



Research paper

Amperometric responses of volatile organic amines in air by using 5-sulpho-salicylic acid modified narrow-gap electrochemical cell

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HIGHLIGHTS

- The bare narrow-gap electrochemical cell responded to volatile organic amines.
- Modification of the cell with 5-sulpho salicylic acid modifying layer increased the sensitivity.
- Pulsed amperometry was more sensitive than constant pulse amperometry.
- Reproducibility was acceptable for *n*-butylamine, triethylamine, and pyridine.

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ABSTRACT

In this article, different kinds of volatile basic organic compounds (*n*-butylamine, morpholine, ethanolamine, triethylamine, pyridine) were investigated by using amperometric techniques with a narrow-gap cell. In case of bare electrode continuous current increase could be observed from beginning of exposure to the saturated vapour of all chemicals during the repetitive amperometric recording at 2 V working potential. The cell did not respond to triethylamine. When the cell was modified with 5-sulpho-salicylic acid the cell responded quickly and it showed high sensitivity to the investigated compounds. Repeatability was investigated which was satisfactory for all compounds except for ethanolamine and morpholine.

1. Introduction

In recent years, there is an increased awareness of the poisoning effects due to the different volatile chemicals. During their storage, some leakage can occur and in case of spills they evaporate in high dose into the environment. In the latter cases, it is almost impossible to avoid the exposure to the workers. On the other hand, leakage causes also detrimental economical defects.

Concerning this problem different types of sensors were developed such as chemiresistors [1–3] optical devices [4–11]. For the detection and measurement of amines, ion mobility spectrometry provides an excellent opportunity [12,13]. Sorption phenomena on surfaces where amines adsorb readily are utilized in quartz crystal microbalance applications [14–16]. They are sometimes used in practise in combination with alarm systems.

For studying voltammetric behaviour of amines during their oxidation were carried out only in liquid phases, mainly in aqueous solutions. For example, at gold electrode in basic solution an oxide layer forms in the anodic potential region which plays a key role in oxidation

of amines [17,18]. Solubilities of aliphatic amines were determined in water with cyclic voltammetry [19], ethylene diamine showed reversible electrochemical behaviour [20], and in nonaqueous solvents diethylenetriamine electrooxidation resulted in an insulating film on the electrode surface [21]. Amine functionalized electrodes can be made by electrochemical grafting of their surface [22–24]. The behaviour of different amines was compared in respect of stability of the hydrochloride salts [25], oxidation in emulsion droplets [26], and lifetime of the formed radical as a consequence of their anodic oxidation [27]. The performance of diamond-based electrodes (boron doped diamond, graphite film electrode) was examined in detail and the products of charge transfer processes could desorb slowly due to the strong interactions with certain sites of the surface [28].

Ultramicroelectrodes are widely used in highly resistive media to detect different substances due to the diminished ohmic potential drop. The gas phase is a typical example and microelectrode cells are used as detectors in gas chromatography [29]. In some works, the exposure to vapours of the mostly used volatile chemicals was studied with voltammetry and amperometry [30] but the signals were in the pico- and

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some nanoampere range using unmodified electrodes, e. g. Pt, Au, carbon microdisc working electrodes involved in an assembly where the distance between working and counter electrodes is in the micrometer scale. The width of interelectrode gap is critical in respect of the sensitivity and response time. So, narrow-gap cells are miniaturized electrochemical sensors. Therefore, weakly accessible places can be monitored with their use making possible local measurements. Narrow-gap microcells are fabricated in different geometries so glass micropipet and sandwich assemblies are used.

When compounds must be detected in air by using voltammetric and amperometric methods some interesting questions arise from the electrochemistry in the gaseous phase. While only the insulating layer separates anode and cathode in the narrow-gap electrochemical cells, there is nothing which can enhance the ionic conductivity through the interelectrode gap. There are more factors that contribute to the development of current signals. In reality, ionic impurities might be present at least in trace amounts everywhere. By exposition to vapours of chemicals a thin condensed layer covers the cell surface and this layer enables the ionic transport across the interelectrode gap by completing the circuit during imposition of the appropriate cell voltage. In narrow-gap cells very high electric field gradients develop due to the very low distance between the electrodes. The dielectric constant of the solvent strongly influences the solvation of ionic impurities so higher permittivity solvents can produce higher current signals. According to the earlier works, the permittivity should be at least 5 to obtain detectable current changes [31]. The liquid itself undergo autoprotolysis injecting further charges into the circuit. The material of the insulating gap might also modify the ionic conductivity due to its hydrophilicity or hydrophobicity. The migration of ionic species might be also facilitated by covering the interelectrode gap with polymers, e. g. polyethyleneoxide.

In this work, a macrodisc-microdisc assembly was used where microdisc served as working electrode and the larger macrodisc electrode was the counter and quasi reference electrode. This geometry is easy to fabricate which proved oneself to be useful in our earlier work where alcohol content was aimed to determine in gasoline samples [32]. This is also practical when the performance of a modifying layer is wanted to be established. Herein, the feasibility of a modifying 5-sulpho-salicylic acid monohydrate modifying layer between the electrodes is discussed in detection of different kinds of nitrogen containing basic compounds which has a crystalline form in ambient conditions (assembly is drawn in Fig. 1).

2. Experimental

2.1. Chemicals and materials

By carrying out the exposure tests pure liquids were used which were the products of Reanal except for triethylamine, the chemical of Sigma Aldrich. Some liquids were put onto the bottom of glass vessels

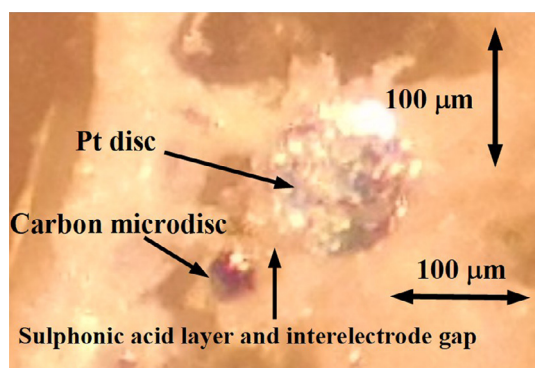


Fig. 1. Illustration of the used narrow-gap cell modified with the sulphonic acid layer between the two electrodes.

and they were closed with their glass caps for one day sufficient for equilibration between the liquid and gaseous phase. By making the narrow-gap cell dental resin was used as insulating matrix made with the mixing of a solid and liquid component (Duracryl Plus, Spofa Dental a. s. Markova 238).

2.2. Apparatus

The measurements were carried out using a potentiostat (Palm Instruments BV, Houten) equipped with a Pocket PC for data acquisition. The carbon microdisc was the working electrode and the Pt disc was the counter and quasi reference electrode involved in the assembly of the narrow-gap cell.

2.3. Preparation of the narrow-gap cell

A Pt wire (100 μm in diameter) and a carbon microwire (30 μm in diameter) were laid down on an insulating sheet made from dental resin (polyacrylate). On one of the ends of the two wires they were fixed with conducting silver epoxy glue and copper wires were glued to them for ensuring the electric leads. The other ends of wires were put as close as possible next to each other on the insulating sheet. The silver epoxy glues were allowed to dry for ~ 12 h. Then the whole assembly was embedded in dental resin. When the resin became solid (~ 10 min curing period) the cell was sanded off on emery paper perpendicularly to the wires. Meanwhile, the process was checked under microscope. The width of the constructed cylindrically shaped cell body was 5 mm, its length was 2 cm. When two discs were obtained next to each other separated by a thin insulating layer the cell was polished with 1 μm alumina powder (Micropolish II, Buehler, US). The cell was washed with deionized water and then ultrasonicated to remove the residual alumina particles which was followed by a washing with deionized water and finally dried.

A hole was drilled into the middle of a plastic sheet and the cell was glued into it. The plastic sheet with the cell was fixed in a scaffold. During the measurements the saturated vapour containing vessels were placed closely under to the plastic sheet while the sensing area of the cell was exposed to the vapour. The measurement setup was the same used in an earlier work [33].

2.4. Preparation of acidic modification layer

By making modification layer from 5-sulpho salicylic acid an aqueous solution was prepared in 0.1 mol/L concentration and ~ 1 μL was placed at the interelectrode gap between the Pt counter/quasi reference and the carbon microdisc working electrode. It was allowed to dry and finally a thin layer of crystalline acid monohydrate covered the interelectrode gap whose width was approximately 50 μm (Fig. 1).

3. Results and discussion

3.1. Evaluation of the bare cell in saturated vapours of basic liquids

The performance of bare cell was firstly evaluated while it was exposed to the saturated vapours of the investigated volatile liquids using constant potential amperometry. In these experiments the cell was placed into the saturated vapours and the amperometric measurements were started imposing 2 V potential onto the carbon microdisc. Fig. 2 shows amperometric curves recorded in vapours of selected chemicals. The recordings began in the ambient air (relative humidity in RH % was around 50 and 60% valid for all studies presented here). These values are characteristic for Central Europe. All exposure tests started mostly after 50 s from starting the measurements and aborted after 70 s. It can be seen that the currents in the ambient air were negligible showing that water content of the air cannot be detected with the used cell. During the 20 s exposure time the ~ 2 nA signal of n-

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