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Cathodic Determination of Tobacco-Specific Nitrosamines in the Presence of 4-Nitroquinoline-N-Oxide. A Theoretical Insight

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Abstract: In this work, the possibility of electroanalytical determination of tobacco-specific nitrosamines (TSN) in the presence of 4-nitroquinoline N-oxide (NQO) was described theoretically for the first time. Electroanalytical detection will be performed by a cathodic process, assisted by vanadium oxyhydroxide, allowing the reduction of NQO by the nitric and N-oxide groups and of TNS by the nitrosamine group. Both processes correspond to reduction peaks, through which it is possible to detect and quantify the concentration of these compounds. The theoretical analysis of the electroanalytical process confirms the effectiveness of vanadium oxyhydroxide for the detection of TNS in the presence of NQO, maintaining the linear dependence between the electrochemical parameter and the concentration in a wide range of parameters.

Keywords: smoking; tobacco-specific nitrosamines; 4-nitroquinoline N-oxide; vanadium oxyhydroxide; electrochemical sensors; electrochemical oscillations; stable steady state.

1. Introduction

Smoking is one of the most serious problems facing humanity [1–4]. It is, in fact, a type of drug addiction that involves the respiratory, digestive, cardiovascular, nervous, and immune systems. Electronic cigarettes, in turn, can simply mask drug addiction without eliminating it. In fact, all the harm that smoking causes to the body is preserved because the composition of the tobacco leaves used in its preparation generally remains intact.

In addition to nicotine, nicotyrine, anabasine, anabatine, and other substances, which are major tobacco alkaloids, tobacco contains toxic compounds, both from natural modification and from burning [5–9]. Among them, tobacco-specific nitrosamines (TNS, Figure 1) deserve special mention because they are partially responsible for the carcinogenic properties of tobacco smoke.

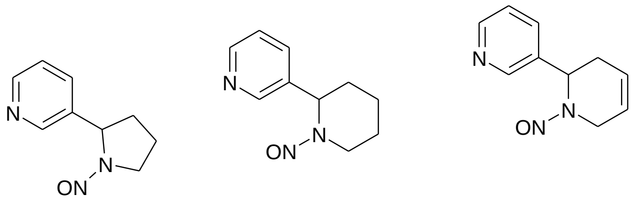

Figure 1. Tobacco-specific nitrosamines (TSN), from left to right – N-nitrosonornicotine, N-nitrosoanabasine, and N-nitrosoanabatine.

These compounds can be obtained in nature from nicotyrine, anabasine, and anabatine by nitrosylation in an acidic medium. The nitrosyl cation, which is obtained within the plant itself from nitrate and nitrite in an acidic medium by reactions (1 – 2):

$$NO_3^- + 4H^+ + 2e^- \rightarrow NO^+ + 2H_2O \qquad (1)$$

$$NO_2^- + 2H^+ \rightarrow NO^+ + H_2O \qquad (2)$$

It then reacts with the secondary amine group, yielding tobacco-specific N-nitrosamines. The reaction of the nitrosyl cation with the aromatic system yields C-nitroso compounds, which are also toxic.

4-Nitroquinoline N-oxide (NQO, Figure 2) can also occur naturally, including in tobacco [10–14], but is usually obtained synthetically as a model compound for cancer investigations.

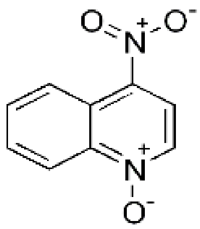

Figure 2. 4-nitroquinoline N-oxide.

In view of the above, the electroanalytical detection of TNS and NQO is actually current [15–18], and considering that all substances are electroactive, the electroanalytical methods, already used for analogous compounds [19-28], could be used in this case.

Considering the presence of acceptor groups in all compounds, we conclude that the use of cathodic reduction methods will be more suitable for the electroanalytical process. Thus, vanadium oxyhydroxide could be used as a plausible electrode modifier for this case. In moderately and slightly acidic, neutral and alkaline solutions (pH<14), it can be easily used for the detection of oxidizing compounds, thus transforming into a tetravalent vanadium compound.

However, the development of new electrosynthesis, electroanalysis, and electrochemical conversion processes requires a prior theoretical investigation of the system's behavior. This investigation allows solving problems such as uncertainty about some details of the electroanalytic process (how electroreduction is carried out in concrete conditions, what modifiers could be used there) and the eventual appearance of instabilities characteristic of the electrooxidation of organic compounds, including electropolymerization [29–32].

Therefore, the general objective of this work is to evaluate, from a theoretical point of view, the performance of the electroanalytical detection of tobacco-specific nitrosamines by vanadium oxyhydroxide. Furthermore, the behavior of this system will be compared with that of similar systems [33-35].

2. Materials and Methods

In a slightly acidic environment, the electrochemical reduction of NQO will occur both by the nitric group and by the N-oxide. The tobacco-specific nitrosamines will be reduced to the corresponding hydrazine derivatives. On the other hand, the trivalent vanadium will be oxidized to tetravalent and, in the electrochemical stage, will be regenerated as per (2):

$$VO_2 + H^+ + e^- \to VO(OH) \quad (3)$$

Or, depending on the pH (4):

$$VO^{2+} + H_2O + e^- \to VO(OH) + H^+ \qquad (4)$$

Thus, the electroanalytical process will be carried out as shown in Figure 3.

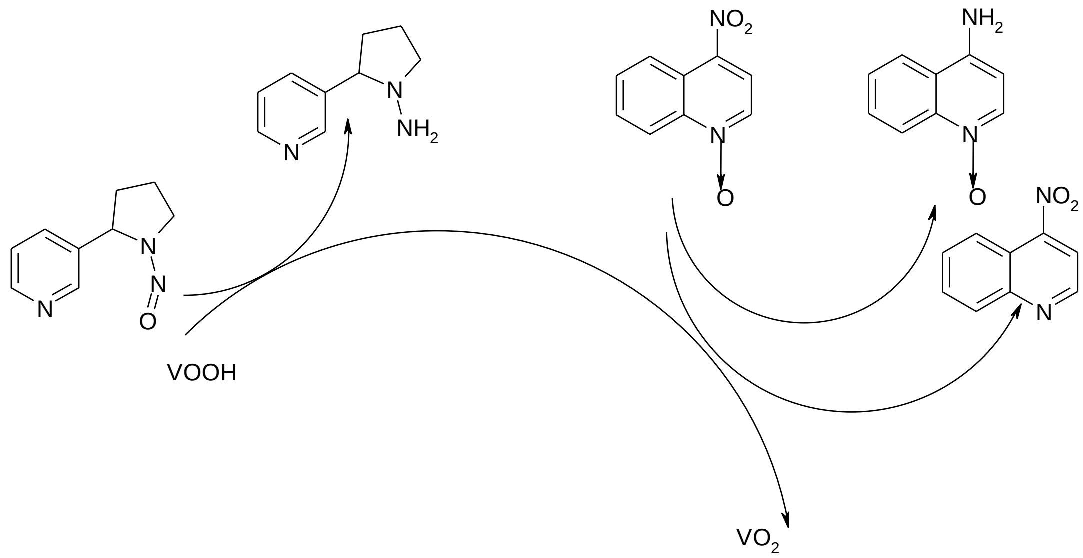

Figure 3. Schematic representation of the electroanalytical process.

Thus, considering certain assumptions [19-21], we describe the behavior of the system through the set of three variables (5):

$$\begin{cases} \frac{dn}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(n_0 - n) - r_{11} - r_{12}\right) \\ \frac{dn*}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(n*_0 - n) - r_{21}\right) \\ \frac{dv}{dt} = \frac{1}{V}(r_{11} + r_{12} + r_{21} - r_r) \end{cases} \quad (5)$$

Where n and n* are the concentrations of the nitro and nitroso compounds in the pre-surface layer, Δ and D are their diffusion coefficients, n 0 and n* 0 are their concentrations inside the solution, v is the degree of coverage of the cathode by vanadium oxyhydroxide, V is its maximum surface concentration and the parameters r are the rates of the corresponding reactions, calculated according to (6 – 9):

$$r_{11} = k_{11}n(1-v)^6 \exp(-an) \qquad (6)$$

$$r_{12} = k_{12}n(1-v)^2 \exp(-an) \qquad (7)$$

$$r_{21} = k_{21}n*(1-v)^4 \exp(-bn*) \qquad (8)$$

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

where the parameters k are constants of the speeds of the respective reactions, the variables a and b describe the parameters, which relate the electrophysical properties of the DCE with the concentration of the analytes, F=N $_A$ *e is the Faraday number, $\varphi_0$is the potential jump, R is the universal gas constant, and T is the absolute temperature of the vessel.

In a slightly acidic environment, corresponding to the liquids in IQOS and electronic cigarettes, the nicotinic derivatives are ionized (which, truth be told, contributes greatly to the assimilation of nicotine by the human body), which increases the probability of the occurrence of oscillatory and monotonic instabilities. Despite the above, even in slightly acidic conditions, the electroanalytical process will be carried out efficiently, as explained below.

3. Results and Discussion

To investigate the behavior of the system with the electroanalytical detection of TNS and NQO, assisted by vanadium oxyhydroxide, we analyzed the set of differential equations (5), in addition to the algebraic relations (6 – 9) through the linear stability theory and bifurcation analysis. The stationary elements of the Jacobi functional matrix can be described as (10):

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

Where:

$$a_{11} = \frac{2}{\delta}\left(\frac{\Delta}{\delta} - k_{11}(1-v)^6 \exp(-an) + k_{11}n(1-v)^6 \exp(-an) - k_{12}(1-v)^2 \exp(-an) + ak_{12}n(1-v)^2 \exp(-an)\right) \qquad (11)$$

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

$$a_{13} = \frac{2}{\delta}(6k_{11}n(1-v)^5 \exp(-an) + 2k_{12}n(1-v) \exp(-an)) \qquad (13)$$

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

$$a_{22} = \frac{2}{\delta}\left(-\frac{D}{\delta} - k_{21}(1-v)^4 \exp(-bn*) + bk_{21}n*(1-v)^4 \exp(-bn*)\right) \qquad (15)$$

$$a_{23} = \frac{2}{\delta}(4k_{21}n*(1-v)^3 \exp(-bn*)) \qquad (16)$$

$$a_{31} = \frac{1}{V}(k_{11}(1-v)^6 \exp(-an) - k_{11}n(1-v)^6 \exp(-an) + k_{12}(1-v)^2 \exp(-an) - ak_{12}n(1-v)^2 \exp(-an)) \qquad (17)$$

$$a_{32} = \frac{1}{V}(k_{21}(1-v)^4 \exp(-bn*) - bk_{21}n*(1-v)^4 \exp(-bn*)) \qquad (18)$$

$$a_{33} = \frac{1}{V}\left(-6k_{11}n(1-v)^5 \exp(-an) - 2k_{12}n(1-v) \exp(-an) - 4k_{21}n*(1-v)^3 \exp(-bn*) - k_r \exp\left(-\frac{F\varphi_0}{RT}\right) + jk_r v \exp\left(-\frac{F\varphi_0}{RT}\right)\right) \qquad (19)$$

To avoid large expressions during the analysis of the Jacobian, we introduce new variables and rewrite the determinant of the matrix as (20):

$$\frac{4}{\delta^2 V}\begin{vmatrix} -\kappa-\Xi & 0 & \Sigma \\ 0 & -\lambda-\Lambda & T \\ \Xi & \Lambda & -\Sigma-T-\Omega \end{vmatrix} \tag{20}$$

Opening the parentheses and exchanging the signs for opposites, we obtain the value of the negative determinant as (21):

$$\kappa(\lambda\Sigma+\lambda T+\lambda\Omega+\Lambda\Sigma+\Lambda\Omega)++\Xi(\lambda T+\lambda\Omega+\Lambda\Omega)\begin{cases} >0, stable\ steady-state \\ =0, detection\ limit \end{cases} \tag{21}$$

If –Det J>0, the Routh-Hurwitz stability criterion comes into effect, corresponding to the stability of the stable, steady state, which, in the absence of side reactions capable of compromising the stability of the analyte and the cathode modifier, corresponds to the linearity of the function between the current and the concentration, providing an effective reading of the analytical signal.

This criterion will be guaranteed to be satisfied if the kinetic parameters of the chemical and electrochemical reactions Ξ, Λ, Ω have positive values (the remaining parameters, present in conditions (21), always have positive values). In fact, if we assume that the mentioned variables have positive values, which happens in the overwhelming majority of cases, the total value of the expression on the left-hand side will shift towards more positive numbers, thus stabilizing the system. This will correspond to the electroanalytical system, controlled both by diffusion and by the kinetics of the analyte reaction, with the process being more diffusional in a medium close to neutral and more kinetic in a slightly acidic medium.

If –Det J = 0, the detection limit will be formed, corresponding to the *monotonic instability*, serving as a margin between the stable and unstable stationary states. At this point, for the system, there are several stationary states, each one unstable, from which the system chooses one. This is destroyed when the system conditions change, and, unlike a stable stationary state, it does not recover, exchanging itself for another, which is also unstable.

The *oscillatory instability* in this system is likely to occur in the case of the Hopf bifurcation. This bifurcation can occur if the elements of the main diagonal of the Jacobian matrix contain positive addends, which describe the positive return connection.

Analyzing the members of the matrix (9), (13), and (17), it is possible to conclude that this instability is possible and can occur through the (co)action of two factors, including the influences of the electrochemical stage on the DCE, described by the positivity of the element $jk_r v\exp\left(-\frac{F\varphi_0}{RT}\right)>0$, if j>0 and those of the chemical steps on the electrophysical properties of the DCE, described by the positivity of the elements $k_{11}n(1-v)^6\exp(-an)>0$, $ak_{12}n(1-v)^2\exp(-an)>0$and $bk_{21}n*(1-v)^4\exp(-bn*)>0$, if a>0 and b>0.

These oscillations are observed in the parametric topological region, far from the detection limit. Furthermore, both theoretical calculations and experimental data confirm that the amplitude and frequency of the oscillations are strongly dependent on the composition of the supporting electrolyte, whose ions also participate in the formation and function of the DCE. At pH values closer to the neutral medium, a=b=0, and the elements containing a and b as the main multiplier annihilate each other, leaving only one factor of the oscillatory behavior and expanding the stable steady-state topological zone. Thus, although the sensor continues to be efficient in slightly acidic media, neutralization of the medium is viable to improve the effectiveness of the electroanalytical process.

4. Conclusions

From the theoretical analysis of the electroanalytical process of detecting tobacco-specific nitrosamines and 4-nitroquinoline oxide, it was possible to conclude that in the present process, the catalytic action of vanadium (III) oxyhydroxide facilitates the achievement and maintenance of the stable, steady state in this system. The electrochemical process is controlled by diffusion and kinetic factors, the impact of the latter being greater in more acidic environments. Oscillatory behavior is possible in this system. It is caused by periodic effects on the structure of the electric double layer. The amplitude and frequency of the oscillations will depend on the composition of the supporting electrolyte. In order to improve the electroanalytical response of the sensor and, therefore, the sensitivity and ease of interpretation of the analytical signal, the use of a neutral medium is recommended.

Author Contributions

Conceptualization, V.V.T.; T.V.M.; P. I. Y; Z.O.K.; Y.G.I.; L.N.N.; N.M.S.; J.I.F.P.M.; methodology, V.V.T.; N.M.S.; Y.G.I.; P.I.Y.; L.N.N.; T.V.M.; J.I.F.P.M. .validation, V.V.T.; T.V.M.; N.M.S.;.L.V.R.; Y.G.I.; P.I.Y.; Z.Z.Y.; V.M.O.; M.P.K.; R. S.; D.M.M.; B.S.S.; L.N.N.; I.O.M.G.; M.J.M.; J.R.G.; J.I.F.P.M.; Z.O.K.; F.S.J.; U.G.M.; I.M.K.; L.O.K.; N.A. S.; N.M.K.; V.O.K. .; formal analysis, V.V.T.; T.V.M.; N.M.S.;.L.V.R.; Y.G.I.; P.I.Y.; Z.Z.Y.; V.M.O.; M.P.K.; R. S.; D.M.M.; B.S.S.; L.N.N.; I.O.M.G.; M.J.M.; J.R.G.; J.I.F.P.M.; Z.O.K.; F.S.J.; U.G.M.; I.M.K.; L.O.K.; N.A. S.; N.M.K.; V.O.K. investigation, V.V.T.; T.V.M.; N.M.S.;.L.V.R.; Y.G.I.; P.I.Y.; Z.Z.Y.; V.M.O.; M.P.K.; R. S.; D.M.M.; B.S.S.; L.N.N.; I.O.M.G.; M.J.M.; J.R.G.; J.I.F.P.M.; Z.O.K.; F.S.J.; U.G.M.; I.M.K.; L.O.K.; N.A. S.; N.M.K.; V.O.K. resources, L.V.R.; Y.G.I.; P.I.Y.; Z.Z.Y.; V.M.O.; M.P.K.; R. S.; D.M.M.; B.S.S.; L.N.N.; I.O.M.G.; M.J.M.; J.R.G.; J.I.F.P.M.; Z.O.K.; F.S.J.; U.G.M.; I.M.K.;. data curation, V.V.T.; T.V.M.; N.M.S.;.L.V.R.; Y.G.I.; P.I.Y.; Z.Z.Y.; V.M.O.; M.P.K.; R. S.; D.M.M.; B.S.S.; L.N.N.; I.O.M.G.; M.J.M.; J.R.G.; J.I.F.P.M.; Z.O.K.; F.S.J.; U.G.M.; I.M.K.; L.O.K.; N.A. S.; N.M.K.; V.O.K. writing—original draft preparation, V.V.T.; T.V.M.; N.M.S.;. J.I.F.P.M.; Z.O.K.;. writing—review and editing, V V.V.T.; T.V.M.; N.M.S.;.L.V.R.; Y.G.I.; P.I.Y.; Z.Z.Y.; V.M.O.; M.P.K.; R. S.; D.M.M.; B.S.S.; L.N.N.; I.O.M.G.; M.J.M.; J.R.G.; J.I.F.P.M.; Z.O.K.; F.S.J.; U.G.M.; I.M.K.; L.O.K.; N.A. S.; N.M.K.; V.O.K. ; visualization, M.V.K,; Y.G.I.; T.V.M.; P. I. Y; Z.O.K.; V.V.K.; K.V.B.; M.P.Z.; O.P.M..;J.I.F.P.M.;J.R.G..; P.I.Y; T.V.V.; J.I.F.P.M.; S.C.O.; J.R.G. supervision. M.V.K,; Y.G.I.; T.V.M.; P. I. Y; Z.O.K.; V.V.K.; K.V.B.; M.P.Z.; O.P.M..;J.I.F.P.M.;J.R.G..; P.I.Y; T.V.V.; J.I.F.P.M.; S.C.O.; J.R.G. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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