic reaction (4):



Schematically, the electrochemical cell, with the reactions occurring therein, is depicted in the Figure 1:



**Figure 1.** Electrochemical membrane cell for adamsite and lewisite electrochemical removal.

The membrane material used to separate the anodic and cathodic cell compartments is generally PVP. If necessary, a double membrane will be used. Arsine, in turn, will leave the system by the exhaustion duct linked to the cathode.

Therefore, taking into account the statements mentioned above and taking some assumptions [16 – 21], we describe the behavior of this system by the equation set (5):

$$\begin{cases} \frac{da}{dt} = \frac{2}{\delta} \left( \frac{A}{\delta} (a_0 - a) - r_a \right) \\ \frac{dl}{dt} = \frac{2}{\delta} \left( \frac{L}{\delta} (l_0 - l) - r_{l1} - r_{l2} \right) \\ \frac{dv}{dt} = \frac{1}{V} (r_a + r_{l1} + r_{l2} - r_r) \end{cases} \quad (5)$$

Herein, A and L are the correspondent diffusion coefficients,  $a_0$  and  $l_0$  stand for their bulk concentrations, a and for their pre-surface concentrations,  $\delta$  for the diffusion layer thickness, v for vanadium dioxide surface coverage degree, V for its maximal surface concentration, and the parameters r are the correspondent reaction rates, calculated as (6 – 8):

$$r_a = k_a a (1 - v)^6 \exp(-\alpha a) \quad (6)$$

$$r_{l1} = k_{l1} a (1 - v)^7 \exp(-\lambda l) \quad (7)$$

$$r_{l2} = k_{l2} a (1 - v)^{10} \exp(-\lambda l) \quad (8)$$

$$r_r = k_r v \exp\left(-\frac{F\varphi_0}{RT}\right) \quad (9)$$

Herein, the parameters k stand for the correspondent reaction rate constants,  $\alpha$  and  $\lambda$  stand for the parameters, relating the double electric layer (DEL) electrochemical and electrophysical properties to ionic forms transformation during the chemical stages involving adamsite and lewisite correspondently, F is the Faraday number,  $\varphi_0$  is the potential slope related to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature.

Taking into account that the ionic compound transformation occurs in this system, the oscillatory behavior will be more probable than in the simple case and of equal probability to similar systems [16–21], in which the steady-state stability topological region remains wide.

This corresponds to the efficient CWA removal process, occurring in mildly acidic and neutral medium, as shown below.

### 3. Results and Discussion

We investigate the steady-state stability for the system with adamsite and lewisite CWA electrochemical removal by linear stability theory and describe the steady-state Jacobian elements as (10):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (10)$$

Herein:

$$a_{11} = \frac{2}{\delta} \left( -\frac{A}{\delta} - k_a(1-v)^6 \exp(-\alpha a) + \alpha k_a a(1-v)^6 \exp(-\alpha a) \right) \quad (11)$$

$$a_{12} = 0 \quad (12)$$

$$a_{13} = \frac{2}{\delta} (6k_a a(1-v)^5 \exp(-\alpha a)) \quad (13)$$

$$a_{21} = 0 \quad (14)$$

$$a_{22} = \frac{2}{\delta} \left( -\frac{L}{\delta} - k_{l1}(1-v)^7 \exp(-\lambda l) - k_{l2}(1-v)^{10} \exp(-\lambda l) + \lambda(k_{l1}a(1-v)^7 \exp(-\lambda l) + k_{l2}a(1-v)^{10} \exp(-\lambda l)) \right) \quad (15)$$

$$a_{23} = \frac{2}{\delta} (7k_{l1}a(1-v)^6 \exp(-\lambda l) + 10k_{l2}a(1-v)^9 \exp(-\lambda l)) \quad (16)$$

$$a_{31} = \frac{1}{v} (k_a(1-v)^6 \exp(-\alpha a) - \alpha k_a a(1-v)^6 \exp(-\alpha a)) \quad (17)$$

$$a_{32} = \frac{1}{v} (k_{l1}(1-v)^7 \exp(-\lambda l) + k_{l2}(1-v)^{10} \exp(-\lambda l) - \lambda(k_{l1}a(1-v)^7 \exp(-\lambda l) + k_{l2}a(1-v)^{10} \exp(-\lambda l))) \quad (18)$$

$$a_{33} = \frac{1}{v} \left( -7k_{l1}a(1-v)^6 \exp(-\lambda l) - 10k_{l2}a(1-v)^9 \exp(-\lambda l) - k_r \exp\left(-\frac{F\phi_0}{RT}\right) + jk_r v \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (19)$$

Avoiding the cumbersome expression during the determinant analysis, we introduce new variables and rewrite the determinant as (20):

$$\text{Det } J = \frac{4}{\delta^2 C} \begin{vmatrix} -\kappa - \Xi & 0 & \Lambda \\ 0 & -\xi - P & \Phi \\ \Xi & P & -\Lambda - \Phi - \Omega \end{vmatrix} \quad (20)$$

Considering that:

$$-\text{Det } J \begin{cases} > 0, \text{ for steady - state stability} \\ = 0 \text{ monotonic instability} \end{cases} \quad (21)$$

Opening the brackets, applying the  $\text{Det } J < 0$  requisite, salient from the criterion, and changing the signs to the opposite, we rewrite the condition set as (22):

$$\kappa(\xi\Lambda + \xi\Phi + \xi\Omega + P\Lambda + P\Omega) + \Xi(\xi\Lambda + \xi\Phi + P\Omega) \begin{cases} > 0, \text{ curve linearity} \\ = 0, \text{ monotonic instability} \end{cases} \quad (22)$$

If  $-\text{Det } J > 0$ , the Routh-Hurwitz stability criterion is valid, and the steady-state is thereby stable, providing an efficient steady-state CWA electrochemical conversion. Moreover, the wide stability region allows us to use this system as an electroanalytical for sensing purposes.

This criterion is readily satisfied if the kinetic parameters  $P$  and  $\Omega$  are positive. In the vast majority of the cases, they both have positive signs. Considering that the other variables in the determinant are positive, it indicates the vast steady-state stability topological region. The electroanalytical process is both diffusion and kinetically controlled, with the prevalence of kinetic factors.

In the absence of the side reactions or other factors capable of compromising the analyte and (or) modifier stability, excluding the reactions foreseen by the mechanism, the linearity between the electrochemical parameter and concentration is observed, providing an efficient analytical signal interpretation, which is important for CWA conversion monitoring.

The condition  $\text{Det } J=0$  corresponds to the detection limit, manifested by the *monotonic instability*. It may be seen as an N-shaped part of the steady-state voltammogram, depicts the margin between stable and unstable states, and corresponds to steady-state multiplicity. In other words, multiple steady-states, each one unstable, coexist at this point.

As for the oscillatory behavior, it is realized beyond the detection limit in the case of the Hopf bifurcation realization. Its realization requires the presence of the positive-callback related positive addendums in main diagonal elements.

Observing the main diagonal elements (11), (15), and (19), we may observe that the oscillatory behavior becomes possible if the kinetic parameters  $\alpha$ ,  $\lambda$ , and  $j$  are positive, which corresponds to the DEL influences of the chemical and electrochemical stages. This factor is typical for similar systems [16–21] and may be described by the positivity of the elements  $\alpha k_a a(1-v)^6 \exp(-\alpha a)$ , if  $\alpha > 0$ ,  $\lambda(k_{l1} a(1-v)^7 \exp(-\lambda l) + k_{l2} a(1-v)^{10} \exp(-\lambda l)) > 0$ , if  $\lambda > 0$  and  $j k_r v \exp\left(-\frac{F\phi_0}{RT}\right) > 0$ , if  $j > 0$ . These elements describe the positive callback, and this callback will depend on the system's characteristics. For example, the oscillation frequency and amplitude will depend on the background electrolyte composition, which has been proven experimentally [16–18] and theoretically [19–21].

The chemical and electrochemical degradation may become parallel in an alkaline medium, especially for lewisite. Nevertheless, it will yield toxic products, like arsenates, being thereby not recommended. This case will be described in one of our next works.

#### 4. Conclusions

From the theoretical description of adamsite and lewisite electrochemical cathodic removal by VO(OH)-modified cathode, it has been possible to conclude that it may be an excellent modifier for removing and quantifying both chemical warfare agents. The electrochemical removal becomes diffusion-controlled or kinetically controlled with the prevalence of the kinetic factor. The oscillatory behavior in this system may be caused by the influence of DEL on electrochemical and chemical stages. The system may be used as an electroanalytical, providing efficient analytical signal interpretation.

#### Funding

This research received no external funding.

#### Acknowledgments

Volodymyr V. Tkach acknowledges the Engineering Faculty of the University of Porto and the University of Trás-os-Montes and Alto Douro for their support during these difficult times for Ukraine and its research.

#### Conflicts of Interest

The authors declare no conflict of interest.

## References

1. Castelvechi, D. The world's top chemical-weapons detectives just opened a brand-new lab. *Nature* **2023**, *617*, 657–658, <https://doi.org/10.1038/d41586-023-01622-9>.
2. McLeish, C.; Johnstone, P.; Schot, J. The changing landscape of deep transitions: Sociotechnical imprinting and chemical warfare. *Environ. Innov. Soc. Transit.* **2022**, *43*, 146–159, <https://doi.org/10.1016/j.eist.2022.03.008>.
3. Martínez, F.J. Containing chemical warfare: anti-gas measures for factory workers, health staff and the general population in Spain during the Rif War (1921-1927). *SHS Web Conf.* **2022**, *136*, 01002, <https://doi.org/10.1051/shsconf/202213601002>.
4. Kumar, V.; Kim, H.; Pandey, B.; James, T.D.; Yoon, J.; Anslyn, E.V. Recent advances in fluorescent and colorimetric chemosensors for the detection of chemical warfare agents: a legacy of the 21st century. *Chem. Soc. Rev.* **2023**, *52*, 663–704, <https://doi.org/10.1039/d2cs00651k>.
5. Muzaffar, S.; Khan, J.; Srivastava, R.; Gorbatyuk, M.S.; Athar, M. Mechanistic understanding of the toxic effects of arsenic and warfare arsenicals on human health and environment. *Cell Biol. Toxicol.* **2023**, *39*, 85–110, <https://doi.org/10.1007/s10565-022-09710-8>.
6. Mallik, S.; Chand Pal, S.; Acharyya, S.; Verma, S.P.; Mandal, A.; Guha, P.K.; Das, M.C.; Goswami, D.K. MOF-Assimilated High-Sensitive Organic Field-Effect Transistors for Rapid Detection of a Chemical Warfare Agent. *ACS Appl. Mater. Interfaces* **2023**, *15*, 30580–30590, <https://doi.org/10.1021/acsami.3c05185>.
7. Wilczynski, W.; Brzeziński, T.; Maszyk, P.; Ludew, A.; Czub, M.J.; Dziedzic, D.; Nawala, J.; Popiel, S.; Beldowski, J.; Sanderson, H.; Radlinska, M. Acute toxicity of organoarsenic chemical warfare agents to Danio rerio embryos. *Ecotoxicol. Environ. Saf.* **2023**, *262*, 115116, <https://doi.org/10.1016/j.ecoenv.2023.115116>.
8. Ahmad, K.; Shah, H.R.; Ahmad, M.; Ahmed, M.; Naseem, K.; Riaz, N.; Muhammad, A.; Ayub, A.; Ahmad, M.; Ahmad, Z. Comparative study between two zeolitic imidazolate frameworks as adsorbents for removal of organoarsenic, As (III) and As (V) species from water. *Braz. J. Anal. Chem.* **2022**, *9*, 78–97, <https://doi.org/10.30744/brjac.2179-3425.AR-112-2021>.
9. Liu, Z.; Liu, H.; Holiharimanana, D.; Wang, H.; Sun, H. Reversible lewisite adsorption/desorption on the transition-metal-doped graphene: first-principle calculations. *Res. Chem. Intermed.* **2023**, *49*, 2875–2887, <https://doi.org/10.1007/s11164-023-05022-6>.
10. Dandekar, A.A.; Vora, D.; Yeh, J.S.; Srivastava, R.K.; Athar, M.; Banga, A.K. Enhanced Transdermal Delivery of N-Acetylcysteine and 4-Phenylbutyric Acid for Potential Use as Antidotes to Lewisite. *AAPS PharmSciTech.* **2023**, *24*, 71, <https://doi.org/10.1208/s12249-023-02527-6>.
11. Hauptman, M.; Woolf, A.D. Chapter 3.4 - British anti-lewisite (dimercaprol). In *History of Modern Clinical Toxicology*, Woolf, A.D., Ed.; Academic Press, **2022**; 243–254, <https://doi.org/10.1016/B978-0-12-822218-8.00050-8>.
12. Vora, D.; Dandekar, A.A.; Srivastava, R.K.; Athar, M.; Banga, A.K. Development and Evaluation of a Topical Foam Formulation for Decontamination of Warfare Agents. *Mol. Pharm.* **2022**, *19*, 4644–4653, <https://doi.org/10.1021/acs.molpharmaceut.2c00636>.
13. Ji, C.; Zhu, Y.; Zhao, S.; Zhang, H.; Wang, S.; Zhou, J.; Liu, X.; Zhang, Y.; Liu, X. Arsenic and heavy metals at Japanese abandoned chemical weapons site in China: distribution characterization, source identification and contamination risk assessment. *Environ. Geochem. Health* **2023**, *45*, 3069–3087, <https://doi.org/10.1007/s10653-022-01382-x>.
14. Fedorov, V.A.; Menschikova, T.K.; Vargunin, A.I.; Brekhovskikh, M.N.; Myslitskii, O.E. Processes and Devices for the Isolation and Purification of Elemental Arsenic and its Compounds. *Theor. Found. Chem. Eng.* **2022**, *56*, 609–612, <https://doi.org/10.1134/S0040579522040091>.
15. de Carvalho, R.C.; Betts, A.J.; Cassidy, J.F. Diclofenac determination using CeO<sub>2</sub> nanoparticle modified screen-printed electrodes – A study of background correction. *Microchem. J.* **2020**, *158*, 105258, <https://doi.org/10.1016/j.microc.2020.105258>.
16. Fadhel, S.; Al-kadumi, A.S.H.; Imran, N.A.; Abdulateef, M.H. A Developed Method for the Estimation of Diclofenac Sodium via Coupling with Diazotized 4-Aminoacetophenone. *Egypt J. Chem.* **2021**, *64*, 3703–3709, <https://doi.org/10.21608/ejchem.2021.68509.3497>.

17. Bahadori, Y.; Razmi, H. Design of an electrochemical platform for the determination of diclofenac sodium utilizing a graphenized pencil graphite electrode modified with a Cu–Al layered double hydroxide/chicken feet yellow membrane. *New J. Chem.* **2021**, *45*, 14616–14625, <https://doi.org/10.1039/d1nj02258j>.
18. Parrilla, M.; Slosse, A.; Van Echelpoel, R.; Montiel, N.F.; Van Durme, F.; De Wael, K. Portable Electrochemical Detection of Illicit Drugs in Smuggled Samples: Towards More Secure Borders. *Chem. Proc.* **2021**, *5*, 44, <https://doi.org/10.3390/CSAC2021-10612>.
19. Santra, S.; Sarkar, B.R.; Doloi, B.; Bhattacharyya, B. Investigation through novel tool-electrode feeding approach on electrochemical discharge machining of glass. *Proc. Inst. Mech. Eng., Part B: J. Eng.* **2023**, *237*, 1207-1219, <https://doi.org/10.1177/09544054221123479>.
20. Tkach, V.; Kucher, M.; Kushnir, M.; Ivanushko, Y.; Akinay, Y.; Karakoyun, N.; Yagodynets, P.; Kormosh, Z. The Theoretical Description for Psilocin Electrochemical Determination over Cobalt Oxyhydroxide. *Orbital Elec. J. Chem.* **2023**, *15*, 27–30, <http://dx.doi.org/10.17807/orbital.v15i1.18012>.
21. Tkach, V.V.; Kushnir, M.V.; Romaniv, L.V.; de Oliveira, S.C.; Ivanushko, Y.G.; Nazymok, Y.V.; Ahafonova, O.V.; Yagodynets, P.I.; da Silva, A.O.; Derevianko, N.P. The Theoretical Description for Ibotenic Acid and Muscimol Electrochemical Determination in Mushroom Pulp and Mushroom-based Alcoholic Beverages on Nano-CuS Composite with Conducting Polymer. *Lett. Appl. NanoBioSci.* **2024**, *13*, 37, <https://doi.org/10.33263/LIANBS131.037>.