

# Detection of Volatile Organic Solvents Using Potentiodynamic Gas Sensors

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**Amperometric electrochemical gas sensors have the advantage of combining good sensitivity and selectivity at relatively low cost. However, their use is restricted to the detection of gases that are very reactive at potentials positive of that at which oxygen is reduced. We describe here a new detection method for less reactive species such as benzene and halogenated hydrocarbons, which cannot be directly oxidized. Instead, the species is continuously adsorbed at a potential below 0.5 V and then oxidized at potentials where oxygen coadsorbs. The oxidation current is corrected for the oxygen adsorption current by performing an additional potential cycle, in which no adsorption is allowed to occur. We have so far obtained sensitivities in the lower ppm range for benzene, toluene, tetrachloroethene, epichlorohydrin, and vinyl acetate; for saturated halogenated hydrocarbons such as CFCl<sub>3</sub>, it is still below 1000 ppm.**

To efficiently control and lower the emissions of toxic and environmentally harmful compounds, the availability of low-cost instrumentation for their continuous detection is highly desirable. In many cases, so-called amperometric gas sensors can be used, e.g., for the detection of Cl<sub>2</sub>, HCl, NO<sub>x</sub>, SO<sub>2</sub>, and formaldehyde in the ppm and sub-ppm ranges.<sup>1</sup>

In these sensors, the gaseous species to be detected is oxidized or reduced under potentiostatic conditions at a porous gas diffusion electrode. The corresponding faradaic current usually is proportional to the concentration of the species in air. This device, therefore, is very simple.

The selectivity and sensitivity of these sensors are optimized not only by the selecting of an appropriate electrocatalyst but also by choosing an appropriate electrode potential, so that primarily the species to be detected reacts at the electrode surface. However, the accessible range of potentials is very limited because the decomposition of the electrolyte, the corrosion of the electrocatalyst, and the reduction of oxygen from air have to be avoided. The corresponding currents would exceed the detection currents by several orders of magnitude. In aqueous electrolyte, using noble metals as the electrocatalyst, the potential window, therefore, is limited to values between 0.9 and 1.5 V (RHE).

Many substances cannot be detected using the amperometric sensors, because they either are too inert (as many halogenated species) or do not react electrochemically in the limited potential window. Among these are many unsaturated compounds, halo-

genated hydrocarbons, and aromatic species. Only in some cases can a chemical converter be used which transfers such species into ones which are electrochemically detectable.<sup>2-4</sup>

It is well known, however, that many of these substances can be oxidized within this accessible potential window after first being adsorbed at lower potentials, e.g., in the double-layer region of Pt. This can be achieved by a potential sweep from the adsorption potential up to 1.5 V, as in usual cyclic voltammetry, and has often been used for the determination of the adsorption isotherm of these species.<sup>5</sup>

The interaction of such organic molecules with noble metal electrode surfaces has been studied by classical electrochemistry<sup>6-8</sup> and radiotracer methods.<sup>9</sup> We have recently studied the adsorption of some organic solvents including benzene,<sup>10-12</sup> toluene,<sup>13</sup> acetone,<sup>14</sup> and halogenated species<sup>11,15-18</sup> on poly- and monocrystalline Pt electrodes, using differential electrochemical mass spectrometry. In all these cases, a complete oxidation of the adsorbate to CO<sub>2</sub> is achieved when sweeping to sufficiently positive potentials.

The oxidation of these molecules occurs at much lower potentials for the adsorbed species than for the free molecules. Moreover, it is complete, yielding CO<sub>2</sub> as the oxidation product, which implies a higher number of electrons usable for the current detection. (For comparison, unadsorbed benzene is oxidized to benzoquinone only at potentials above 1.5 V.) In the case of associatively (or  $\pi$ -) bound adsorbates such as benzene, this is, of course due to the weakening of the internal molecular bonds

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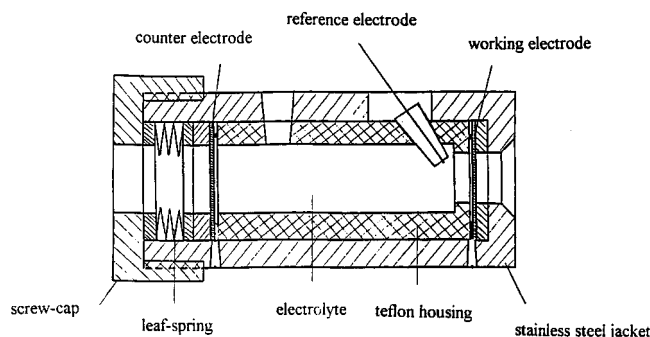


Figure 1. The sensor cell.

upon adsorption (cf., e.g., ref 19). A continuous adsorption and oxidation at a constant potential in the accessible potential window is not possible because an oxidized benzene molecule, which is oxidized to  $\text{CO}_2$ , is immediately replaced by adsorbing oxygen atoms or OH species (formed from water). An adsorption of molecules such as benzene, therefore, is achieved only after reduction of the adsorbed oxygen, i.e., in the double-layer region. For a continuous detection of such molecules, the potential of the sensing electrode, therefore, has to be steadily cycled between an adsorption potential and the oxidation potential.

Adsorption of organic species at Pt electrodes (in a usual electrochemical H cell) was already used for the (noncontinuous) determination of organic contaminants in water.<sup>20</sup> Potential pulses and linear potential sweep voltammetry have been applied for the pulsed amperometric detection (PAD) of organic compounds in liquid chromatography.<sup>21,22</sup> Here, however, the main purpose of the potential pulses is to clean the electrode from adsorbed organic species. Such adsorbates would inhibit the faradaic electrode reaction used for the amperometric detection itself ("fouling"). In some cases, however, PAD also makes use of the current connected to the oxidation of the organic adsorbate.<sup>23</sup>

The determination of  $\text{CO}_2$  in air has been described using an approach very similar to that used in this work:  $\text{CO}_2$  was reductively adsorbed at 50 mV vs RHE from air; the adsorbate was then oxidized after a potential step to more positive potentials.<sup>24</sup> It was thus possible to detect  $\text{CO}_2$  concentrations above 0.5%.

We will show in the following that, using automatic data processing and an appropriate sensor cell, it is possible to detect continuously many toxic species down to concentrations of 1 ppm in air.

## EXPERIMENTAL SECTION

The electrochemical sensor cell used here is very similar to the usual amperometric cells (Figure 1). The sensor electrode (working electrode) consists of a thin Pt or Pd layer (50–80 nm), sputtered onto a porous Teflon membrane (Goretex, thickness approximately either 50  $\mu\text{m}$  or 1 mm, nominal pore diameter 0.2  $\mu\text{m}$ ). A similar electrode also served as the counter electrode. As the reference electrode, a dynamical hydrogen electrode was

used (Pt disk of 1 mm diameter, constant current of 5–10  $\mu\text{A}$  between this and the counter electrode). The cell body is made of Teflon. It is surrounded by a steel construction. The seals are tightly pressed against the membrane with the help of leaf springs. This is necessary for minimizing edge effects and for preventing the cell from leakage. The diameter of the working electrode is a compromise, such that (1) edge effects due to creeping of the electrolyte are minimized (which is the case for large diameters) and (2) the resistance across the electrode is low enough that identical potentials everywhere on the electrode surface are obtained quickly after a potential step (which is the case for low diameters). So far, 6 or 8 mm proved to be best. The diameter of the counter electrode usually was 12 mm.

For the potentiostatic control, simple homemade potentiostats were used (10 mA maximum output current, 15 V maximum output voltage).

A Keithley (PCIP-AWFG) digital function generator was used for the potential program.

Test gases were prepared by mixing nitrogen or synthetic air with either the corresponding pure gas, a gas with a certified concentration in nitrogen, or nitrogen saturated with the corresponding solvent. Saturation of nitrogen with solvents was achieved by continuously bubbling nitrogen through the solvent (usually at 0 °C with a flow rate between 0.5 and 100 mL/min); the partial pressure then corresponds to the vapor pressure of the solvent (at 0 °C). These gas flows were adjusted using flow meters (UCAR). Total flow rate usually was 1 L/min.

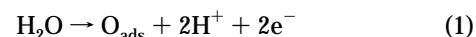
The electrolytes used were 5 M  $\text{H}_2\text{SO}_4$  or 1.6 M  $\text{MgClO}_4 + 1$  M  $\text{HClO}_4$ , unless otherwise noted. These electrolytes were chosen due to their hygroscopicity, which prevents their drying out when exposed to ambient air.

## RESULTS AND DISCUSSION

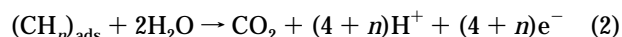
The potential program is shown in Figure 2. First, the substance (e.g., tetrachloroethene) is allowed to adsorb during the adsorption time  $t_{\text{ad}}$  (1) at the adsorption potential  $E_{\text{ad}}$  (e.g., 100 mV). During the adsorption of chlorinated species, C–Cl bonds are reductively cleaved.<sup>11,15,17</sup> In the case of tetrachloroethene, also the C–C bond is cleaved to some extent, leading to a variety of adsorbed species, e.g.,  $\text{CH}_n$ . During this adsorption time, oxygen from air is also continuously reduced, leading to a large reduction current, but this has no influence on the adsorption behavior.

The potential is then stepped to a potential just below the onset of the oxidation (2a). (The spike 2b is due to the charging of the double layer during the potential step.) Oxidation of the adsorbate to  $\text{CO}_2$  is achieved during the subsequent potential sweep (3a), giving rise to the current peak (3b).

During this sweep, oxygen (or OH) is adsorbed from water, e.g., according to



In parallel, the adsorbed organic species (such as  $\text{CH}_n$  formed from tetrachloroethene) is oxidized to  $\text{CO}_2$ , e.g.:



The corresponding anodic currents are superimposed and lead

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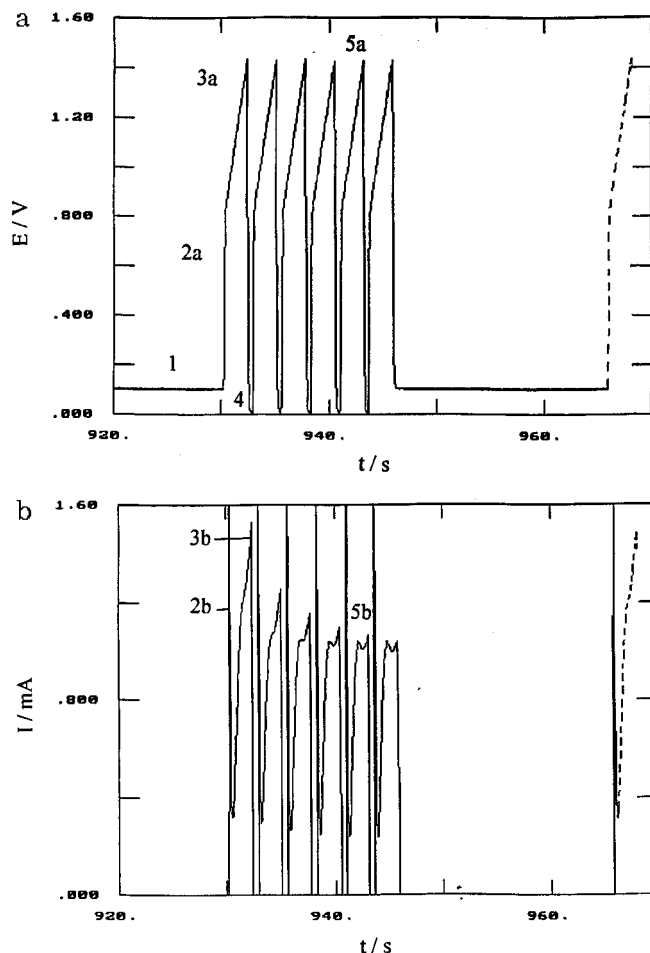


Figure 2. (a) Potential–time program applied to the working electrode of the sensor (see text). (b) Resulting current (WE, 8 mm; electrolyte, 5 M H<sub>2</sub>SO<sub>4</sub>;  $t_{\text{ad}} = 20$  s,  $t_{\text{red}} = 0.5$  s;  $E_{\text{ad}} = 100$  mV;  $E_{\text{red}} = 0$  V;  $v = 300$  mV/s). The dotted line is the start of the next macrocycle.

to the current peak (3b). The adsorbed oxygen is reductively desorbed during the potential step to  $E_{\text{red}}$  (e.g., 0 mV) (4). This step has to be long enough to ensure complete reduction of adsorbed oxygen, but so short that the amount of newly adsorbed organic species is negligible. Depending on the organic species and the anodic potential limit, oxidation of the adsorbate is not complete after one oxidation cycle. Therefore, five more such oxidation cycles, each of them followed by a reduction step, are applied (“microcycles”). During the last oxidation sweeps (5a), the current (5b) is due only to oxygen adsorption (eq 1). In the absence of organic species, of course, all currents during the microcycles, including that during the first one, are identical and equal to that shown in Figure 2 as 5b.

Therefore, after subtraction of the current 5b from the current 3b in the first oxidation sweep, the current that is merely due to oxidation of the organic adsorbate (eq 2) is obtained. For a continuous measurement, this sequence is repeatedly followed by another overall potential cycle (“macrocycle”), starting with the adsorption step.

The amount of adsorbate formed during such an adsorption step directly depends on the concentration of the species in the gas phase and, therefore, serves as a measure for the concentration. This amount of adsorbate can be calculated from the oxidation charge after integration of the current difference between the first and the fifth sweeps. However, since the sensor

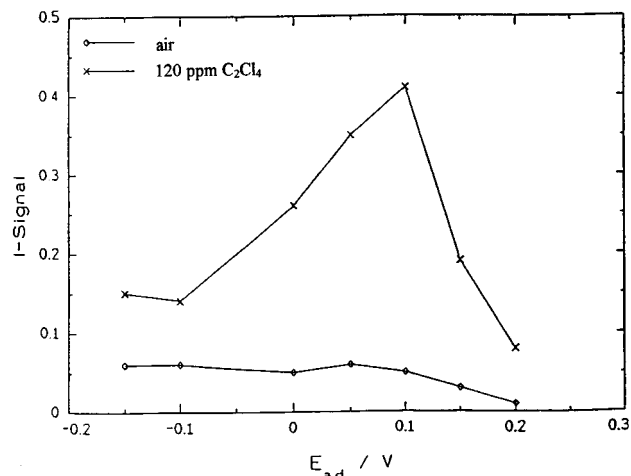


Figure 3. Dependence of the sensor signal for 120 ppm tetra-chloroethene in air on the adsorption potential (WE, 8 mm; electrolyte, 1.6 M MgClO<sub>4</sub> + 1 M HClO<sub>4</sub>;  $t_{\text{ad}} = 20$  s,  $t_{\text{red}} = 0.5$  s,  $E_{\text{red}} = 100$  mV;  $v = 300$  mV/s)

has to be calibrated anyway, it is sufficient to determine the current values at a given potential  $E_{\text{det}}$  (e.g., the current at the anodic potential limit).

Since the true surface area of the porous working electrode is not very reproducible and also might change during the lifetime of the sensor, it proved to be advantageous to divide this current difference ( $I_{\text{ox}}^1 - I_{\text{ox}}^5$ ) by the oxygen adsorption current in the fifth cycle ( $I_{\text{ox}}^5$ ). Thus, a dimensionless signal is obtained:

$$S = \frac{I_{\text{ox}}^1 - I_{\text{ox}}^5}{I_{\text{ox}}^5} \quad (3)$$

The following criteria are useful for optimizing for the parameters of the potential program.

**Adsorption Potential  $E_{\text{ad}}$ .** Should be such that the adsorption rate is high; depends on substance; typically 50–500 mV.

**Potential Sweep Rate.** The higher the sweep rate, the shorter is a complete potential cycle, and the faster is the response time of the sensor. However, in order to achieve an extensive oxidation during the first sweep, the sweep rate is limited to a few hundred millivolts per second.

**Upper Potential Limit.** The higher it is, the more complete is the oxidation of the adsorbate in the first sweep. However, corrosion of the catalyst starts around 1.45 V.

**Reduction Potential  $E_{\text{red}}$ .** For simplicity, it is identical to  $E_{\text{ad}}$ . Alternatively, it could be optimized to a value where adsorption of organic substance is slow but reduction of adsorbed oxygen is fast (e.g., 50 mV).

**Reduction Time  $t_{\text{red}}$ .**  $t_{\text{red}}$  has to be long enough to ensure complete reduction of the adsorbed oxygen. On the other hand, adsorption of the new substance should be avoided. If reduction is not complete, less oxygen is adsorbed during the subsequent sweep, and a high sensor signal is generated, even if no organic substance is present. If the reduction time is too long, adsorption of the organic substance leads to a value of the current in the fifth sweep that is too high, thus decreasing the sensitivity.

The dependence of the sensor signal on the adsorption potential for tetrachloroethene is depicted in Figure 3. The shape of the resulting curve is identical to that of the potential

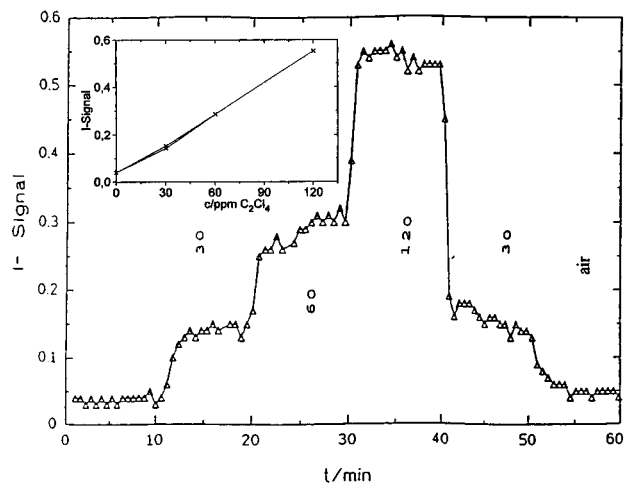


Figure 4. Response of the sensor to various concentrations of  $C_2Cl_4$  (0, 30, 60, 120, 30, 0 ppm in air, each concentration for 10 min). (Inset) Concentration dependence of the sensor signal ( $E_{ad} = 50$  mV;  $E_{red} = 50$  mV; other parameters as before).

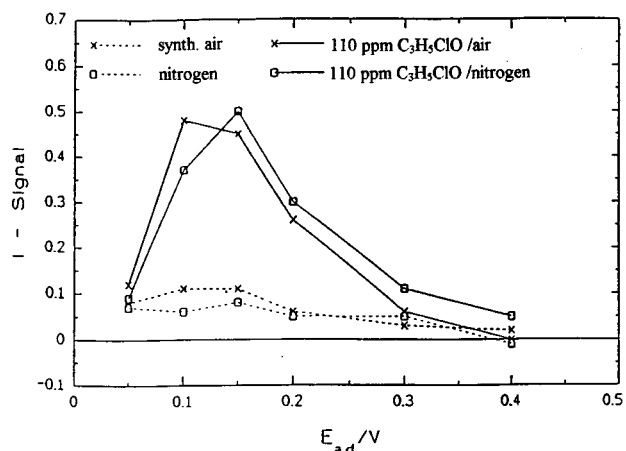


Figure 5. Same as Figure 3 for 110 ppm epichlorohydrin in air ( $\times$ ) and  $N_2$  ( $\square$ ). (WE, 8 mm; electrolyte, 5 M  $H_2SO_4$ ,  $t_{ad} = 20$  s,  $E_{det} = 1.15$  V,  $v = 300$  mV/s).

dependence of the rate of tetrachloroethene adsorption on a smooth polycrystalline Pt electrode from solution.<sup>25</sup> In short, the adsorption rate is highest at the potential of zero charge at Pt. Also, at more negative potentials, hydrogenation competes with adsorption; at more positive potentials, the adsorption rate decreases because the adsorption is a reductive process. Figure 4 shows that the response time of the sensor is essentially given by the duration of one complete potential cycle. Here, each triangle corresponds to one macrocycle and a value calculated according to eq 3. The dependence on concentration is linear (Figure 4, inset).

A similar potential dependence is obtained for epichlorohydrin (Figure 5). Comparison of the two curves of epichlorohydrin in nitrogen and in air shows that the presence of oxygen shifts the curve by only 20–30 mV to lower potentials. This means that adsorption is not influenced by the comparatively large oxygen reduction currents at the adsorption potential; i.e., the  $iR$  drop was low enough not to shift the effective electrode potential significantly.

In the case of benzene, the sensor signal is nearly independent of the value of the adsorption potential over the whole double-

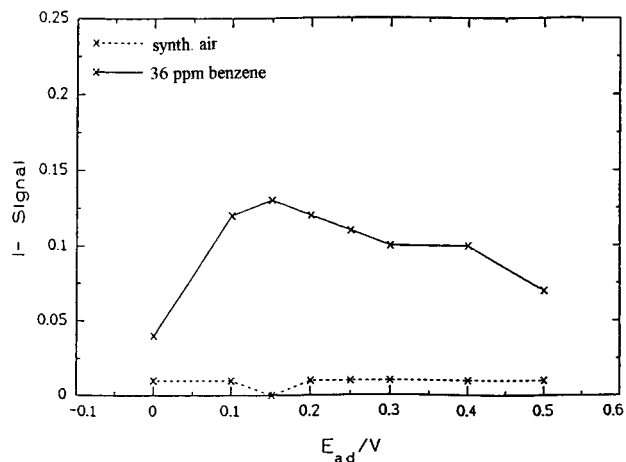


Figure 6. Dependence of the sensor signal on the adsorption potential for 36 ppm benzene in air (5 M  $H_2SO_4$ ;  $t_{ad} = 5$  s;  $E_{det} = 1.44$  V).

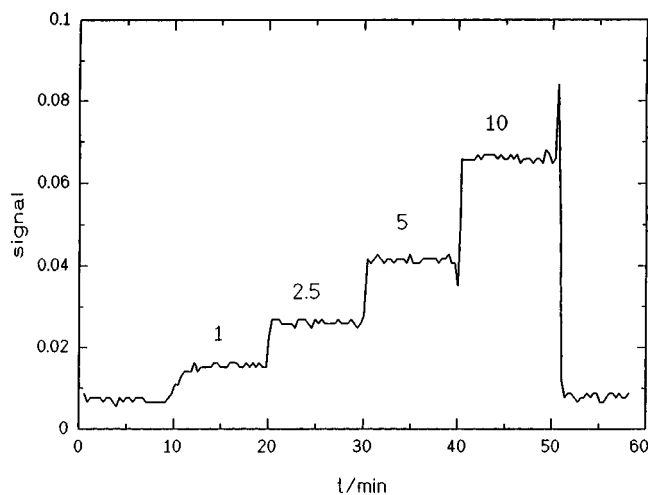


Figure 7. Response of the sensor to various concentrations of benzene (5 M  $H_2SO_4$ ;  $E_{ad} = 200$  mV;  $t_{ad} = 5$  s).

layer region (Figure 6), as is also expected from the diffusion-limited adsorption rate in this potential region (cf. ref 5). A similar potential dependence was obtained for vinyl acetate. For chlorobenzene, a potential dependence in between that of tetrachloroethene and benzene was found. The sensor is quite sensitive; 1 ppm of benzene can be clearly detected (Figure 7). However, it is also obvious that the dependence on concentration is not linear in this case. This is, especially at higher concentrations, due to a saturation of the electrode surface with adsorbate. This deviation from linearity might also originate from the fact that we use the current at a single potential for the detection instead of the oxidation charge, i.e., the integrated oxidation current.

To detect saturated fluorochlorinated hydrocarbons, alkaline electrolytes have to be used, because adsorption is too slow in acid solution.<sup>18</sup> Best sensitivity was achieved using Pd as the electrocatalyst in 5 M KOH. We were thus able to clearly detect 300 ppm of F-11 ( $CCl_3F$ ), a value still well below dangerous concentrations and also low enough to detect leakages.

Of course, the lifetime of such a sensor is a critical problem. It is largely affected by the anodic potential limit, and potentials higher than 1.45 V have to be strictly avoided. So far, we have achieved lifetimes of 3 months with constant sensitivity within about 10% (except for the first week, during which a more drastic

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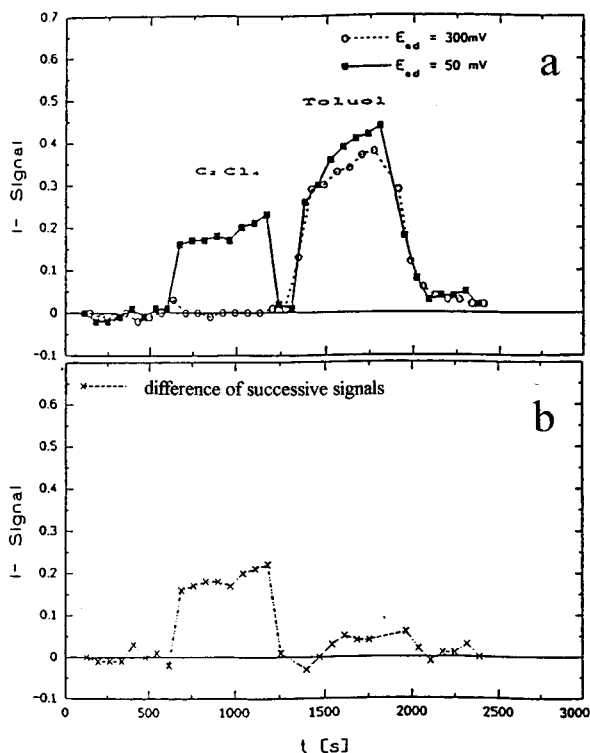


Figure 8. Selective detection of  $C_2Cl_4$  and toluene by alternating adsorption potentials. The sensor was exposed first to 120 ppm  $C_2Cl_4$  in air, then again to pure air followed by 35 ppm toluene. (a) Sensor signal at  $E_{ad}^1 = 50$  mV (■) and  $E_{ad}^2 = 300$  mV (○). (b) Difference of two subsequent sensor signals  $S(E_{ad}^1) - S(E_{ad}^2)$  (×) (1 M  $HClO_4$ ;  $t_{ad} = 20$  s;  $t_{red} = 0.5$  s;  $E_{red} = 0$  V).

decrease of about 30–40% is observed). During this time, the potential program was constantly applied. (However, only during ~20 h/week was an adsorption time of 5 or 20 s was used. During the other times, the adsorption period was increased to 60 s.)

The different dependences of the adsorption rate and the sensor signal on the adsorption potential (cf. Figures 3 and 5) can be used to discriminate between different substances, as is demonstrated in Figure 8. Here, the adsorption potential was alternately switched between two different values in subsequent adsorption cycles. At one of these ( $E_{ad}^1 = 50$  mV), both tetrachloroethene and toluene are adsorbed. At the other ( $E_{ad}^2 = 300$  mV), toluene is equally well adsorbed, but tetrachloroethene hardly adsorbs (cf. Figure 3). Like before, each of the data points represents one cycle consisting of one adsorption step and six oxidation sweeps. As expected, a signal during exposure to tetrachloroethene is obtained only in those cycles in which the adsorption potential is 50 mV (full squares in Figure 8).

During exposure to toluene, a signal is obtained at both adsorption potentials. The values obtained for  $E_{ad} = 300$  mV yield a signal that is selectively sensitive to toluene. When calculating the difference of the signals obtained at both adsorption potentials, the signals nearly cancel in the case of toluene, but not in the case of tetrachloroethene. This difference, therefore, can be used as a selective sensor signal for toluene.

Other adjustable electronic parameters can also be used for a further increase in selectivity. Although the oxidation of the adsorbed species during anodic potential sweep extends over a fairly large potential range for all the species studied, the exact shape is different; i.e., some of the adsorbates formed are oxidized to a larger degree at lower potentials than others. So far, only

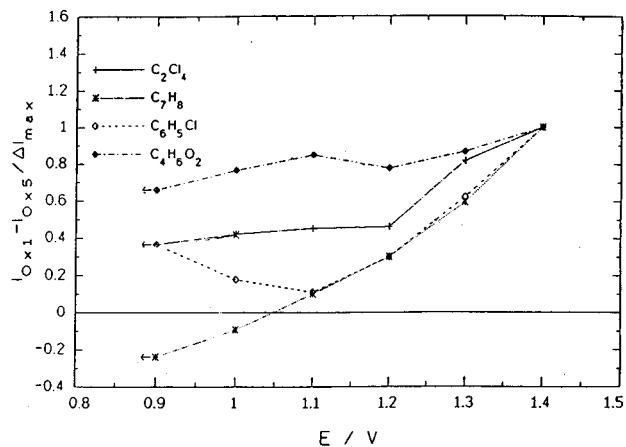


Figure 9. Dependence of the sensor signal on the potential at which the oxidation currents  $i_{ox}^1$ ,  $i_{ox}^2$  and  $i_{ox}$  are determined for 35 ppm toluene, 40 ppm chlorobenzene, 60 ppm vinyl acetate, and 120 ppm tetrachloroethene. All values were normalized to 1.4 V.

the current value  $E_{det} = 1.44$  V was used. However, the potential dependence can be used for a further optimization of sensitivity. As an example, Figure 9 shows the dependence of the sensor signal on the value of the potential at which the oxidation current is determined ( $E_{det}$ ). The shape of the curves is exactly what one would expect from cyclic voltammetry; e.g., for toluene<sup>13</sup> and tetrachloroethene,<sup>15</sup> adsorption of toluene inhibits oxygen adsorption below 1 V, leading to negative values in Figure 9, whereas tetrachloroethene is already oxidized at potentials below 1 V.

Here, all signal values were normalized to a value of 1 at the anodic potential limit. It can be seen that the signal for toluene is highest at 1.4 V, whereas for vinyl acetate the value of the signal is nearly identical for detection potentials between 0.9 and 1.4 V. Although these substances have a similar dependence on adsorption potentials, it is, therefore, possible to adjust the electronic parameters in a sensor so that it distinguishes between these two.

It should be stressed that this kind of sensor selectively detects species that strongly adsorb. As we have verified, it is not (or only weakly) sensitive to such substances as CO and NO, which are oxidized during the anodic potential sweep, even without being adsorbed at a lower adsorption potential. This is because the current due to the continuous faradaic oxidation in these cases is identical in the first and the following oxidation sweeps and, therefore, cancels when forming the difference. Furthermore, adsorbed CO is oxidized below 1 V, as is well known. This also applies to methanol.

Cross-sensitivities toward ethanol are important, because it is an abundant nontoxic solvent. It is also oxidized in a continuous faradaic reaction below and above 1 V. Additionally, the largest part of its adsorbate is oxidized below 1 V. A part of its adsorbate, however, is only oxidized at potentials in the oxygen adsorption region.<sup>26</sup> For 1000 ppm ethanol, we therefore obtained a sensor signal  $S = 0.07$ , simulating the presence of, e.g., 44 ppm tetrachloroethene.

Where this cross-sensitivity is a problem, the sensor program can be refined in such a way that the sensor can distinguish between tetrachloroethene and ethanol. By refining the applied potential program, the sensor can be used to detect both a species like tetrachloroethene, which is oxidized only after adsorption,

(26) Schmiemann, U.; Müller, U.; Baltruschat, H. *Electrochim. Acta* **1995**, *40*, 99.

and ethanol, which is also oxidized from solution. For this purpose, the potential is stopped at 1 V for 3 s during each of the potential sweeps. During this stop, ethanol is oxidized, but tetrachloroethene (including its adsorbate) is not.

The corresponding oxidation current at the end of this stop (for the above-mentioned example, 0.12 mA for 1000 ppm of ethanol) serves as the signal for the detection of ethanol, very similar to the situation in commercial amperometric sensors for ethanol, where ethanol is oxidized at a constant potential.

A suitable electronic device then recognizes from this current that ethanol is present and that, therefore, the sensor signal calculated from the potential sweeps according to eq 3 does not indicate the presence of tetrachloroethene or a similar species.

## CONCLUSION

Many organic solvents, which are not reactive in the potential window accessible in amperometric sensors, can be detected by using an appropriate potential program. Selectivities can be optimized and adjusted to a specific application by choosing the parameters of this potential program. It is an important advantage of this sensor that this can be done by varying the electronic parameters without changing the sensor itself; i.e., the user will be able to switch between substances to be detected.

We are optimistic to further increase the lifetime of currently 3 months by further optimizing the electrode preparation and

better controlling the electrode potentials. A slight decrease of the anodic potential limit should also be possible and prolong the lifetime. The sensitivities are high enough for nearly all practical applications.

The sensitivity of the sensor can be adjusted by choosing an appropriate adsorption time. Thus, it can be increased at the expense of the response time. It is a disadvantage of the sensor described so far that the sensitivity and the response time are fixed. A more serious problem is the possible saturation at high concentrations and/or long adsorption times when the coverage with the organic species approaches a monolayer.

A solution to this problem will be presented in a forthcoming paper.<sup>27</sup> There, we will show that the increase in coverage during the adsorption period can be monitored using impedance measurements. The adsorption can then automatically be stopped as soon as a certain coverage is reached. The adsorption time is automatically adjusted to the concentration, resulting in a wide dynamic range.

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(27) Oelgeklaus, R.; Baltruschat, H., submitted.

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