



The electrochemical determination of formaldehyde in aqueous media using nickel modified electrodes

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ABSTRACT

Glassy carbon (GC) electrodes were modified with nickel metal via a simple deposition procedure, followed by enrichment of the nickel in a potassium hydroxide solution to deliver the catalytic nickel hydroxide species (Ni(OH)₂). In solutions of 1 M KOH, the nickel modified GC electrode (Ni-GC) contained a reproducible detection limit of the order of 1.1×10^{-5} M for formaldehyde additions. This is comparable and, in many cases, surpasses, platinum group metal modified electrodes. The potentiometric analytical method also allowed for the accurate determination of “unknown” formaldehyde concentrations, over a linear range of 1×10^{-5} – 1×10^{-3} M and a sensitivity of $22.7 \pm 3.8 \mu\text{A}/\text{mM}$. Furthermore, the Ni-GC electrode showed negligible response to formate and methanol, even when they were present in concentrations 10 times greater than the formaldehyde. The electrochemical performance was compared to a simple colorimetric approach to formaldehyde determination, wherein a detection limit of 6×10^{-6} M was obtained.

1. Introduction

Formaldehyde is used worldwide in large quantities as a raw material in the production of chemicals and plastics manufacturing, as well as in various household products [1]. This extensive industrial and domestic usage means that it is present in workplace air spaces, industrial waste materials, and also a prevalent contaminant in ground water due to dumpsite leaching [1–3]. Formaldehyde is also a potential product in the electrocatalytic conversion of CO₂ to produce useful hydrocarbon synthetic fuels, such as methanol and methane, directly from renewable electricity [4]. The complex multi-proton, multi-electron reduction of CO₂ yields an array of small organic products; the first three water-soluble products being formate, formaldehyde and methanol [4]. A simple, selective and effective means of identifying and quantifying these small organic molecules, in a typically complex reaction medium, is a fundamental issue [5] – most notably for formaldehyde [6–8]. Developing methods to selectively, accurately and rapidly identify and quantify these products would therefore be of great advantage to CO₂ reduction research, not to mention a valuable analytical development in wastewater treatment and analysis [9,10].

Varieties of analytical strategies exist to determine formaldehyde, with emphasis typically being on the determination of gas phase formaldehyde. Of the liquid phase determinations, the most notable technique is the derivatization of the carbonyl compound with 2,4-

dinitrophenylhydrazine (2,4-DNPH). This compound is commonly known to produce Brady's reagent for the qualitative determination of aldehydes. It is also the reagent stipulated by the U.S. Environmental Protection Agency [11] to be used quantitatively in conjunction with high performance liquid chromatography (HPLC). The analytical method requires a lengthy derivatization process and the use of reversed-phase (RP-HPLC) [4,11,12]. The approach is the analytical state-of-the-art, and obtains detection limits of 10^{-10} M in an optimized system [13]. However, recent safety concerns have rendered this technique a somewhat problematic approach to formaldehyde determination, due to the flammable and explosive properties of the 2,4-DNPH when allowed to dry out in poor storage conditions. Consequently, purchasing the solid reagent is now difficult.

Similar to the 2,4-DNPH derivatization method, a lesser reported derivatization approach which is solely spectrophotometric is the adapted Hantzsch reagent method reported by Nash [14]. This approach uses the reaction between formaldehyde and acetylacetone, acetic acid and ammonium acetate to form diacetyldihydrolutidine (DDL), a yellow derivative of the formaldehyde with a high extinction coefficient.

Electrochemical approaches would better suit quantification of the complex electrolyte expected of CO₂ reduction samples. Such samples are unsuitable for chromatographic machinery, and sample preparation would potentially cause sample loss. A small body of research exists in

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the field of electrochemical formaldehyde determination, with approaches typically using platinum [15,16], palladium [17–21] or gold [22] electrocatalysts. Typically these studies are conducted in sulfuric acid or sodium hydroxide solution, and use various nanoarchitectures and complex fabrication methods in their design. Detection limits are typically of the order of 10^{-5} M, though some palladium electrodes have been reported to determine formaldehyde concentrations as low as 10^{-11} M [16].

Nickel modified electrodes in alkaline solution are well-known catalysts towards small organic molecules. The Ni(III) species in the oxidised NiOOH readily reacts with organic compounds, oxidizing the organic analyte and reforming the Ni(OH)₂ species [23–26]. Despite the wealth of literature utilizing the Ni(OH)₂ redox catalyst in alcohol and glucose oxidation [27–29], very few researchers have considered the electrochemical oxidation of formaldehyde. Of the few that have [30–32] their focus has been on large concentrations in fuel cell assessment, as opposed to being used for formaldehyde detection [33]. As one would expect, the nickel catalyst strongly responds to the presence of formaldehyde. This is to be expected, as the formaldehyde forms a gem diol in water, and such polyol species are highly responsive to the nickel catalyst [26].

Here in we report a simple, low cost nickel modified glassy carbon electrode and its application to formaldehyde determination. For parity, the analysis of formaldehyde by a spectrophotometric method is also discussed, and the merits and disadvantages of the two techniques considered.

2. Experimental

2.1. Reagents and equipment

Ammonium acetate, acetic acid, sodium acetate, and acetylacetone were reagent grade from Sigma Aldrich (UK) and used as received. Ni(NO₃)₂ was purchased from Sigma Aldrich (UK) and KOH was purchased from Fisher Scientific. All solutions were prepared using Milli-Q® ultrapure water of resistivity 18.2 MΩ cm.

The formaldehyde additions were made using a standardized formaldehyde stock solution. Formaldehyde (HCOH) was purchased from ACROS Organics (37 > wt%, stabilized with 5–15% methanol). A 0.05 M stock solution was prepared for use in electroanalytical experiments using Milli-Q® ultrapure water. The stock was standardized following the US EPA Method 554 [34]. Anhydrous sodium sulfite (98%) and hydrochloric acid (37%) were purchased from Sigma Aldrich (UK) and used as received.

To determine formaldehyde concentrations in a real water sample, pond water was obtained from the university campus, filtered to 0.45 μm, and spiked with a volume of formaldehyde stock solution.

Prior to use, all glassware was soaked for 8 h in 3 M hydrochloric acid followed by 3 rinses with Milli-Q® ultrapure water (18.2 MΩ; organic carbon < 2 ppm). All electrochemical measurements were made using an Ivium EmSTAT 3+ (Alvatek, UK) in conjunction with the software PSTrace. The working electrodes were glassy carbon (3 mm ø), counter electrode was a platinum wire (CH Instruments, both purchased from IJ Cambria Scientific Ltd, UK), and a Ag/AgCl reference electrode (BASi, Alvatek, UK). UV–vis experiments were made using a Jenway 7315 Spectrophotometer.

2.2. Electrochemical method

The nickel modified glassy carbon (Ni-GC) electrode was fabricated via the electrodeposition of nickel at -1.3 V vs. Ag/AgCl from a 1 mM Ni(NO₃)₂ in 0.1 M acetate buffer deposition solution. The freshly polished GC electrode was held at potential from 30 or 600 s under constant stirring and under a nitrogen atmosphere. At higher deposition times a thin metal film was visible across the GC surface.

Following deposition, the Ni-GC electrode was removed from the

deposition solution, washed with Milli-Q® ultrapure water, and then placed in a 1 M KOH solution for conditioning. The electrode was cycled between 0.15 and 0.55 V in the alkaline medium ca. 200 times at a scan rate of 100 mVs⁻¹. This allowed for the crystalline phases of the Ni(OH)₂ to settle into the aged beta phase [23–26].

At a holding potential of ca. 0.46 V vs. Ag/AgCl, determined from cyclic voltammograms in the presence of formaldehyde, a potentiometric calibration plot was obtained over various linear ranges. In a standard three-electrode set-up, under constant, fast stirring, additions of formaldehyde were made to the 1 M KOH solution at intervals of 20–30 s. A calibration plot was then produced based on the average current of the time interval of each addition. The method was then repeated with formaldehyde-spiked pond water.

2.3. Spectrophotometric method

2.3.1. By UV detection

A six-point calibration was made diluting the 35% formaldehyde stock with Milli-Q® ultrapure water. Aqueous formaldehyde calibration standards were reacted with equal amounts of Hantzsch reagent containing 15% w/v ammonium acetate, 3% v/v acetic acid and 2% v/v acetyl acetone, heated for 30 min in a water bath at 40 °C and allowed to cool to room temperature (20 °C) for 30 min. The resultant yellow solution, 3, 5-diacetyl-dihydrolutidine (DDL) was then analysed by spectrophotometry at a wavelength of 412 nm.

2.3.2. Coupled with HPLC

Following reaction of the formaldehyde with the Hantzsch reagent, the DDL solution was transferred to a GC vial and complementary DDL determination was performed using HPLC. Samples were run on an Agilent 1220 HPLC (Hanover, Germany) fitted with an Agilent Poroshell 120 EC-C18 column (3.0 × 50 mm; 2.7 μm particle size), using a variable wavelength detector monitoring absorbance at 412 nm. 20 μL of sample was injected. The solvents were acetonitrile (B) and water (A).

3. Results and discussion

3.1. Electrochemical determination of formaldehyde

3.1.1. Nickel deposition and conditioning

In accordance to the method outlined in the experimental section, glassy carbon electrodes were modified with nickel films to produce a Ni-GC electrode. Optimisation of the deposition procedure found -1.3 V vs Ag/AgCl to be the best deposition potential, with a deposition time of 60 s. It was necessary to avoid the formation of bubbles (caused by the reduction of water) on the electrode surface to ensure a smooth deposition of nickel. Deposition for 300 s or more generated a relatively thick metal film on the electrode surface. Although the quantity of nickel was evidentially greater, the Ni-GC electrodes were found to be less durable to repetitive testing with more material.

Fig. 1 shows a typical cyclic voltammogram for the Ni-GC electrode in KOH solution on the first cycle after deposition, and the final, 200th cycle. The enrichment step is required with Ni-modified electrodes to ensure that the Ni(OH)₂ layer is formed and present in the stable β-crystalline structure [23–26]. The anodic shift and growth of the broad Ni(OH)₂ peak as the nickel oxidises to NiOOH is evident in Fig. 1. Approximately 200 cycles over the potential window ensured that the redox couple was stable and unchanging for the subsequent formaldehyde additions.

3.1.2. Calibration plots and detection limits

Fig. 2 shows an overlay of cyclic voltammograms (CVs) taken of the Ni-GC electrode with increasing additions of 0.5 mM formaldehyde. The electrocatalytic response to formaldehyde additions is evident in the forward scan, with the peak potential shown to shift positively with

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