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## Fast responding ephedrine detection with miniaturized surface ionization gas sensors

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### Abstract

We report on novel kinds of miniaturized gas sensors whose operation is based on the principle of surface ionization (SI). In SI gas sensing adsorbed analyte species are ionized at a heated solid surface and the formed ions are extracted towards an oppositely charged collector electrode positioned a short distance from the emitting surface. Here, we show that SI sensors allow for a fast, sensitive and selective detection of illicit drugs in the presence of large concentrations of solvent water.

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### 1. Introduction

Gas sensors are indispensable for the detection of hazardous, toxic and explosive substances. Other target substances of interest are illegal drugs and other controlled goods. All applications require high sensitivity, selectivity and speed of response. Miniaturized metal oxide (MOX) gas sensors do not usually exhibit the required degree of selectivity as the detection criterion of combustibility is shared by an extremely wide variety of target and background gases. Safety and security relevant gases are usually relatively reactive gases with low activation energy for respective chemical reaction. Positive surface ionization reaction favors gas species with low ionization energies. Less reactive background and interfering gases in comparison exhibit relatively high ionization energies. Ionization energy, therefore, is

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a much more useful detection criterion than combustibility. For this reason we have engaged in systematic research on SI processes on noble metal and metal oxide surfaces [1, 2].

In this paper we present the results of ephedrine (EP) detection experiments and show that this stimulant can be sensitively, selectively and rapidly detected against a background of less relevant background species, particularly solvent water.

**2. Sensor architecture**

The principle architecture of a SI gas detector is shown in Fig.1a. A heated emitter layer (Pt, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, other oxides) is deposited onto a heater substrate and contacted in a similar way as in a conventional resistive-type (RES) MOX gas sensor. In order to observe SI currents, a negatively biased counter electrode is positioned at a short distance (~1mm) above the emitter layer. Under forward bias and under exposure to an easily positively ionizable gas, analyte ion currents can be observed which rapidly increase with increasing emitter temperature.

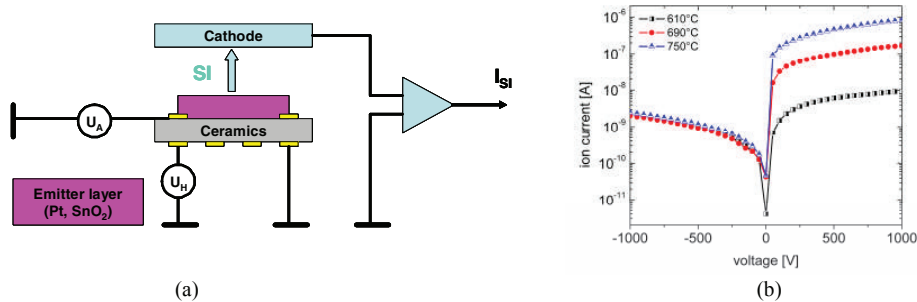


Fig. 1. (a) Principle architecture of a SI gas sensor; (b) Surface ionisation current/voltage characteristics as observed at different emitter temperatures. The analyte gas was ethene (E<sub>I</sub> ~11.5eV) and the emitter layer was a 13mm<sup>2</sup> screen-printed Pt.

The data in Fig.2 below show that SI currents usually exhibit Arrhenius-type temperature dependence. The most striking observation is that analytes with amine functional groups exhibit particularly low activation energies. Restricting SI emitter temperatures to the range of operation temperatures normally employed in the case of RES gas sensors (400-500°C), there is a spectacular selectivity to analytes with amine function groups.

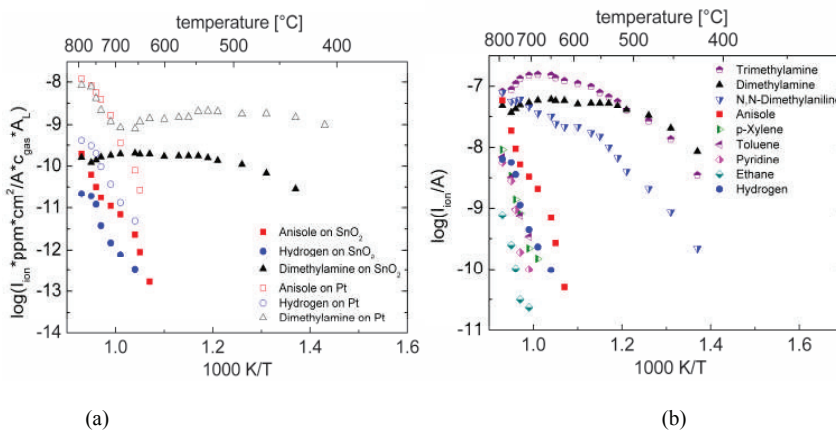


Fig. 2. (a) Temperature-dependence of SI currents as extracted from Pt and SnO<sub>2</sub> emitter layers. SI currents are normalized to the emitter area and the analyte gas concentration; (b) Temperature-dependence of SI currents as extracted from a SnO<sub>2</sub> emitter layers for a larger range of analytes.

### 3. Ephedrine detection experiments

Considering the high selectivity to amines, we have engaged into the detection of ephedrine (EP) and ephedrine-chloride (EPCl), a stimulant structurally similar to amphetamine and methamphetamine.

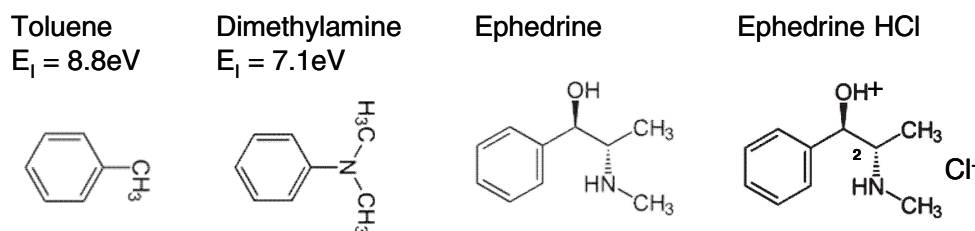


Fig. 3. A range of analyte molecules with particularly low ionisation energies. The ephedrine-type stimulants exhibit the same kind of easily ionisable amine side-groups as dimethylamine.

A severe problem is that these analytically relevant substances do not naturally abound in gas or vapor form. EP, rather, is a white, sticky solid and EPCl is a salt. In order to detect such substances, these need to be collected in particle form and vaporized for detection. Direct vaporization is possible in the free-base form (EP, MP 40°C) and salt form of ephedrine (EPCl, MP 220°C). EPCl is soluble in water and is in addition in water solution form evaporable.. Fig.4 shows how these substances were collected and prepared for SI gas detection.

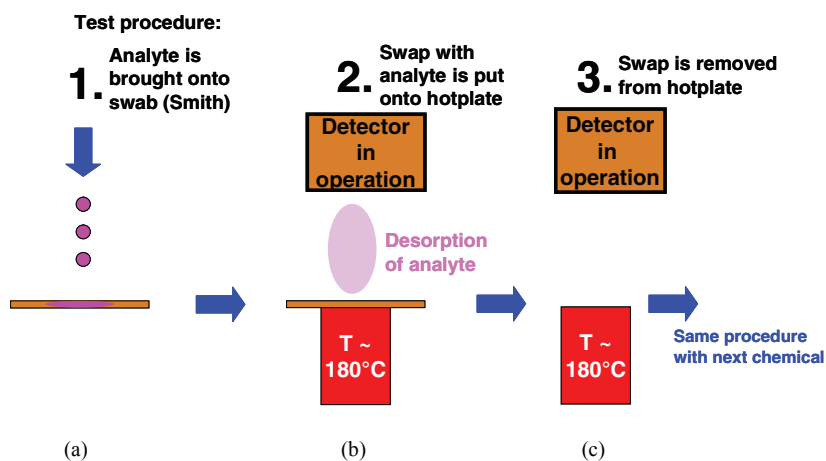


Fig. 4. (a) collection of solid/liquid analyte, (b) flash evaporation of analyte, (c) preparation for next detection run.

Results obtained in a series of detection events are shown in Fig.5. Analyte evaporation was started at the points of time indicated with downward pointing arrows and the SI response to the evaporation flash was observed. Short, high-intensity currents were observed upon detecting EP in its free-base form. The SI pulses terminated after a few seconds after the EP had been completely evaporated. EPCl as solid particles and dissolved in water evaporated much more slowly in the form of a continued set of very short micro-flashes. Detection ended when the EPCl-containing pad was removed from the heat rod, indicated by upward arrows. There is no difference between EPCl in solid particle form and in water-dissolved

form. Most interestingly, control experiments with pure water did not produce any sizeable SI response. This latter result proves the excellent selectivity of the SI detection process. The analytically relevant EPCI, obviously, can easily be detected within a huge background of solvent (water). This high degree of selectivity arises from the vastly different ionisation energies of EPCI ( $\sim 7\text{eV}$ ) and  $\text{H}_2\text{O}$  ( $\sim 12.5\text{eV}$ ). EP and EPCI detection experiments performed with a permeation tube dosage apparatus yielded minimum detectable concentrations of EP in the order of 500ppb and 50ppb in the case of EPCI.

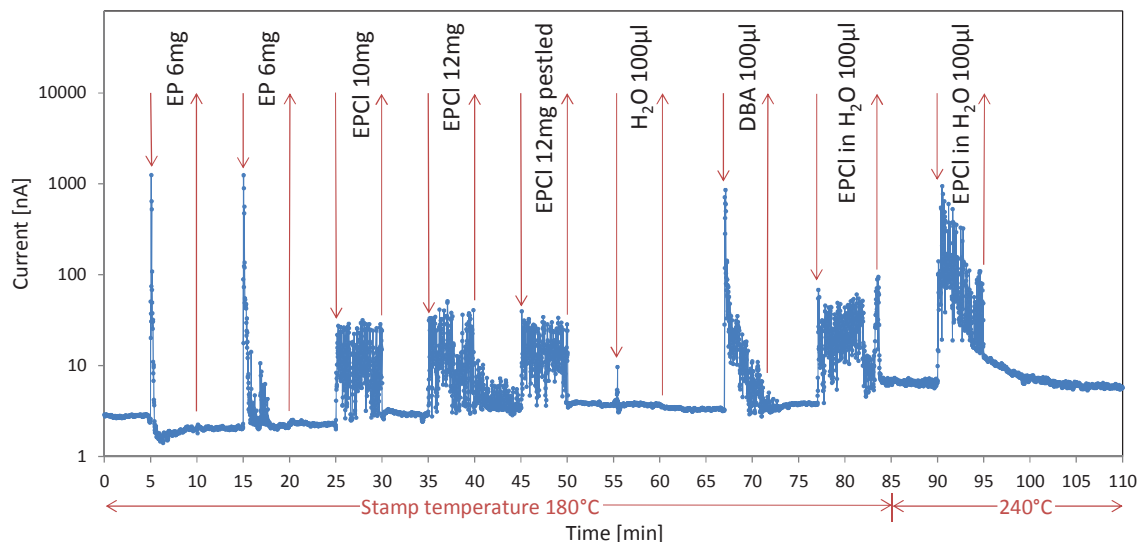


Fig. 5. SI current responses observed upon evaporating small samples of EP, EPCI, DBA, and water. Emitter layers were nanostructured  $\text{Fe}_2\text{O}_3$  and thin-film  $\text{SnO}_2$ .

#### 4. Conclusions

- Low ionisation-energy gases can be sensitively and selectively detected against large backgrounds of analytically less important background gases;
- Selectivity toward solvents can facilitate effective detection of dissolved salt-form analytes;
- SI response and recovery time constants are fast ( $< 1\text{s}$ );
- Applications to illicit drug detection appear to be feasible.

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#### References

- [1] Hackner A, Habauzit A, Müller G, Comini E, Faglia G, Sberveglieri G. *IEEE Sensors Journal*, 9, 2009; 1727-1733.
- [2] Hernandez-Ramirez F, Prades JD, Hackner A, Fischer T, Müller G, Mathur S, Morante JR. *Nanoscale*, 3, 2011; 630-634.