



# Novel hydrazinium polyacrylate-based electrochemical gas sensor for formaldehyde



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## ABSTRACT

A disposable electrochemical sensor was developed for convenient detection of gaseous formaldehyde. The sensor is composed of a three-electrode screen printed system modified with hydrazinium polyacrylate which was synthesised to serve a dual purpose, i.e. as formaldehyde accumulation/derivatisation medium, and as polyelectrolyte enabling voltammetric measurements. It exhibited a linear response in the examined concentration range of 4–16 ppm gaseous formaldehyde in combination with 120 min accumulation; also sub-ppm concentration levels could be detected when the exposure time was extended.

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## 1. Introduction

Formaldehyde is considered as one of the most important (indoor) pollutants due to its high toxicity and potential carcinogenicity. Gaseous formaldehyde originates from a variety of different sources, such as industry (e.g. resin production), traffic, forest fires, and tobacco smoke. It can also be emitted from different objects, e.g. new furniture and polymeric materials undergoing the degradation process [1–3], thus it can be used as a marker molecule for material degradation.

The most common analytical method used for formaldehyde detection is its derivatisation with 2,4-dinitrophenylhydrazine combined with high-performance liquid chromatography and UV detection [4]. For gas-phase analysis formaldehyde is first collected at different sorptive media (e.g. in impingers, denuders or on solid sorbents), which contain or are impregnated with the derivatising agent [5]. Although this method is reliable and precise, it requires relatively expensive instrumentation and can only be performed in a laboratory environment. The development of novel formaldehyde detection approaches and sensors thus presents an attractive topic. The already existing sensors vary in the measurement principle ranging from spectrometric, piezoresistive and colorimetric to amperometric and conductometric [6], the latter being the most widely investigated; metal oxide films/nanostructured metal

oxides are commonly used in this case as sensing layers. Although relatively high sensitivity can be achieved using this methodology, its inherent drawbacks are the need for elevated temperatures and difficulties associated with measurements in humid environments [7,8]. To overcome the operation at high temperatures, conductive polymer-based sensing layers were introduced for detecting volatile organic compounds (VOCs), e.g. formaldehyde. Upon interaction with the polymer, the analyte alters the polymer's physical properties, manifesting in the change of conductivity or in the shift of transmission spectrum [8].

The formaldehyde gas sensors of different types, e.g. amperometric, conductometric and colorimetric, often involve the enzyme formaldehyde dehydrogenase [9–13]; however, due to potential issues with the stability of enzyme-based sensors, their use is not always appropriate for all environments/applications. The enzyme-free electrochemical sensors with improved performance are therefore emerging [14,15], although voltammetric formaldehyde gas sensors are still very rare. An interesting example was introduced by Gębicki [14], using a platinum working electrode, ionic liquid as the electrolyte, and a polydimethylsiloxane membrane to constitute a prototype gas sensor for formaldehyde.

In this work a new concept of a multipurpose polymeric sensing layer for room-temperature voltammetric detection of gaseous formaldehyde is introduced. A synthesised polymeric modification/sensing coating, which combines analyte accumulation capacity and its derivatisation via a well-known hydrazine-based reaction, and at the same time acts as the polymeric electrolyte enabling voltammetric measurements, was developed and studied

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to prepare a simple and inexpensive (disposable) sensor for gaseous formaldehyde detection.

## 2. Experimental

Commercially available screen printed electrodes were used as the substrate, with carbon working ( $d=4$  mm) and counter electrodes, and silver quasi-reference electrode (DropSens, Oviedo). The electrochemical cell was comprised of these three electrodes covered with an in-house synthesised sensing coating acting as the analyte accumulation/derivatisation medium and polymeric electrolyte. Two different polymers were used in this study, i.e. polyacrylic acid (PAA,  $M=450,000$  g mol<sup>-1</sup>, Aldrich) and hydrazinium polyacrylate (HPA), both 1% aqueous solutions. The three-electrode system was coated with 20  $\mu$ L of 1% HPA or PAA solution and dried overnight. All solutions used in this work were prepared using Milli-Q water ( $R=18.2$  M $\Omega$ ). Polyacrylic acid was used as received and dissolved in water. Hydrazinium polyacrylate was prepared in the laboratory by first dissolving polyacrylic acid in water and subsequently neutralising it with equimolar amount of hydrazine hydrate (50–60% N<sub>2</sub>H<sub>4</sub>, Aldrich).

Cyclic voltammetric measurements were carried out using Autolab PGSTAT 30 (Eco Chemie, Utrecht). Gaseous formaldehyde was prepared in flasks using formaldehyde solutions of corresponding concentrations obtained by water dilution of 37% formaldehyde (Merck, Darmstadt); concentration in the gas phase was calculated according to Henry's law [16].

Infrared spectra of polymer electrolytes were recorded with a Bruker model IFS 66/S after casting them on a silicon wafer from their aqueous solutions and drying. The spectra were recorded over the range of 4000–400 cm<sup>-1</sup>.

## 3. Results and discussion

Aldehydes are known to spontaneously react with hydrazine, forming different hydrazones, depending on the aldehyde in question. This reaction is of great importance in analytical chemistry for chromatographic analysis [4]; however, due to the C=N double bond, hydrazones can be electrochemically reduced to alkyl-hydrazines meaning that, e.g. formaldehyde derivatisation can be used beneficially in voltammetric detection protocol. In this work, hydrazine was integrated into an appropriate polymeric medium/electrolyte and used for simultaneous accumulation and derivatisation of formaldehyde, whereas the polymeric compound functioned also as the electrolyte. Since hydrazones are preferably reduced in an acidic environment, polyacrylic acid was selected as a simple proton conductive polymer, which does not react with formaldehyde on its own, excluding possible side reactions, but could be easily functionalised with hydrazine forming hydrazinium polyacrylate (HPA) and thus locking the hydrazine into the polymer structure via ionic bonding.

When the so-prepared sensor was exposed to gaseous formaldehyde, hydrazone species was formed in the polymeric electrolyte, which was then electrochemically reduced, displaying a reduction peak at ca. -0.6V, as can be seen in Fig. 1 (together with a background response). On the contrary, when the electrode was modified with sole polyacrylic acid, i.e. without the hydrazinium group, no signal could be observed for formaldehyde, as demonstrated in the inset of Fig. 1.

Characterisation of the synthesised polymeric material employed as the modification/sensing coating was carried out via recording the IR spectra of PAA and its hydrazinium counterpart HPA, as depicted in Fig. 2. A typical IR spectrum of PAA [17] (upper spectrum) was obtained with characteristic O–H bands at 3100, ~2590 and 850 cm<sup>-1</sup>; C–H bands at 2940, 1452 cm<sup>-1</sup>;

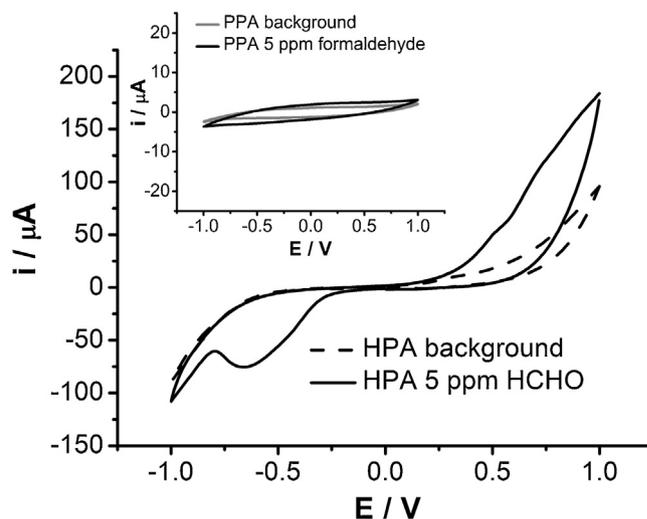


Fig. 1. Cyclic voltammograms recorded at the HPA-modified electrode in the absence (dashed line) and presence (solid line) of 5 ppm HCHO<sub>(g)</sub>; inset shows PPA-modified electrode under the same conditions; exposure time of 120 min, scan rate of 100 mV s<sup>-1</sup>.

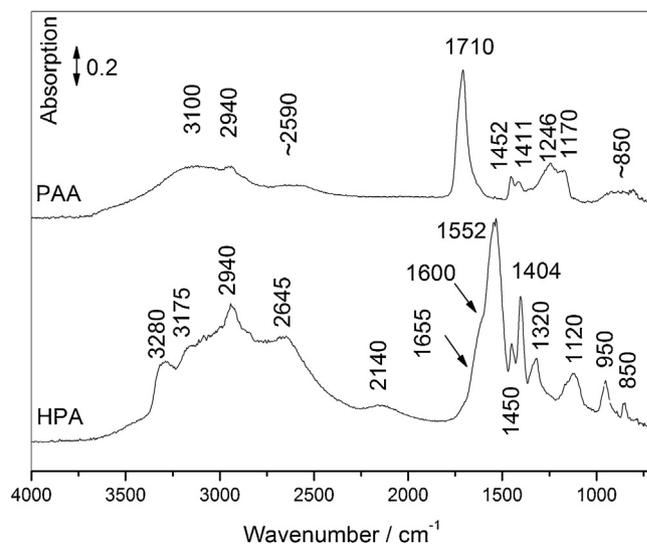
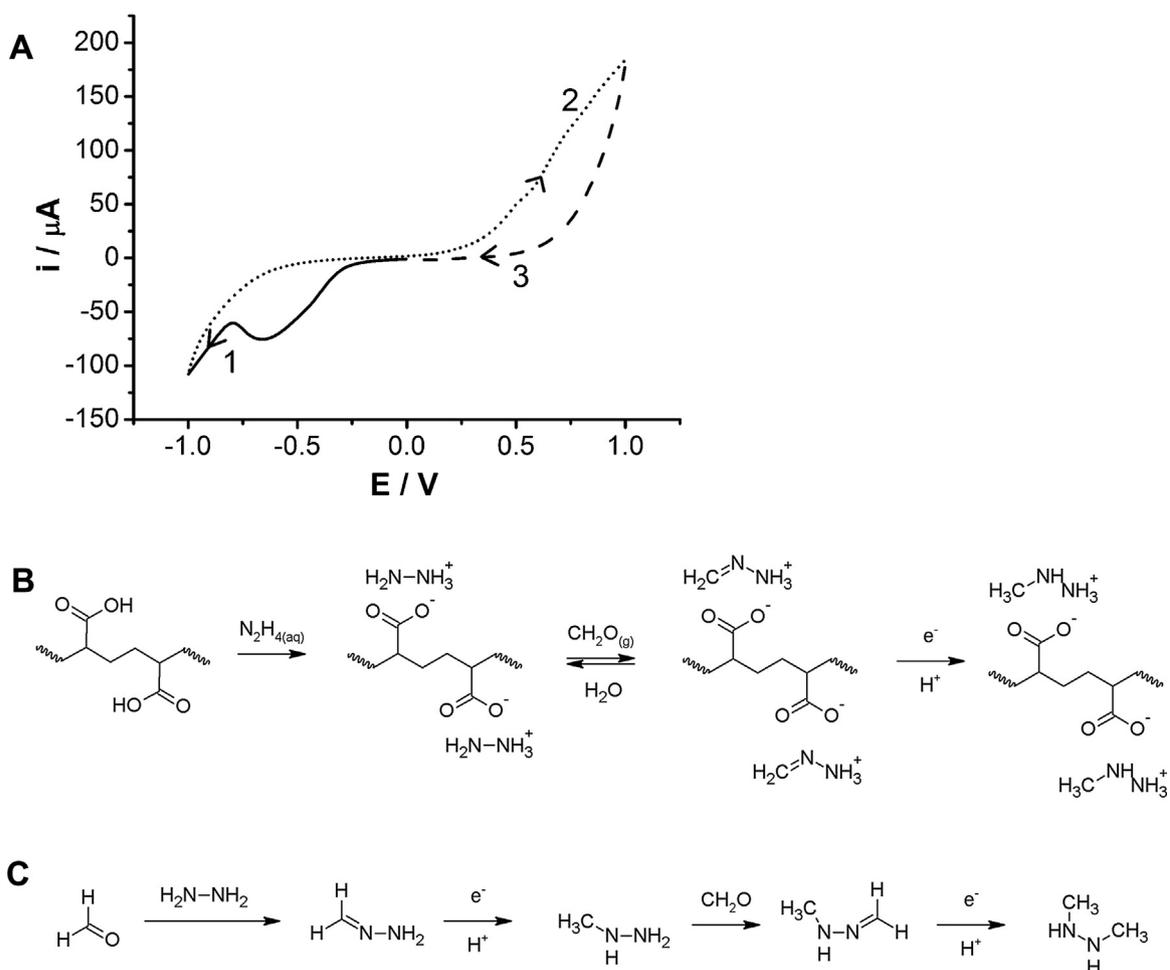


Fig. 2. IR spectra of polyacrylic acid and hydrazinium polyacrylate.

C=O stretching at 1710 cm<sup>-1</sup>, and different C–O bands at 1411, 1246, and 1170 cm<sup>-1</sup>. When an equimolar amount of hydrazine hydrate was added into the solution of PAA, a more complex IR spectrum emerged (bottom spectrum); it comprised several N–H bands at 3280, 3175, 1655, 1600, 1552, 1320, 1120, 950 and 850 cm<sup>-1</sup>; N–N bands at 1552 and 1140 cm<sup>-1</sup>; O–H bands at 2645 and 2140 cm<sup>-1</sup>; and C–H bands at 2940, 1450, 1404 cm<sup>-1</sup>. These bands are consistent with the previous IR spectroscopic studies of hydrazine [18], hydrazones [19] and hydrazinium carboxylates [20].

To investigate and optimise the electroanalytical performance of the novel gas sensor, the potential range of voltammetric scans was examined through following the hydrazone reduction signal in the presence of formaldehyde. The potential range was varied from -1.0V to 0.0V up to -1.0V to (+1.5) V in 0.25V increments starting at 0.0V with the first vertex potential maintained at -1.0V (Fig. 3A, step 1). In the case of scanning in the range of -1.0V to 0.0V, a strong signal of formaldehyde (i.e. hydrazone reduction) was recorded only during the first cathodic scan, and disappeared during the second scan; however, the signal increased



**Fig. 3.** Cyclic voltammetric steps: (1) solid line – scan from 0.0V towards the first vertex potential of  $-1.0$  V, i.e. detection scan with formaldehyde signal recorded at ca.  $-0.6$  V; (2) dotted line – anodic scan from  $-1.0$  V to the second vertex potential, which was optimised in the range of 0.0 V to  $+1.5$  V; (3) dashed line – scan from the second vertex potential back to 0.0 V (A); proposed mechanisms of the reaction between formaldehyde and hydrazine taking place in the polymer (B) and in the solution (C).

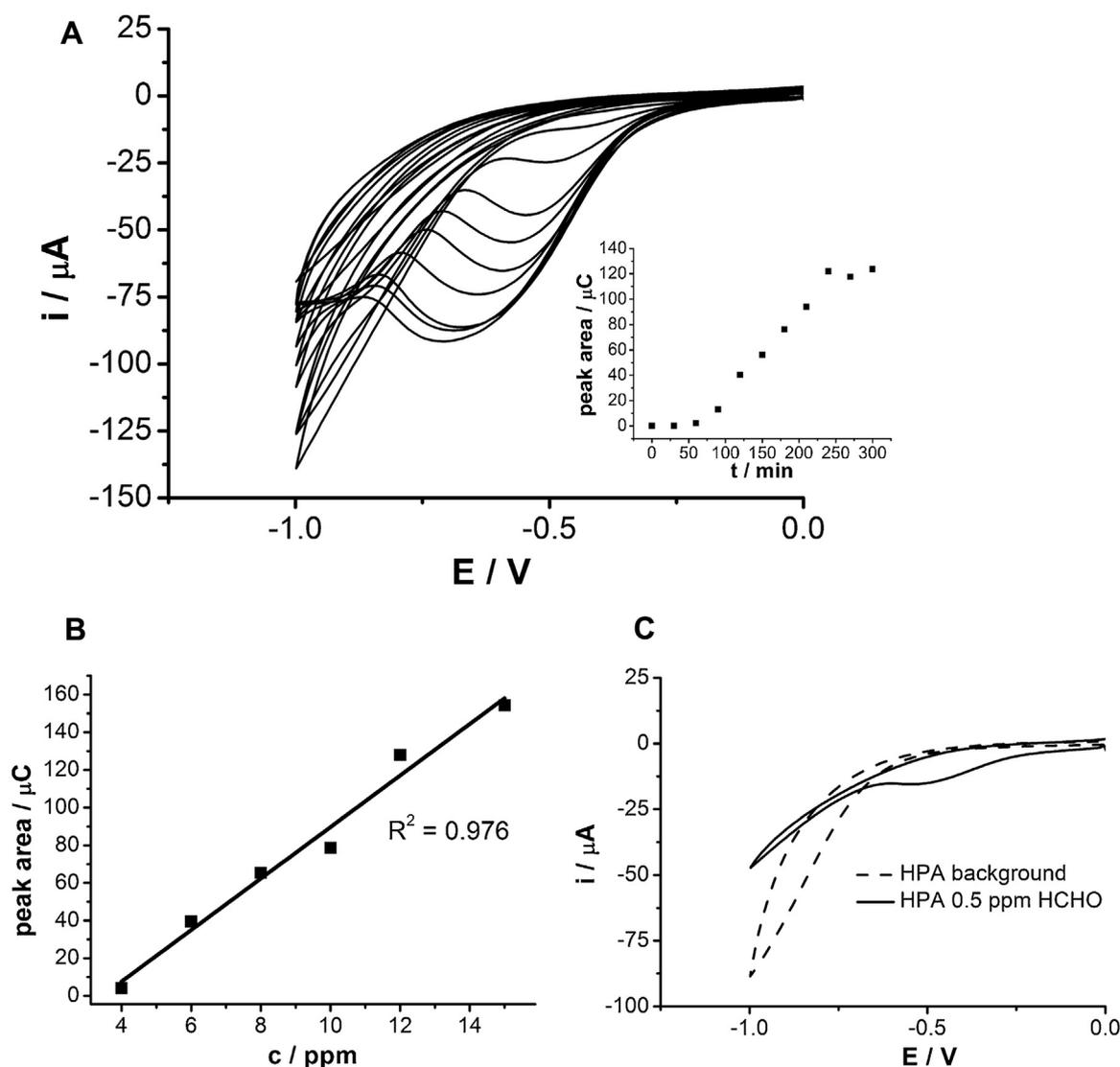
when the anodic vertex potential was increasing towards  $+1.0$  V, and decreased again at higher, i.e. more positive potentials (Fig. 3A, step 2). For example, when compared to the applied anodic (second) vertex potentials of, e.g.  $+0.75$  V or  $+1.25$  V, the increase of signal at anodic potential of  $+1.0$  V was almost three-fold. The optimal performance, i.e. the highest signal of formaldehyde was thus achieved when the measurement was carried out using cyclic voltammetric scan in the range of  $-1.0$  V to  $(+1.0)$  V, implying that the re-oxidation reaction is an important part of the process and further studies are needed to better understand the detailed reaction scheme. Importantly, in conventional detection of aqueous formaldehyde in the solution containing hydrazine, the reaction pathway allows only two step reaction with formaldehyde after which hydrazine is irreversibly transformed/consumed. In the proposed novel sensing approach, the hydrazine is ionically bonded to polyacrylic acid forming HPA (i.e. is protected at one side), which reacts with formaldehyde yielding hydrazone species that are still bonded to skeleton of PAA (Fig. 3B), thus we can speculate that the second step, which irreversibly transforms hydrazine in the conventional scheme (Fig. 3C), probably does not occur. Therefore we can assume that in this case, the HPA can further undergo several oxidation-reduction cycles which can be beneficially exploited for detection of formaldehyde.

In addition, the sensor exhibited reversible operation, due to relatively slow but reversible nature of the formaldehyde–hydrazinium reaction; when it was transferred into a formaldehyde-free environment, the signal started to attenuate

and finally disappeared after few repetitive cycles (within 120 min with measurements taken every 30 min). When formaldehyde was reintroduced, the signal appeared again corroborating the sensor's reversible and reusable character.

Further studies offered additional insight into the sensor's electroanalytical performance. During the sensor exposure to formaldehyde, two processes are obviously taking place simultaneously, i.e. formaldehyde absorption and formaldehyde reaction with hydrazine to form hydrazone. As shown in Fig. 4A, the signal increased with increasing the time of accumulation/exposure to formaldehyde and started to level off at prolonged accumulation times due to saturation. As expected, the time until saturation/equilibrium was observed strongly depended on the formaldehyde concentration, e.g. for 5 ppm gaseous formaldehyde the levelling off occurred after 240 min; therefore, during calibration, the adequate (and the same) time of exposure to the analyte must be considered. Since the sensor-to-sensor repeatability was satisfactory (RSD of 15% for 10 measurements carried out with 10 different sensors, each in its own flask), the sensor calibration was conducted with seven different sensors exposed to formaldehyde (background and six increasing concentrations), as depicted in Fig. 4B. The sensors exhibited satisfactory linear behaviour in the concentration range of 4–16 ppm associated with 120 min accumulation/exposure and  $R^2$  of 0.976.

Since the signal strongly depends on the accumulation/exposure time, the detection of lower concentrations can be achieved by its prolongation. Sub-ppm gaseous concentrations can be read-



**Fig. 4.** Cyclic voltammograms of 5 ppm gaseous formaldehyde for increasing accumulation/exposure time together with the inset showing the corresponding signal area plot (A); the signal area plot for increasing concentrations of gaseous formaldehyde in the range of 4–16 ppm (B); cyclic voltammograms in the presence of low (0.5 ppm) concentration of gaseous formaldehyde (solid line) together with background (dashed line); scan rate of  $100 \text{ mV s}^{-1}$ .

ily measured, e.g. 500 ppb of formaldehyde can be detected after 64 h exposure with a signal roughly equivalent to 4 ppm at 2 h exposure, as demonstrated in Fig. 3C. On the other hand, higher concentrations of formaldehyde can also be measured in connection with correspondingly shorter accumulation/exposure times. No deterioration of the sensor operation was observed in the frame of our experiments, even during prolonged exposure associated with low concentration measurements and when examining the reusability of the sensor via exposing it to formaldehyde and formaldehyde-free atmosphere repeatedly. The main benefits of the proposed sensor, besides simple and straightforward preparation, are its operation at room temperature, pre-concentration capability, favourable low limit of detection and linear range which can be improved, if necessary, by adjusting exposure time. This gives the sensor a wide range of usability, for example to detect the commencement of the material degradation in, e.g. museum collections.

#### 4. Conclusions

A novel formaldehyde gas sensor was developed using a screen printed carbon electrode as the substrate, which was surface mod-

ified with a hydrazinium polyacrylate sensing layer. Hydrazinium polyacrylate is used to accumulate formaldehyde and derivatise it to hydrazone, which can be determined through its reduction using cyclic voltammetry, and at the same time, it acts as the polymeric electrolyte. The preliminary investigation implies promising electroanalytical characteristics of the proposed sensor for measuring gaseous formaldehyde in a wide concentration range. The examination of other aldehydes as potential analytes/interferences is in progress.

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