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Voltammetric Determination of Dissolved Nitrous Oxide

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The platinum disk electrode has been tested as a working electrode for the cathodic reduction of N_2O in aqueous solutions using 0.2 M K_2SO_4 as supporting electrolyte, buffered at pH = 12, and a scan rate of 100 mV s^{-1}. The well-resolved cathodic peaks were observed for the solutions of N_2O in the concentration range of 0 – 10.34 mM. A strong linear correlation was seen between the cathodic peak current and N_2O concentration. The detection limit of the developed method amounts to $c(N_2O)$ = 0.0104 mM, and the quantification limit amounts to $c(N_2O)$ = 0.0191 mM. The error of these determination methods was between 4.0 and 5.1 % for higher N_2O concentrations ($c(N_2O) > 1$ mM) and 7.4 to 12.3 % for N_2O concentrations below 0.5 mM. The presence of O_2 and CO_2 did not influence the determination of N_2O in solution.

Keywords: Nitrous oxide, platinum electrode, voltammetric determination, cathodic reduction, solution

1. INTRODUCTION

Under ambient conditions, nitrous oxide (N_2O, dinitrogen oxide, laughing gas) is a colorless, non-flammable, non-toxic gas, exhibiting a slightly sweet odor and taste. It is stable and chemically inert at ordinary temperatures. However, at elevated temperatures N_2O is a powerful oxidizer similar to molecular oxygen [1]. Decomposition to N_2 and ½ O_2 commences at around 600 ºC [2]. Most common synthetic pathways yielding N_2O involve controlled thermal (~220-250 ºC) decomposition of ammonium nitrate, reductive coupling of nitric oxide, and nitrate reduction during adipic acid production [2]. Naturally, N_2O is formed from microbial activity (nitrification and denitrification) in soils and aquatic systems (oceans). Also, trace amounts are found in the Earth's atmosphere. Atmospheric concentrations of N_2O are around 350 ppb and are increasing at a rate as high as 0.3 % per year [3]. Nitrous oxide has a negative impact on the atmosphere by causing ozone depletion contributing to global warming, and it is 300 times more persistent in the atmosphere than CO_2 [4]. It is therefore necessary to monitor, reduce, and control N_2O emission. Natural sources of N_2O comprise 70% of total atmospheric emission. Anthropogenic sources, which comprise 30% of total atmospheric N_2O emission, include agricultural soil management (excessive use of fertilizers), biomass burning, industrial processes, fossil fuel combustion, and wastewater treatment plants [5, 6].

With respect to different sources of N_2O and its forms (free or dissolved), it is necessary to develop detection methods that are fast and reliable. The methods most commonly used for N_2O detection and quantification include gas chromatography [7, 8] and IR spectroscopy [9-11]. Electrochemical methods of analysis are mostly developed for measuring dissolved N_2O in aqueous solutions and have major advantages such as rapidity, simplicity, sensitivity, and relatively low cost [12].

Electroreduction of nitrous oxide has been investigated in various types of noble metal working electrodes (platinum, gold, and silver) using various supporting electrolytes (KCl, KOH, NaOH; K_2SO_4), and over a wide potential range (from -0.6 to -1.6 V) [1, 13-19]. A few authors describe the use of modified commercially available Clark electrodes for N_2O amperometric measurements [14, 15, 17]. Andersen et al. developed a commercially available electrochemical microsensor for N_2O quantification in aqueous media[19].

In this study, we investigated the electrochemical reduction of N_2O in aqueous solutions on the platinum disk electrode.

2. EXPERIMENTAL

2.1. Reagents and materials

All reagents were of analytical grade and were used without further purification. Stock solutions of supporting electrolytes were prepared with high purity water from a Millipore Milli-Q system (resistivity greater than or equal to 18 MΩ cm). Reagents used for stock solutions were obtained from Kemika (Zagreb, Croatia) and are as follows: K_2SO_4 (c = 0.5 M), NaOH (c = 5.0 M), KOH (c = 2.0 M), KCl (c = 2.5 M), KNO_3 (c = 0.1 M), NaH_2PO_4 (c = 0.25 M), Na_2HPO_4 (c = 0.25 M), and Na-ascorbate (c = 0.5 M).

Different compositions and concentrations of supporting electrolytes were obtained by diluting and combining the abovementioned stock solutions. The pH of the supporting electrolytes was adjusted using KOH and NaOH stock solutions as well as commercial buffer solutions (pH = 4, 7, 8, 9) obtained by Metrohm (Switzerland). Gaseous N_2O and Ar (Messer Griesheim, Germany), both of purity 5.0, were used for the preparation of saturated N_2O solution and for sparging (Ar) when investigating interferences.

2.2. Apparatus and measurements

All electrochemical measurements were performed using a EA164 Quad Stat software controlled four-channel potentiostat (eDAQ, Denistone East, NSW, Australia), and a 821 e-corder (eDAQ) unit was used for collection, display and analysis of signals. A conventional three-electrode system was used for voltammetric measurments consisting of platinum disk (2 mm in diameter) working electrode, Ag/AgCl reference electrode, and a platinum plate was used as the counter electrode.

2.3. Procedure

Cyclic voltammetry was used to investigate the influence of ionic strength, pH, and scan rate on the shape, height, and shift of voltammetric wave. Cyclic voltammetric experiments were performed at a polarization voltage range of ± 1.0 V.

Linear sweep voltammetry was used for measuring dissolved N_2O in model solutions. All electrochemical experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

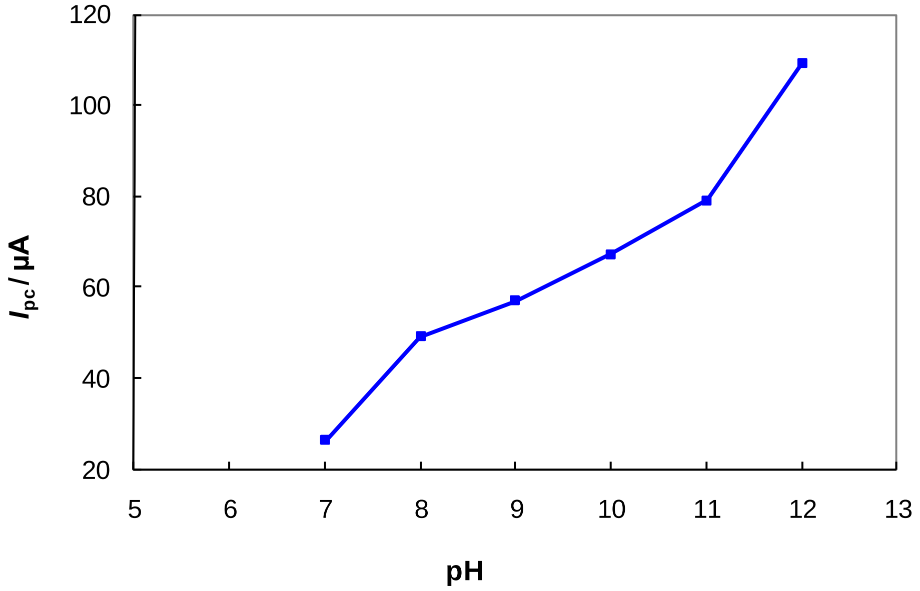
3.1. Selection of supporting electrolyte

A number of supporting electrolytes were tested including the following: K_2SO_4 (at 4 concentration levels, c = 0.05, 0.1, 0.2 and 0.3 M), KOH (c = 1 M), KCl (c = 0.5 M) + KOH (c = 0.5 M), KCl (c = 0.1 M), NaH_2PO_4 (c = 0.1 M) + Na_2HPO_4 (c = 0.1 M), KNO_3 (c = 0.1 M), and K_2SO_4 + Na-ascorbate. In general, a somewhat higher sensitivity and better peak shape was obtained in K_2SO_4 solutions. A significant increase in cathodic peak current was observed when concentrations of supporting electrolytes were increased in the range of c(K_2SO_4) = 0.05 - 0.2 M, whereas further concentration increases (from 0.2 to 0.3 M) did not significantly affect the cathodic peak current. Because electrolytes added to N_2O water solution depress its solubilty [2], 0.2 M K_2SO_4 was chosen as the supporting electrolyte for the rest of the measurements.

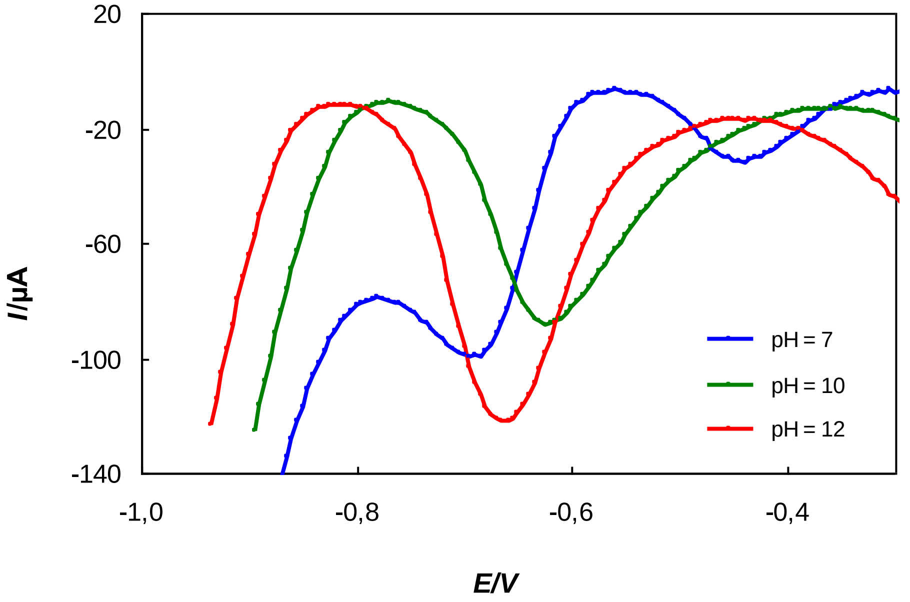
3.2. Influence of pH

The influence of pH on the response of N_2O at the platinum electrode was investigated at pH = 4, 7, 8, 9, 10, 11, and 12. The results show that the peak currents increased with increasing pH, whereas the cathodic peak shifted to more negative potential values (Figure 1).

The characteristic N_2O cathodic peak was not observed below pH = 7, which is in agreement with the previous investigations [1, 13, 15, 16, 18, 19] claiming that N_2O electrochemical reduction occurs only in strong alkaline media. Therefore, the solution of K_2SO_4 at pH = 12 has been used as the supporting electrolyte for further investigations.



A)



B)

Figure 1. The influence of pH of the supporting electrolyte on a) the peak current response b) the response of N_2O at the platinum disk working electrode, $c(N_2O)$ = 7.76 mM, $c(K_2SO_4)$ = 0.2 M, v = 100 mV s^{-1}

3.3. Effect of scan rate

The effect of scan rate on the N_2O response (c = 5.17 mM) was investigated using cyclic voltammetry at scan rates v = 10, 20, 40, 50, 80 and 100 mV s^{-1}. The dependence of the cathodic peak current on the square root of the scan rate is shown in Figure 2. It can be seen that a linear correlation exists between variables in the scan rate range of 10 to 100 mV s^{-1} (R^2 = 0.9834). The linearity is expected for diffusion-controlled reduction processes. The intercept on the Y-axis indicates that processes apart from diffusion influence N_2O reduction [20]. This is in accordance with former investigations indicating that N_2O reduction at platinum electrode is carried out also by an adsorption process [1, 18].

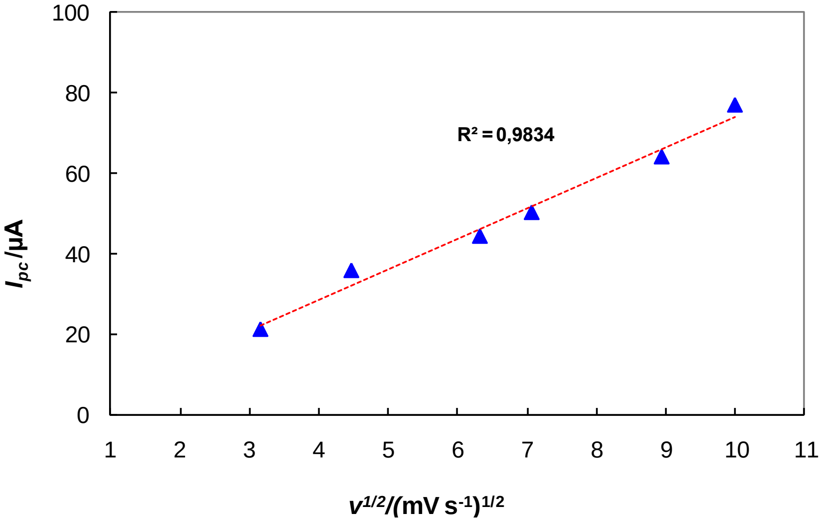


Figure 2. Dependence of the cathodic peak current on the square root of the scan rate, $c(N_2O)$ = 5,17 mM, $c(K_2SO_4)$ = 0.2 M, pH = 12.

The cyclic voltammograms of N_2O solutions, shown in Figure 3, perfomed at scan rates v = 10, 50, and 100 mV s^{-1} indicate an increase of cathodic peak current with an increasing scan rate. At the same time, the cathodic peak potentials shifted toward more negative potential values, which indicates irreversible electrochemical reactions.

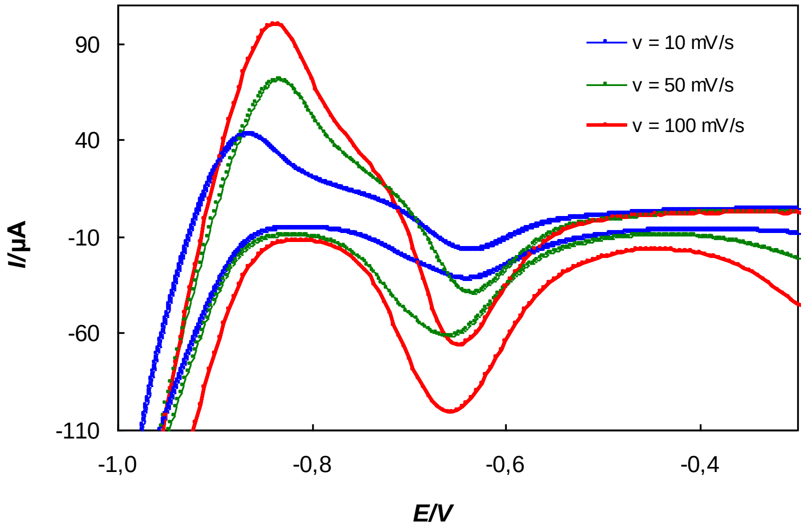


Figure 3. The effect of scan rate on the response of N_2O at the platinum disk electrode, $c(N_2O)$ = 5.17 mM, $c(K_2SO_4)$ = 0.2 M, pH = 12, v = 10, 50, and 100 mV s^{-1}.

3.4. Interferences

Generally, the interfering agents are all reducing agents and species that can be electrochemically reduced on the platinum electrode at potentials close to the reduction potential of N_2O. Carbon dioxide does not interfere because the measurements are performed in strong alkaline media, where CO_2 is easily converted to CO_3^{2-}. Oxygen does not influence the N_2O determination because its peak separation potentials on the platinum electrode are sufficiently different from those of N_2O. This was confirmed by performing the measurements in oxygen-free distilled water, which was obtained by the sparging of distilled water with argon. Nitric oxide (NO) ,due to its short half-life and high reactivity, is rarely found in a free form. Also, it is easily oxidized, appearing in aqueous absorbtion media as nitrite and nitrate, and it is detected by various methods. Nitrogen dioxide (NO_2) hydrolyzes with disproportionation to give nitric acid. Ascorbic acid seriously disturbs determination of N_2O and must be absent in the solution to be analyzed.

3.5. Determination of N_2O

3.5.1. Response characteristics of the platinum electrode

The determination of N_2O in aqueous solutions using the platinum disk electrode was accomplished by linear sweep voltammetry (LSV), and the corresponding voltammograms are shown in Figure 4.

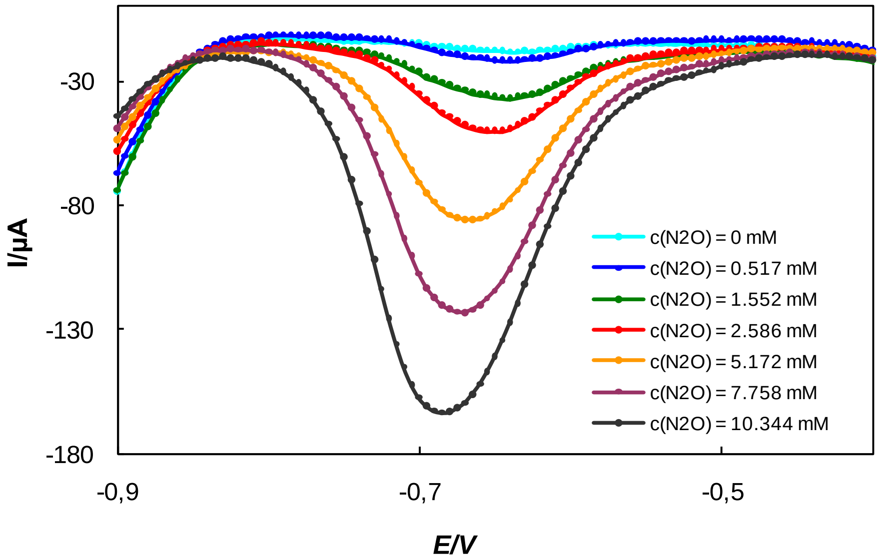


Figure 4. LSV of N_2O solutions of different concentrations, $c(N_2O) = 0 – 10.34$ mM, $c(K_2SO_4) = 0.2$ M, pH = 12, $v = 100$ mV s^{-1}.

Well-resolved cathodic peaks are obtained for the solutions of N_2O in the concentration range $c(N_2O) = 0 – 10.34$ mM. The calibration curve displaying the dependence of cathodic peak current against N_2O concentration is shown in Figure 5. The strong linear correlation is seen between the cathodic peak current and N_2O concentration in the above concentration range defined by the following equation:

$I_{pc} = 2.19 – 14.12 \times c(N_2O)$

where I_{pc} is cathodic peak current (μA), $c(N_2O)$ is the concentration of dissolved N_2O (mM).

The regression statistics of LSV responses of platinum electrode toward the solutions of N_2O for the above concentration range is shown in Table 1.

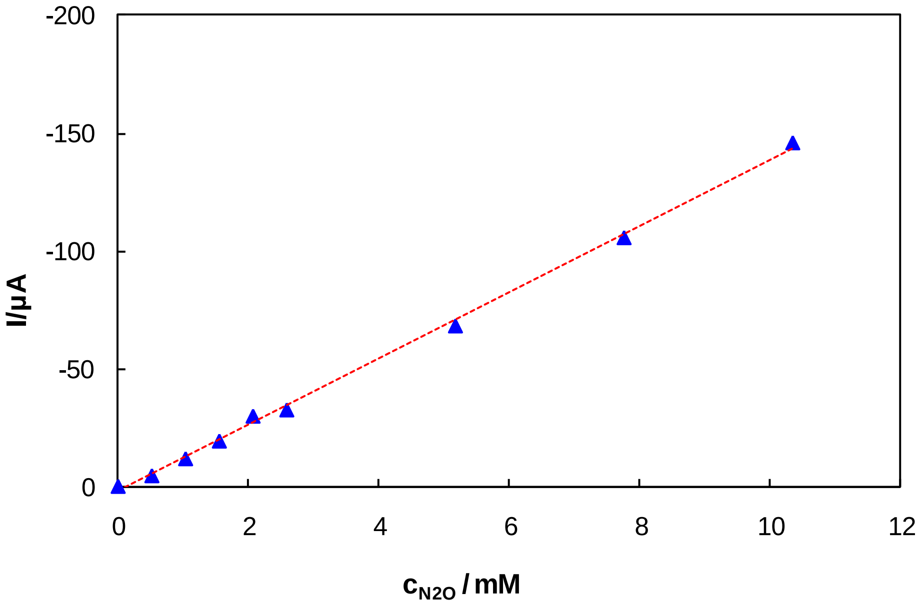


Figure 5. The response currents of the platinum electrode towards the solutions of different N_2O concentrations using linear sweep voltammetry $c(K_2SO_4) = 0.2$ M, pH = 12, $v = 100$ mV s^{-1}.

Table 1. Regression statistics of the platinum electrode LSV responses in the solutions of different N_2O concentrations, $c(N_2O) = 0 – 10.34$ mM, $c(K_2SO_4) = 0.2$ M, pH = 12, $v = 100$ mV s^{-1}.

Parameters	Values
Slope (S)	-14.12
SE_S	0.21
CI_S (p = 0.05)	0.50
Intercept (I)	2.19
SE_I	1.01
CI_I (p = 0.05)	2.39
Correl. Coef. R^2	0.9985

SE = standard error *CI* = confidence interval

To determine the sensitivity, detection, and quantification limits of these N_2O measurements, the response characteristics of the platinum electrode was specifically investigated in the lower N_2O concentration regions (*c*(N_2O) = 0 – 0.517 mM). The resulting LSV responses are shown in Figure 6, and the related calibration curve is shown in Figure 7.

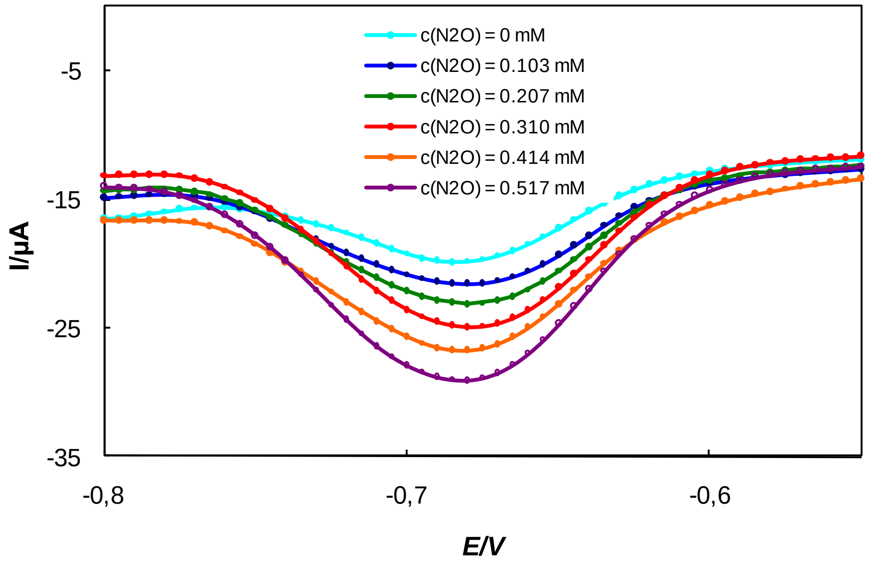


Figure 6. LSV of N_2O solutions of different concentrations, *c*(N_2O) = 0 – 0.517 mM, *c*(K_2SO_4) = 0.2 M, pH = 12, *v* = 100 mV s^{-1}.

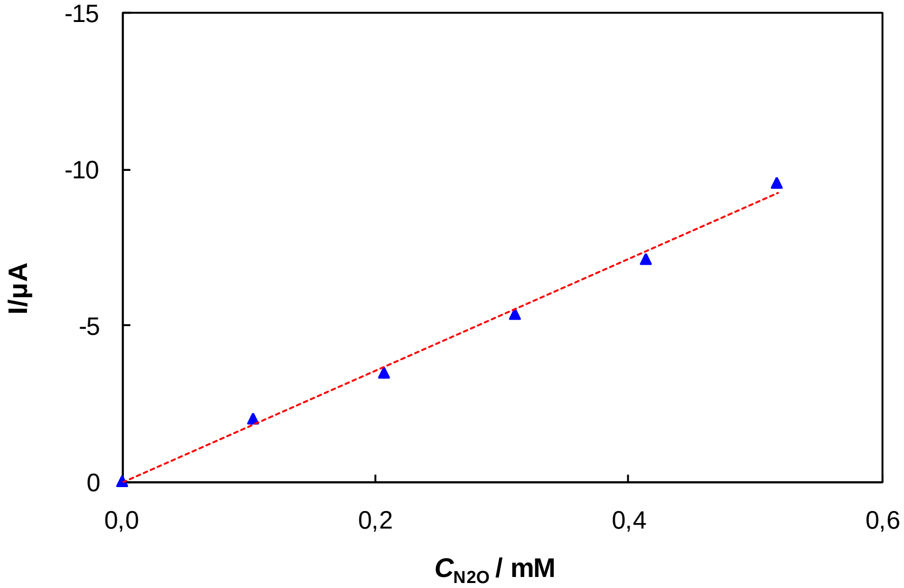


Figure 7. The LSV response characteristics of the platinum electrode towards the solutions of lower N_2O concentrations, *c*(N_2O) = 0 – 0.517 M, *c*(K_2SO_4) = 0.2 M, pH = 12, *v* = 100 mV s^{-1}.

The corresponding regression statistics are shown in Table 2. There is a linear correlation between cathodic peak current and lower N_2O concentration defined by the following equation:

$$I_{pc} = 0.12 - 18.14 \times c(N_2O)$$

The detection and quantification limit of the developed method amounted to $c(N_2O) = 0.0104$ mM and $c(N_2O) = 0.0191$ mM, respectively.

Table 2. Regression statistics of the platinum electrode responses towards the solutions of lower N_2O concentrations using LSV, $c(N_2O) = 0 - 0.517$ mM, $c(K_2SO_4) = 0.2$ M, pH = 12, $v = 100$ mV s^{-1}.

Parameters	Values
Slope (S)	-18.14
SE_S	0.92
CI_S (p = 0.05)	2.92
Intercept (I)	0.12
SE_I	0.31
CI_I(p = 0.05)	1.00
Correl. Coef. R^2	0.9924

SE = standard error *CI* = confidence interval

3.5.2. Accuracy of the determination

The accuracy of the voltammetric N_2O determination using the developed method was tested by the standard addition method. The results are shown in Table 3. The obtained recoveries can be considered as satisfactory for the determination of gaseous samples, such as N_2O, with an error between 4.0 and 5.1 % for higher concentrations ($c(N_2O) > 1$ mM). For the N_2O concentrations below 0.5 mM, deviations from the true values totalled 7.4 to 12.3 % (for the lowest concentration measured, $c(N_2O) = 0.103$ mM). The confidence interval given in Table 3 relates to 95% confidence level.

Table 3. The results and statistics of the voltammetric N_2O determination.

Added (mM)	**Found (mM)**	**Recovery* (%)**	**Stand. dev.**	**Confid. interval**
0.103	0.116	112.3	0.010	± 0.008
0.310	0.287	92.6	0.013	± 0.012
0.517	0.485	93.7	0.019	± 0.017
1.034	0.987	95.5	0.029	± 0.026
2.586	2.455	94.9	0.045	± 0.040
5.172	4.967	96.0	0.064	± 0.056

* average values of 5 measurements

4. CONCLUSIONS

Cyclic voltammetry was used to investigate the electrochemical behavior of N_2O at a platinum disc electrode. The optimum supporting electrolyte was selected. The influence of pH and scan rates on the magnitude and position of the cathodic reduction peak was investigated. The platinum N_2O electrode was characterized by linear sweep voltammetry, and the linear response region, the detection and quantification limits were determined. The presence of O_2 and CO_2 did not influence the determination of N_2O in solutions.

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