Sensors and Actuators B 156 (2011) 673–679

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

# *Vic*-dioximes: A new class of sensitive materials for chemical gas sensing

Mika Harbeck[a,*], Zafer Şen[a], Ilke Gürol[a], Gülay Gümüş[a], Emel Musluoğlu[a], Vefa Ahsen[a,b], Zafer Ziya Öztürk[a,c]

[a] *TÜBITAK Marmara Research Center, Materials Institute, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey*
[b] *Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, 41400 Gebze, Kocaeli, Turkey*
[c] *Gebze Institute of Technology, Department of Physics, P.O. Box 141, 41400 Gebze, Kocaeli, Turkey*

## ARTICLE INFO

*Article history:*
Received 12 October 2010
Received in revised form 9 February 2011
Accepted 11 February 2011
Available online 17 February 2011

*Keywords:*
Chemical gas sensor
*Vic*-dioxime
H bonding
Volatile organic compound
Quartz crystal microbalance

## ABSTRACT

*Vic*-dioximes, a class of organic chemical compounds, are proposed and characterized for the first time as sensitive materials for volatile organic compound sensing with sorption based chemical gas sensors. Their peculiar sensing properties described in this work originate in the oxime functional group which is a powerful H bond donor interacting strongly but reversibly with H bond acceptors. These specific interactions result in a high preferential enrichment of analyte molecules with H bonding acceptor capabilities in the sensitive material. Accordingly, sensitivity and selectivity for these compounds of *vic*-dioxime based sensors are high. The advantageous sensing properties are demonstrated in this work with quartz crystal microbalance sensors using 11 selected volatile organic compounds and a set of *vic*-dioximes varied in their substituents. *Vic*-dioximes with short alkylthiol substituents were found highly sensitive to such H bond acceptors as organic amines, alcohols, and esters with partition coefficients up to 26,000. At the same time they showed low affinity for aromatic compounds and chlorocarbons. *Vic*-dioximes are considered powerful sensing materials and interesting for practical use in chemical gas sensor arrays.

## 1. Introduction

Sorption based chemical sensor are most adequate for gas sensing applications targeting semi-volatile to volatile organic compounds (VOCs). Generally, several partially selective but complementary sensing materials on a suitable transducer, e.g. mechanical, optical or electrical, are combined to form a sensor array. The response data of the sensors taken during exposure to sample gases or vapors are then processed and evaluated using specialized algorithms. This concept is dubbed in popular terms "electronic nose". However, the large variety of possible target analytes and cross-interferents requires a similar variety in the sensing properties of the materials and sensors. Consequently, materials of ever increasing sensitivity and, more important, also selectivity towards certain analytes or analyte classes of interest are being developed [1–5].

Here we propose and describe for the first time the use of *vic*-dioximes (glyoximes) for VOC gas sensing applications. The oxime functional group is the origin of the remarkable sensing properties, as it can engage in H bonding with Brønsted and Lewis bases such as amines or alcohols. This class of compounds has not been described previously as sensitive material for chemical gas sensors other than a single report in the form of their very stable metal complexes [6]. *Vic*-dioximes are generally investigated and used as metal complexes or in their function as metal ion complexants, e.g. in analytical chemistry [7–9] or in the extraction of heavy metals from solutions [10,11]. Besides, metal complexes of *vic*-dioximes are studied, among others, in their electrochemical behavior [12], as potential catalysts [13] or biological model compounds [14].

In this work the glyoxime base compound was modified with alkylthio substituents of different chain length. In contrast to many other known substances with H bonding capabilities the compounds described here are easily available through a simple chemical synthesis procedure. The materials were tested in their responses to selected analytes spanning a wide range of chemical classes including strong and weak H bonding partners using quartz crystal microbalance (QCM) transducers.

## 2. Experimental

### 2.1. Sensitive materials

A *vic*-dioxime is a molecule with two neighboring oxime groups (=N–OH) and thus a derivative of glyoxime (ethanedial dioxime). In total six different *vic*-dioximes with *n*-alkylthiol (R–S) substituents

---

[*] Corresponding author. Tel.: +90 262 677 3123; fax: +90 262 641 2309.
*E-mail addresses:* mika.harbeck@mam.gov.tr (M. Harbeck), zafer.sen@mam.gov.tr (Z. Şen), ilke.gurol@mam.gov.tr (I. Gürol), gulay.gumus@mam.gov.tr (G. Gümüş), emel.musluoglu@mam.gov.tr (E. Musluoğlu), ahsen@gyte.edu.tr (V. Ahsen), zozturk@gyte.edu.tr (Z.Z. Öztürk).

0925-4005/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2011.02.017

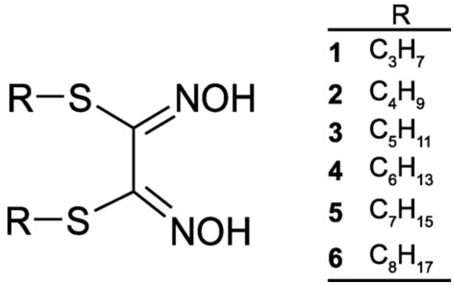

**Fig. 1.** Chemical structure of a *vic*-dioxime with two substituents R–S in 1,2 positions: R is an *n*-alkyl chain from $C_3H_7$ to $C_8H_{17}$.

of different chain length ($R{=}C_3H_7$–$C_8H_{17}$) in 1,2 position were synthesized and tested in their gas sensing properties. The chemical structure of such a substituted glyoxime molecule is presented in Fig. 1. The code numbers **1**–**6** used here for identification of the compounds indicate the difference in alkyl chain length: **1** is the *vic*-dioxime with two propylthio and **6** with two octylthio substituents. The chemical synthesis of the compounds was achieved following literature procedures described in [15] using the sodium salt of the respective thiol and 1,2-dichloroglyoxime.

### 2.2. QCM sensors

AT-cut quartz crystals of 10 MHz fundamental frequency (Klove Electronics B.V., the Netherlands) were used as transducers. With the help of an air-brush coating system the sensing materials were deposited from solution on both sides of the transducer. During the coating the frequency of the QCM was monitored and coating was stopped when a frequency shift of 11 kHz was reached (each side). Sensors were freed from remaining solvent in a dry air stream prior to use.

### 2.3. Sensor testing set-up and procedures

The same automated gas mixing system, QCM sensor systems, and experimental conditions as described in [4,5] were used for the sensor tests. Typical experiments of sensor test consisted of repeated exposure to analyte gas (normally 20–30 min) and subsequent purging with pure air to reset the baseline. The sensing materials were characterized using acetonitrile (ACN), ethyl acetate (EtOAc), ethylbenzene (EB), *n*-heptane (*n*C7), methanol (MeOH), *o*-xylene (*o*XLN), *n*-propanol (*n*PAOH), toluene (TLN), trichloromethane (TCM), trichloroethylene (TCE), and triethylamine (Et3N) vapors. The VOCs were selected to represent common chemical classes and to cover a wide range of chemical properties as expressed in their linear solvation energy relationship (LSER) parameters [16]. The concentrations were adjusted to levels between 5% and 25% of the vapor pressure of the respective analyte at −10 °C in five concentration steps. The humidity background was changed between 15–75% r.h. in three levels. Additionally, nitrobenzene (NB) and *iso*-propanol (iPAOH) sensor data in dry air was acquired to provide more input values for the response modeling. For NB the vaporization temperature was +10 °C due to the higher freezing point. During the measurement the sensor chamber was kept at 22 °C at all times. The sensors were prepared and tested in duplicates and the measurements were repeated at least once.

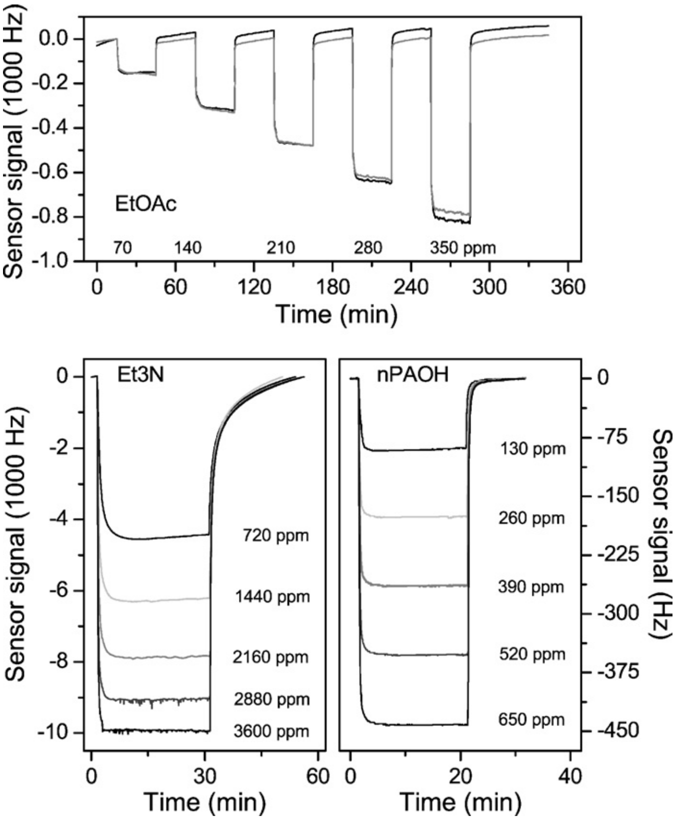

**Fig. 2.** (Top) Transient signals of two QCM sensors with **1** to pulses of EtOAc vapor. (Bottom) Superimposed response curves of a QCM sensor with **1** to pulses of (left) Et3N and (right) *n*PAOH vapors.

## 3. Results and discussion

### 3.1. Gas sensing performance of vic-dioximes

The QCM sensors prepared with the oxime compounds were exposed to the different vapors in increasing concentration steps and at different background humidity levels to study the gas sensing properties of the *vic*-dioximes. Generally, the gas sensing characteristics of the compounds in terms of baseline stability, response and recovery times, and repeatability were good. Sensors with short chain substituted *vic*-dioximes exhibited the best sensing performance judged on the quick responses and recoveries as well as the magnitude of the responses.

In Fig. 2(top) the simultaneous transient responses of two 10 MHz QCM sensors coated with 11 kHz of compound **1** on both sides to pulses of EtOAc vapor in increasing concentrations are presented. The raw data is plotted without any corrections, only the last sensor reading before the first analyte exposure was used as zero reference and subtracted from all data points. The two sensors show nearly the same performance with only little variation from each other. The responses of both sensors lie within 3% of the average value. The graphs of Fig. 2 (bottom) depict the superimposed response curves acquired during exposure to five concentrations of Et3N (left) and *n*PAOH (right) vapors. Each response is equally well behaved with only some changes in response and recovery times. This illustrates the good response and recovery characteristics of the *vic*-dioximes based sensors. The response times ($t_{95}$) decrease with increasing analyte concentration. In the examples, $t_{95}$ times decrease from 177 s via 120, 97, and 56 to 42 s for Et3N and from 63, 49, 48, and 48 to 42 s for *n*PAOH. Recovery times are longer and in the range from 963 to 735 s for Et3N and 74 to 46 s for *n*PAOH. Most response times ($t_{95}$) are below or near 1 min as shown for *n*PAOH