

DETECTION OF PHOSGENE BY USING TiO₂/INDICATOR NANOCRYSTALLINE THIN FILMS

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Summary: *A new optical solid sensor device for detection of phosgene in chloroform has been developed by incorporating the Harrison's reagent (a solution of diphenylamine and dimethylaminobenzaldehyde in ethanol), to nanocrystalline TiO₂ thin films.*

The TiO₂ thin films were prepared by depositing the 18NR-T Transparent Titania Paste from Dyesol onto a glass substrate through the screen printing method. The active area of the films was 0,16 cm² with a thickness of 1,8 μm. The composite was obtained by immersion into a solution of the Harrison's reagent during 15 minutes.

As real target analyte we have used chloroform stabilized with amilenes which is known to be slightly decomposed in phosgene and HCl, if storage conditions are not appropriated. We have used chloroforms from different manufacturers were the initial presence of phosgene was checked by using test strips wetted with the indicator.

Further decomposition of chloroform was photoinduced by using a solar simulator. Nanocrystalline films were used to detect in situ the formation of phosgene by measuring their absorbance spectra under exposure to the sample vapors. A new band at ~450 nm appears in the spectrum due to the presence of phosgene. The response intensity (absorbance at 450 nm) has been found to be concentration-dependent with response films varying from 1 to 8 minutes.

To the best of our knowledge this is the first solid optical sensor of phosgene. Currently we are working in the detection limits and other operation parameters of this new sensor.

1 INTRODUCTION

Phosgene was used in I World War as a biological weapon due to its high toxicity. The lethal dose for human being is 2 ppm. [1] Phosgene has several lung irritant effects, including pulmonary edema and asphyxia [2,3] but the irritant effects or symptoms appear a few hours after the exposition. This is the reason why an early detection is very important.

Although there are several commercially available phosgene sensors on the market, most of them are based on complex and time-consuming techniques such as gas chromatography or mass spectroscopy. Other simpler and faster methods based on color reactions such as the detection with phosgene-indicator strips. Obviously, these methods do not allow automation. Although many fluorescent sensors have been developed for a variety of chemical warfare agents existing in the atmosphere, [4,5,6] there is no one available for the detection of phosgene.

Unfortunately, most of the reported sensors cannot meet the requirement for an optical solid sensor. In recent years, optical sensors have attracted much interest in gas sensors because of their easy preparation and high stability as well as easy to measure spectroscopic properties.

In this work, we report a new optical solid phosgene sensor based on the chemical reaction between phosgene and Harrison's reagents.

The optical solid sensor device has been developed by incorporating the Harrison's reagent into nanocrystalline TiO₂ thin films. In order to study its detection capabilities, the absorbance spectra of the film were recorded under exposure to the sample vapors.

As real target analyte we have used chloroform stabilized with amylene, which is known to be slightly decomposed in phosgene and HCl if storage conditions are not appropriated.

2 RESULTS AND DISCUSSION

In order to test the initial amount of phosgene in chloroform, test strips wetted with the phosgene indicator (Harrison's reagent) were exposed to the sample vapors and color changes were detected by naked-eye, as it is shown in Figure 1.

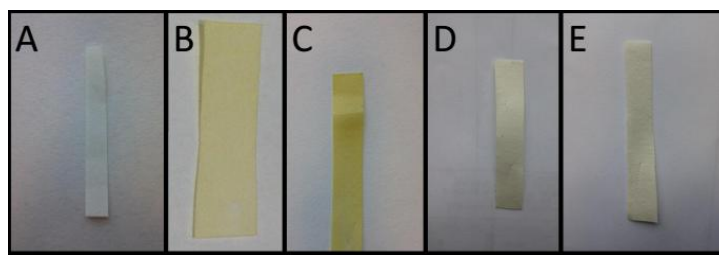


Figure 1: Strips previously wetted with Harrison's reagents for two minutes, before (A) and after two minutes of exposure to the vapors from different chloroforms from SIGMA ALDRICH (B and E, Ref: 472476), PANREAC (C, Ref: 133101.1611), and LABKEM (D, Ref: CHLF-S0T-1K0)

After the exposure to the headspace vapors from different bottles of chloroform, the strips exposed to B and C turned from white to yellow revealing the presence of phosgene due to some decomposition of the solvent. In contrast, strips exposed to chloroforms D and E did not make any change of color indicating that there is no evidence of chloroform decomposition in these bottles.

The TiO₂ thin films were prepared by depositing the 18NR-T Transparent Titania Paste from Dyesol onto a glass substrate through the screen printing method. The active area of the films was 0,16 cm² with a thickness of 1,8 μ m.



Figure 2: TiO₂/indicator thin films prepared by depositing the 18NR-T Transparent Titania Paste from Dyesol onto a glass substrate through the screen printing method

In order to determine the optimal time for the infiltration of the reagent into the TiO₂ thin

films, UV-vis spectra were recorded at different infiltration time as it is shown in Figure 3. Firstly, we see that as the infiltration time increase, the absorbance of the Harrison's reagent in the film grows up to a maximum at 15 minutes. After that, the absorbance decreases. Therefore we can conclude that the optimum time for the infiltration is 15 minutes. Additionally, TiO₂/indicator thin films were found to be very stable after one week with the respective spectra remaining unaltered after this time (data not shown).

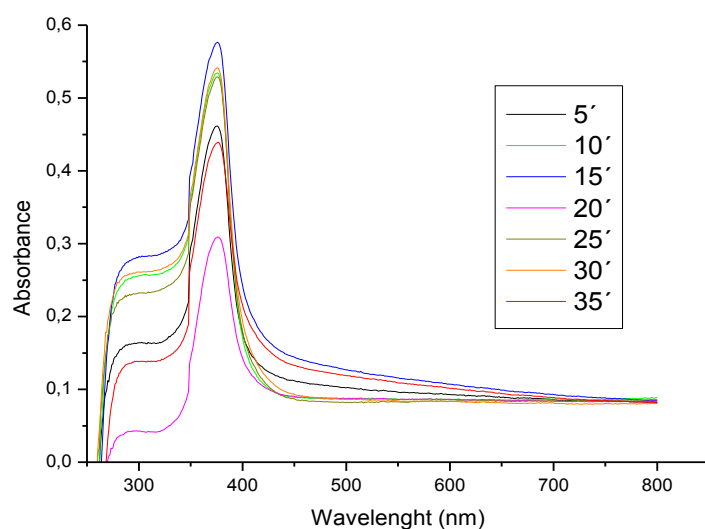


Figure 3: TiO₂/indicator thin films spectra after different infiltration times in Harrison's reagent solutions

In order to increase the amount of phosgene generated in the chloroform samples, the solvent was irradiated with a solar simulator thus photoinducing further decomposition.

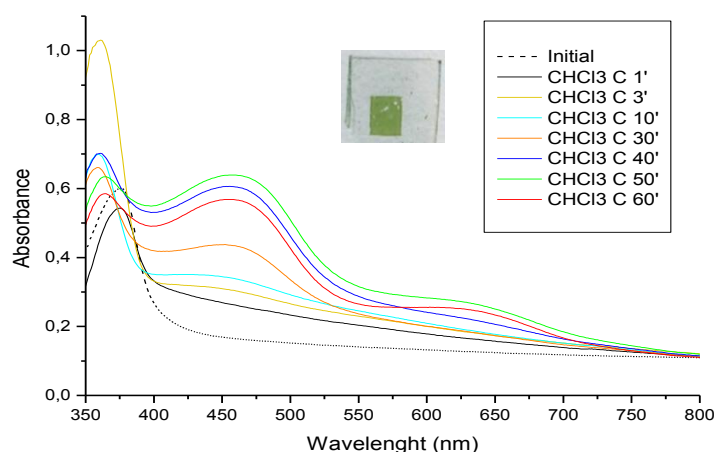


Figure 4: Absorbance spectrum evolution of TiO₂/indicator thin films exposed to chloroform C after different irradiation times. Inserted image taken for the film after the exposure to 50' irradiated chloroform C

As can be seen the absorbance at 450 nm increases with the irradiation time due to the appearance of increasing amount of phosgene in the sample. A new peak appears at 650 nm

probably due to the presence of HCl.

In order to study the concentration dependent of the sensor we have used the irradiation time of the sample as a direct indicator of the amount of generated analyte. In this way, the previous results have been interpreted in terms of the Langmuir adsorption isotherm. This isotherm has been successfully used to account for the adsorption of different types of molecules either from gas or liquid media onto different solid materials [7,8,9] and can be expressed as:

$$\frac{n_{ads}}{N_s} = \frac{\lambda c}{1 + \lambda c} \quad (1)$$

Where n_{ads} is the number of the absorbed molecules, proportional to the peak area, N_s is the number of adsorption sites available on the TiO₂ surface, λ is a constant relating to the adsorption capacity of TiO₂/indicator, and c is the analyte concentration. In this case, we assume that concentration of generated phosgene is time-dependent. In our study, we expose the samples to a solar simulator with standard calibration, 1 sun (100 mW/cm²) and these samples maintain their linear properties.

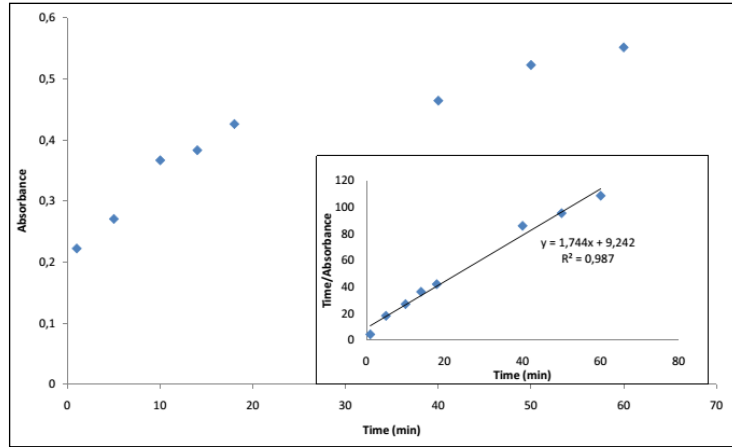


Figure 5: Langmuir adsorption plot for TiO₂/indicator thin films upon exposure to phosgene generated with different irradiation times

As can be seen in Figure 5, our data fit quite well with the isotherm demonstrating the sensor applicability for calibration purposes.

As mentioned before, the chloroform decomposition chemical reaction produces phosgene and HCl. In order to verify that the absorbance peak at 450 nm is related to the phosgene appearance instead of HCl, we exposed the TiO₂ /indicator thin film to a saturated HCl atmosphere.

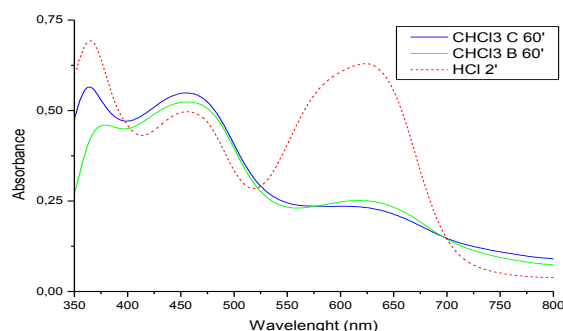


Figure 6: Absorbance TiO_2 /indicator thin films spectra after the exposure to saturated HCl vapors and the headspace vapors from chloroform C and B exposed at solar simulator for 60 minutes

Figure 6 shows that after exposure to HCl atmosphere, the absorbance peak at 625 nm increase notably. Therefore, we could conclude that the absorbance peak at 450 nm reveals the presence of phosgene and the peak at 650 nm would be due to HCl, with only a slight contribution to the peak at 450 nm.

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