

Overview on solid-state dosimeter-type gas sensors

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Abstract:

Based on irreversible analyte accumulation in the sensitive layer, dosimeter-type gas sensors are promising for the long-term monitoring of low levels of analytes. Thereby, the analyte dose can be detected either during progressive analyte sorption or release with a direct correlation between the sensor response and the cumulated analyte amount. A short overview on various solid-state resistive dosimeter-type sensors for several gaseous analytes is given in order to demonstrate the potential of this cumulative sensing principle. The focus is on a NO_x sensor based on chemical NO_x storage with linear characteristics concerning the NO_x dose allowing for additional information on the actual NO_x concentration from the signal derivative.

Key words:

Low level detection, long-term monitoring, accumulation mode, exposure monitoring, real-time gas dosimeter, chemiresistor.

Introduction

In the field of exhaust or air quality monitoring, the focus is rather on mean values or amounts of analyte exposure (= dose) than on the timely course of the concentration. The mathematical integration of concentration-related sensor responses to determine the dose over longer periods is error-prone. Especially for low analyte levels, the analysis often suffers from noise, zero-level drifts as well as from slow response and recovery times.

On the contrary, real-time dosimeters are particularly suitable for the long-term monitoring of low level exposures without mathematical operations since the sensor response correlates directly with the analyte dose. Average concentrations of highly diluted gases (e.g. the hourly mean value [1-3]) can be determined easily from the sensor response accounting for the duration of exposure. Due to their irreversible analyte sorption capability, dosimeters are also denoted as (ac-) cumulating [2-5] or integrating [3,6,7] devices.

Analyte accumulation in the sensitive layer can be realized by chemical reactions [2,6,8,9], or by apparently irreversible sorption processes [7,10,11]. Therefore, the proper choice of the sensitive material is essential to obtain a dosimeter-type sensing behavior under the applied conditions [3,10].

After an introduction to the dosimeter-type sensing principle, a short overview on resistive gas dosimeters for various analytes is given. The diverse functionalities of a NO_x dosimeter based on chemical NO_x storage are described in detail.

Background on the dosimeter-type sensing principle

Similar to passive samplers, dosimeter-like gas sensors are operated in two alternating steps as shown in Fig. 1. During the sorption period, analyte molecules are progressively accumulated in the adsorbent layer followed by a short-term regeneration to release the formerly sampled molecules.

An analyte loading level dependent physical property of the adsorbent serves as sensor signal R . In resistive dosimeters the resistance R might serve as measurand. R increases with proceeding exposure and recovers as the initial state of the adsorbent is restored. Therefore, analyte detection might be performed either during sorption [6,7,12] or release [13]. Mainly optical [2,5,9], gravimetric [8], and recently impedimetric [1,6,12,14-17] dosimeters are reported.

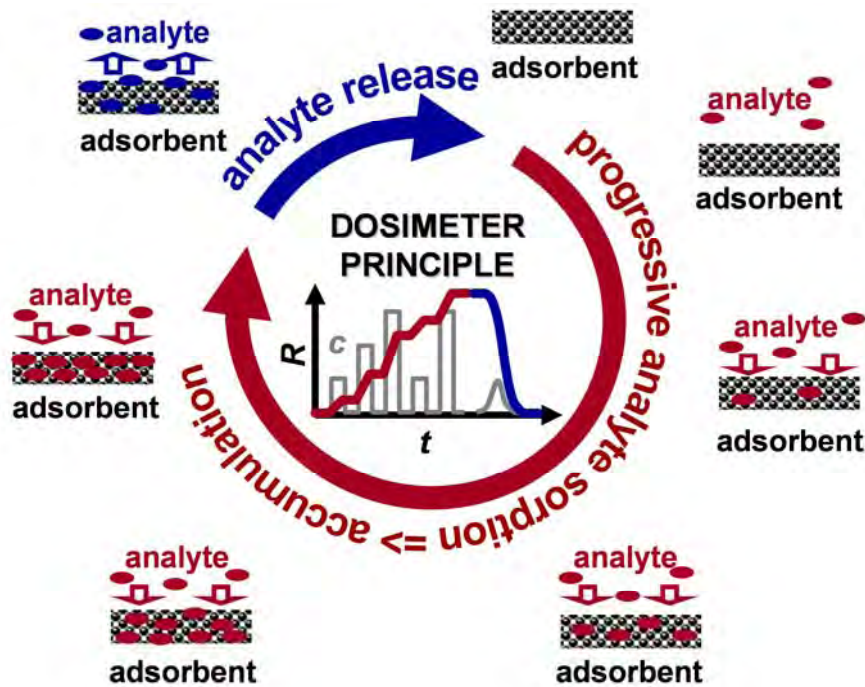


Fig. 1. Principle of dosimeter operation: alternating analyte sorption and regeneration periods with an exposure dependent sensor response R .

The direct amount sensing characteristics of a resistive dosimeter during analyte sorption are sketched in Fig. 2 for a constant gas flow rate [18]. Then, the dose or cumulated amount A is proportional to the timely integral of the exposed concentration c in the unit $\text{ppm}\cdot\text{s}$ [3,5,12]. Consequently, the measurand R (e.g. the resistance) increases irreversibly in the presence of analyte [7,8,15,16]. Ideally, the analyte sorption rate of the adsorbent is proportional to c resulting in a linear characteristic line between R and the dose A [3,18]. Due to this proportionality, the course of the analyte concentration can be obtained from the signal derivative dR/dt [2,3,7,10]. The amount-sensitivity S_A is given as dR/dA [3-5,9], e.g. in $\%/\text{ppm}\cdot\text{h}$ or $\%/\mu\text{l}$, and is proportional to the common concentration-sensitivity S_c [4].

Once the sorption sites of the adsorbent are saturating, the analyte accumulation rate decreases. Regeneration needs to be initiated to recover the performance of the dosimeter [3,4,6,7,10]. Depending on the interaction between the adsorbent and the analyte, analyte release might occur e.g. thermally [3,11,17,19], or upon exposure to UV light [16,17]. Otherwise the dosimeter is a disposable device allowing only for a one-shot detection [8,10]. Advantageously, the zero level of the dosimeter-type sensor response is self-redefined by regeneration, avoiding long-term signal drifts [3].

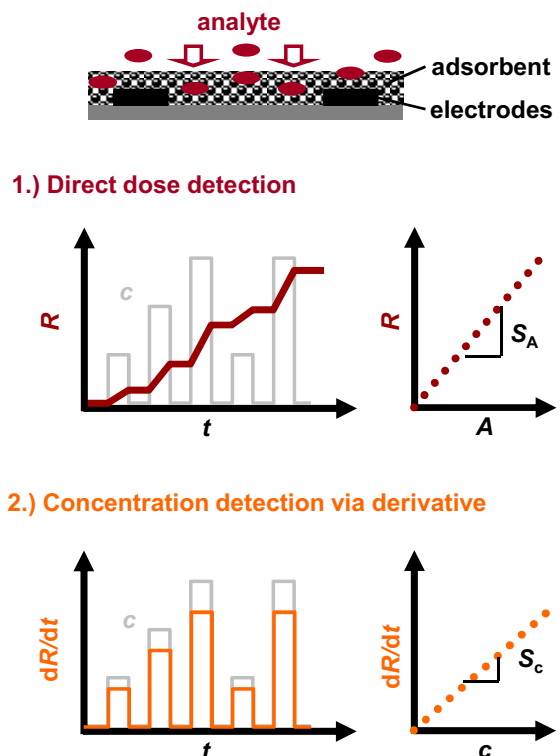


Fig. 2. Evaluation of sensor response R in the sorption mode to determine: (1) directly the analyte dose and (2) indirectly the timely analyte concentration.

The resistive accumulating NO_x sensor

As a first example for solid-state gas dosimeters, a NO_x accumulating device is described.

The NO_x sorption capability of the presented NO_x dosimeter is based on a lean NO_x trap known from automotive catalysts. In the temperature range of 350 to 450 °C, NO and NO₂ are oxidized and stored chemically by a carbonate to nitrate conversion under excess oxygen [6]. The resistivity of the adsorbent decreases with progressive nitrate formation [6,14]. This enables dosimeter-type total NO_x detection under NO_x oxidizing and sorption conditions [3,4,11,20] with a comparable sensitivity to NO and NO₂ [3,4]. NO_x release via nitrate decomposition is achieved upon heating to 650 °C [20] or in reducing atmospheres [3,6] enabling a periodic recovery of the storage sites and of the sensitivity.

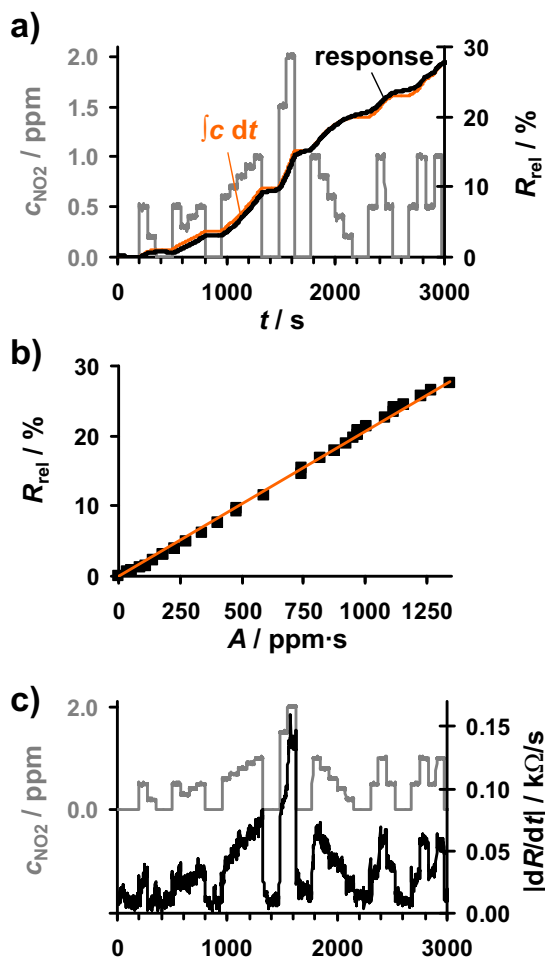


Fig. 3. Low level NO₂ detection (0.2 to 2 ppm for 75 s): a) response R_{rel} proportional to $\int c_{NO_2} dt$, b) amount related characteristic line, c) derivative $|dR/dt|$ proportional to c_{NO_2} . Adapted from [3].

The suitability of the NO_x dosimeter for the long-term NO₂ detection with concentrations in the sub-ppm range is shown in Fig. 3 [3]. The absolute value of the relative resistance change R_{rel} is monitored as sensor response during intervals with 0.2 to 2 ppm NO₂ as indicated in Fig. 3a. R_{rel} increases stepwise in the presence of NO₂. More precisely, R_{rel} follows the course of the timely integral of the concentration c that is representing the cumulated NO₂ amount A . The resulting characteristic line in Fig. 3b clarifies the linear correlation between R_{rel} and A up to about 30 % with a sensitivity of 0.021 %/ppm·s. The time derivative of the resistance $|dR/dt|$ in Fig. 3c is almost proportional to course of the concentration $c(t)$.

Fig. 3 reveals that in contrast to common gas sensors, the presented NO_x dosimeter detects directly and time-continuously the cumulated amount of NO₂ in the sorption mode, while the actual concentration can be estimated from the slope (timely derivative). Concerning NO₂, the EU emission legislation permits a 1-hour value of 200 µg/m³ and an annual mean value of 40 µg/m³ [21]. According to the linear measurement range reported in Fig. 3, the 1-hour value could be monitored linearly by the NO_x dosimeter for about 3.7 h without regeneration and the annual value for even 18.5 h.

In accordance to the catalytic properties, it was demonstrated that the sensitivity of the NO_x dosimeter increases with temperature while the linear measurement range decreases [3,22]. At 650 °C, the resistance changes reversibly in NO_x indicating missing NO_x accumulation properties and thermodynamic instability of nitrates [20]. The presence of oxygen is essential, but variations of O₂ and CO₂ in a wide concentrations range have no significant effect on the dosimeter-like NO_x sensing characteristics [6]. The missing oxidizing properties of pure carbonates enable NO₂ dosimetry without NO sensitivity [14,23]. SO₂ deteriorates the NO_x sorption capacity and affects the resistivity requiring regeneration at elevated temperatures and in reducing atmospheres [24]. Hence, SO₂ dosimetry can be achieved with the same setup [24].

It was shown that the arrangement of the adsorbent in the gas flow influences the NO_x sorption [18,20]. One can distinguish between an amount detector due to complete NO_x uptake or a flow rate independent concentration integrator [18]. A rotational symmetry of the transducer geometry was found to be particularly advantageous for analyte sorption in dosimeters [20]. The self-heated tubular ceramic platforms allowed for a sensitivity

adaption by an easy adjustment of the temperature of the adsorbent and periodic thermal regeneration. Differently heated zones in the tubular setup equipped with various adsorbent layers are intended to enlarge the functionality.

Additionally, the NO_x dosimeter characteristics can be adapted by the adsorbent thickness as explained in detail in [4]. The test series included adsorbent layers of 30, 60 and 90 μm deposited on electrodes with 100 μm spaces. All samples show NO and NO_2 cumulative sensing behavior and a linear sensing characteristics independent on the NO_x species. However, the sensitivity increases with the inverse thickness. Independent on the thickness, the linear measurement range is limited by 30 % sensor response and consequently decreases with increasing sensitivity.

Overview on other resistive gas dosimeters

As already mentioned, the dosimeter's response correlates with analyte loading state of the adsorbent. The loading state is dependent on the analyte exposure, in particular the concentration and the duration. In the following further examples of solid-state dosimeters based on resistive measurement principles are given. The adsorbent materials range from polymers to ceramics and metals and analyte detection is achieved either during analyte sorption or release at various temperatures.

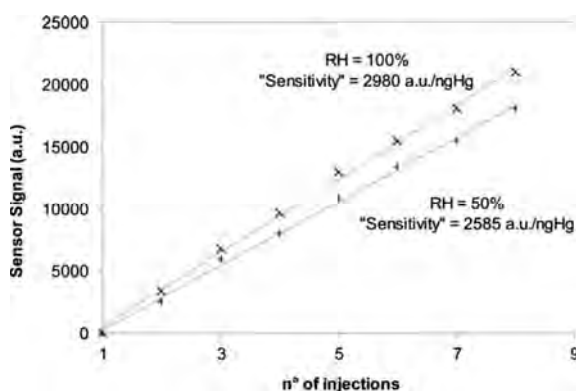


Fig. 4. Resistive dosimeter to monitor the personal exposure to gaseous mercury by a thin gold film. Reprinted from Ref. [1], Copyright (2007), with permission from Elsevier.

Mattoli et al. [1] developed a low-cost, wearable dosimeter based on thin gold films. This dosimeter is proposed for the long-term and

real-time monitoring of the personal exposure to gaseous mercury in indoor applications. Upon diffusion controlled sampling of Hg^0 in the sampling chamber, amalgam is formed on the gold film and the resistance increases. Fig. 4 reveals the dosimeter-like sensing characteristics by a dependency of the sensor response on the number of consecutive injections of 12 ng Hg^0 .

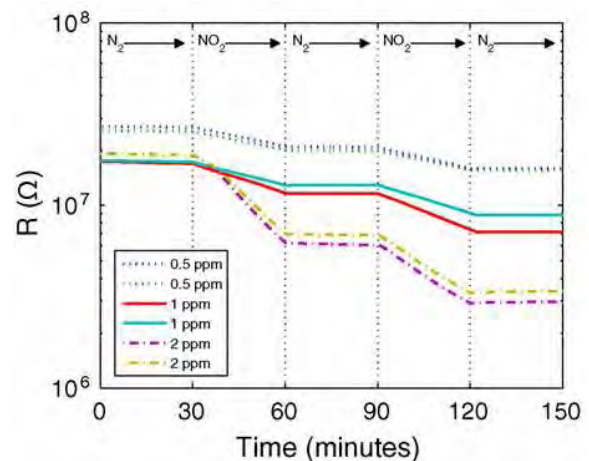


Fig. 5. Low level NO_2 dosimeter based on iron (II) phthalocyanine operated at room temperature. Reprinted from Ref. [7], Copyright (2010), with permission from Elsevier.

Iron phthalocyanine (FePc) is applied as NO_2 sensitive chemiresistor by Shu et al. [7]. Forming a charge carrier complex, NO_2 as electron acceptor results in an increase in the conductivity. As shown in Fig. 5, FePc allows for resistive-type low level NO_2 dosimetry at room temperature since the NO_2 adsorption is irreversible in the non-saturated state. Higher temperatures accelerate the adsorption-desorption kinetics, the adsorbent can be regenerated, and the resistance correlates with the NO_2 concentration. Like for the NO_x dosimeter in Fig. 3c, the derivative of the dosimeter-type sensor response is evaluated to obtain concentration information.

Recently, Hennemann et al. [12] reported on the H_2S dose sensing characteristics of CuO nanofibers. Forming CuS in H_2S , the conductivity increases by several orders of magnitude. After reaching the percolation threshold, H_2S can be electrically detected stepwise as shown in Fig. 6. While H_2S accumulates on CuO at 160 °C, the nanofibers are regenerated at 350 °C.

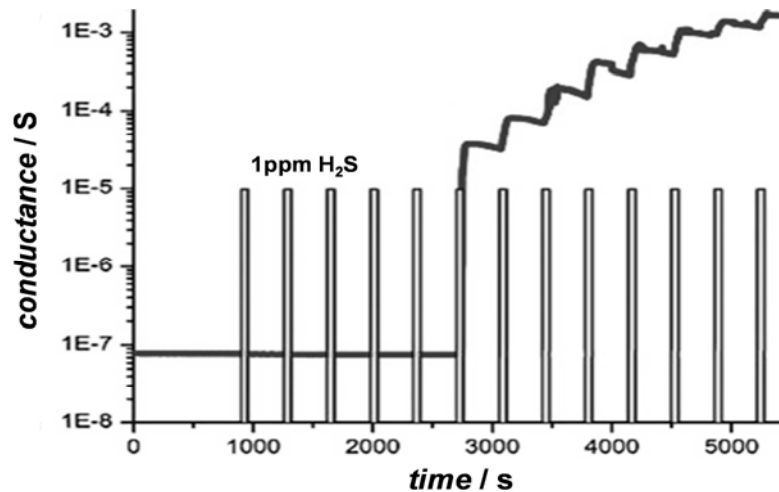


Fig. 6. H_2S dosimetry by electrospun copper oxide nanofibers at $160\text{ }^\circ\text{C}$ in $1\text{ ppm } H_2S$ pulses being affected by a percolation threshold. Adapted from [12].

Helwig et al. [19] published a review article on the low temperature response of semiconductor gas sensors. Comparing the sensitivity to gaseous species of several semiconducting materials below $150\text{ }^\circ\text{C}$ reveals, that the dosimeter-like sensing properties originate from acid or base reactions. The electrolytic dissociation of the analyte in adsorbed water at the surface results in a pH change affecting the electrical properties of the semiconductor. The sensor response is recovered in UV light or O_3 . Additionally, the thin water layers at the surface may serve as single-use sensitive layers by alternately condensing and evaporating water [25].

While the latter dosimeters detect the analyte amount in the sorption mode, Kubinski et al. [13] introduce a NH_3 dosimeter operated during the release of the formerly sorbed analyte.

Conclusions

The operation principle of gas dosimeters is described in detail. Further, examples for resistive-type gas dosimeters are given. Dosimeters are operated either in the analyte sorption or release mode. Both allow for the detection of the analyte dose, but only the former gives real-time and time-continuous information on the analyte exposure evolution.

Solid-state gas dosimeters are beneficial in the field of long-term monitoring of low levels of analytes compared to common gas sensors. The sensor response correlates directly with the cumulated amount. This enables dose detection without the need for a mathematical integration

of concentration-related signals. Those are often affected by noise or long-term drifts upon exposure to low levels of analytes. Hence, the analyte accumulating character of dosimeters enhances the accuracy of the determination of mean values or doses. Additionally, the course of the analyte concentration can be estimated from the signal derivative if the dosimeter provides linear sensing characteristics unaffected by varying flow rates.

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