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## Acousto-electrical and surface plasmon resonant responses from NOX-doped Langmuir-Blodgett films of macrocycles

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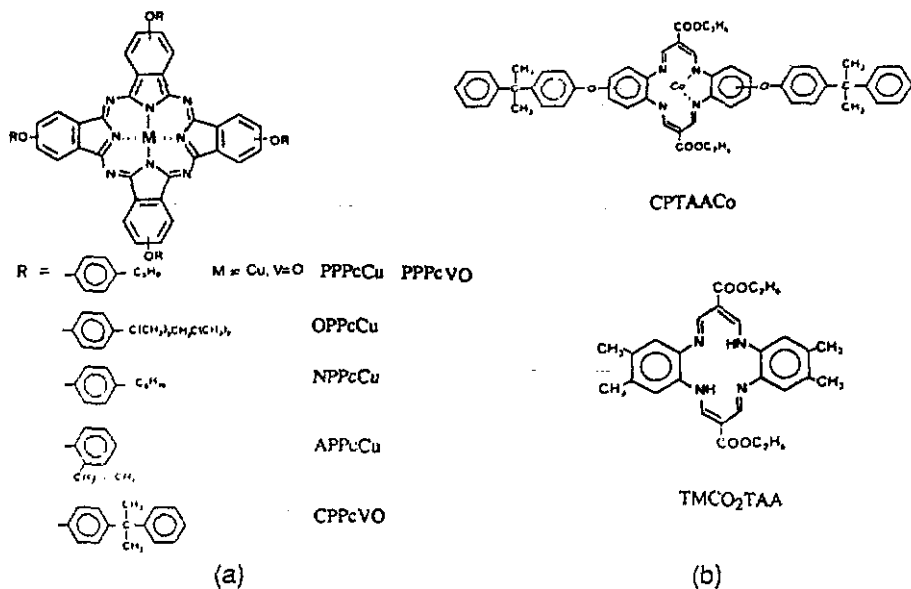
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**Abstract.** The adsorption of nitrogen dioxide gas by Langmuir-Blodgett (LB) films of derivatives of phthalocyanine and dibenzotetra-aza-annulene has been monitored using quartz crystal oscillators, surface acoustic wave devices and surface plasmon resonance. Significant responses were observed from these films at relatively low concentrations of NOX (5-200 ppm) and some possible advantages of using thin LB films have been indicated.

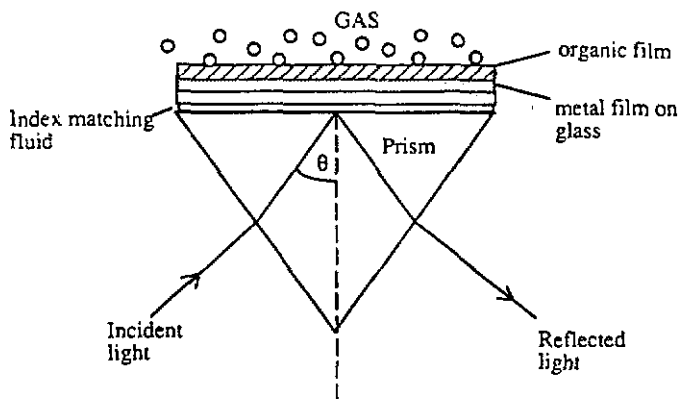
### 1. Introduction

A significant amount of work has been undertaken on the application of macrocyclic compounds to gas detection [1], most of which has been concerned with exploiting the semiconductive properties of the phthalocyanines [2]. Our recent work has involved the use of acousto-electric devices (quartz crystal oscillators and surface acoustic wave devices) and an optical technique, surface plasmon resonance (SPR), to monitor the adsorption of nitrogen dioxide (NOX) by Langmuir-Blodgett (LB) films of new derivatives of phthalocyanine (Pc) and dibenzotetra-aza-annulene (TAA) (figure 1); conductivity measurements have also been made [3]. Surface acoustic wave (SAW) and quartz crystal sensors operate by microgravimetry; they respond to minute increases in mass, caused by the adsorption of gas onto a surface layer, by decreasing their resonant frequency. In an SPR sensor, shown in figure 2 in the so-called Kretschmann geometry, light is coupled to a thin metal film sandwiched between two materials of different dielectric constant. At a specific angle,  $\theta$ , which is greater than the critical angle, the incident light induces collective oscillations of the free electrons at the metal surface, which is seen as a sharp minimum in the reflectance (figure 3). The evanescent field of the resonance travels into the adjacent dielectric, thus the angle,  $\theta$ , is highly susceptible to changes in the refractive index or the thickness of that dielectric. If a thin, gas adsorbing film is coated onto the metal and interacts with a gas, then any change in its refractive index will produce a measurable change in  $\theta$  (figure 3(b)).

The nature and morphology of the organic thin film greatly influences the adsorption kinetics [4]. In this work LB films were used because they may hold the potential to provide a higher degree of ordering and a better-defined film structure for gas adsorption. Previous gas-sensing studies using LB films of Pcs with quartz oscillators [5], SAW devices [6] and SPR [7] have shown promising results. The use of LB films of TAAs for gas sensing has not been previously reported.



**Figure 1.** Phthalocyanine and dibenzotetraaza-annulene derivatives: (a) substituted Pcs and (b) TAAs.



**Figure 2.** The surface plasmon resonance (SPR) experiment (Kretschmann configuration).

## 2. Experimental details

The TAA and Pc syntheses, which have been reported elsewhere [8], were based on standard procedures [9-11].  $TMCO_2TAA$  and some cumylphenoxy Pcs [9, 12] have been prepared by other workers.

The LB technique of preparing thin multilayer films by the sequential deposition of monolayers is well documented [13]. Further details concerning LB films of macrocycles are described in our recent work on porphyrins [14] and TAAs [15]. The LB films were

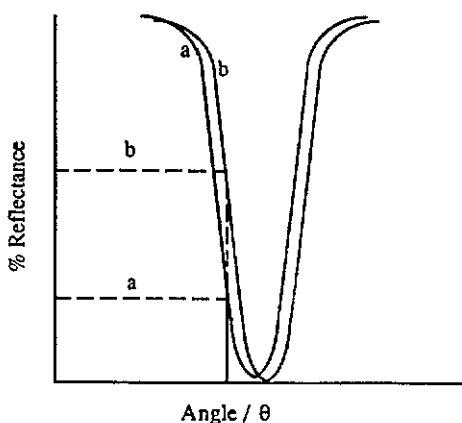


Figure 3. SPR minimum: (a) before gas exposure and (b) after gas exposure.

prepared using a Nima technology LB deposition system with a subphase of cadmium chloride solution ( $2.5 \times 10^{-4} \text{M}$ ) at a pH of 5.6 and at surface pressures of  $25 \text{ mN m}^{-1}$  for the Pcs and  $\text{TMCO}_2\text{TAA}$  and  $20 \text{ mN m}^{-1}$  for CPTAACo. These Pc derivatives and  $\text{TMCO}_2\text{TAA}$  tended to form aggregates which rendered their Langmuir films too rigid to transfer as LB multilayers, therefore, they were deposited as mixed films in a matrix of cadmium stearate. CPTAACo formed multilayer films without the addition of cadmium stearate [15]. For SPR, one monolayer of pure material was deposited onto a gold film coated with a layer of cadmium stearate. The uniformity of film transfer was confirmed using visible absorption spectroscopy and microgravimetry. x-ray diffraction indicated structural order in the films.

All gas-sensing experiments were carried out at room temperature. NOX was supplied from a calibrated cylinder (BOC special gases) and diluted with dry air. Quartz oscillator measurements were made using 9 MHz quartz crystals. The sample crystal and an uncoated reference crystal were enclosed in a small flow cell and their frequency changes were monitored simultaneously using a frequency counter (Philips PM6661). The frequency/mass relationship, for AT cut quartz operating in thickness shear mode, given by the Sauerbrey equation is

$$\Delta f = -2.3 \times 10^{-6} f_0^2 \Delta m / A$$

where  $\Delta f$  is the change in frequency (Hz),  $f_0$  is the resonant frequency of the crystal (Hz),  $\Delta m$  is the change in mass and  $A$  is the area of the adsorbing layer ( $\text{g cm}^{-2}$ ). The resolution of the system was 2 Hz, giving a detection limit of  $9.4 \text{ ng cm}^{-2}$ . SAW devices are able to operate at much higher frequencies, thus allowing a much higher sensitivity. The analogous equation for the frequency/mass dependence of an ST cut quartz SAW device is

$$\Delta f = -1.26 \times 10^{-6} f_0^2 \Delta m / A.$$

For these experiments a dual delay line SAW device [6] of ST cut quartz, with two pairs of 100 finger pair aluminium IDTs ( $4 \mu\text{m}$  wide and  $4 \mu\text{m}$  apart), operating at 98.6 MHz

was used (figure 4). With a resolution of 2 Hz, the detection limit was  $0.16 \text{ ng cm}^{-2}$ . One side of the device was coated with an LB film leaving the other side uncoated as a reference channel. The device was enclosed in a flow cell and its response to NOX was monitored using a high-resolution counter (Philips PM6654).

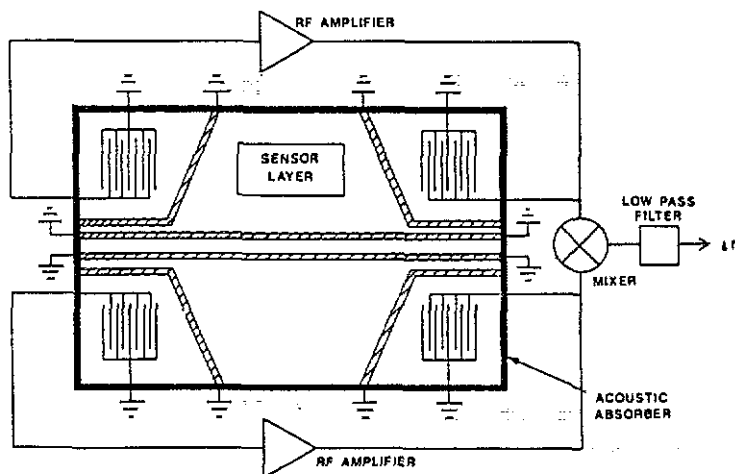


Figure 4. 98.6 MHz dual delay line SAW device.

The SPR sensor was of a fan-beam configuration comprising a diode laser source of wavelength 820 nm, focused to a convergent beam, and a 256-component photodetector array. The substrates were of glass, coated with 50 nm of gold. A small gas-flow cell was clamped to the surface of the substrate. The effect of NOX interaction with the film was observed by monitoring the resulting change in reflectance at a fixed angle on the resonance curve just to the left of the minimum (figure 3).

### 3. Results and discussion

#### 3.1. Acousto-electrical measurements

Large changes in frequency, in response to concentrations of NOX from 10 to 50 ppm, were observed for both classes of macrocycle. Initial exposure to NOX produced little response, but after prolonged exposure, the rate of response increased and greater sensitivity to lower concentrations of gas was observed. This initialization effect is similar to that observed in conductivity measurements [4]. As expected, the SAW devices showed a greater sensitivity than the crystal oscillators. The results obtained on exposure of the quartz oscillators and the SAW devices to NOX are shown in figure 5 and table 1 respectively. In most cases no correlation between frequency and concentration could be obtained; however, a five-layer film of PPPcVO (figure 6) and a two-layer film of CPTAACo (figure 7), after initialization gave, for three successive exposures, linear plots of log frequency/log concentration. This indicates that very thin LB films may permit faster attainment of equilibrium and simpler, more reproducible adsorption kinetics. Although the thicker films gave a greater change in frequency

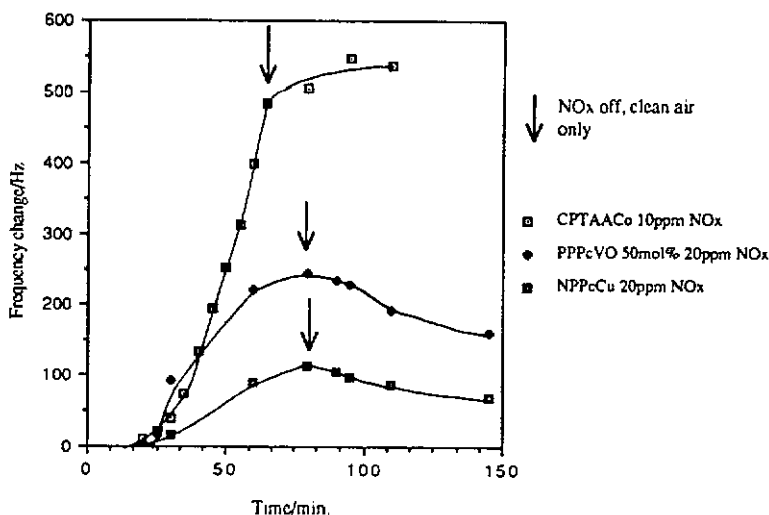


Figure 5. Response to NO<sub>x</sub> of LB films of Pcs and TAAs on quartz oscillators.

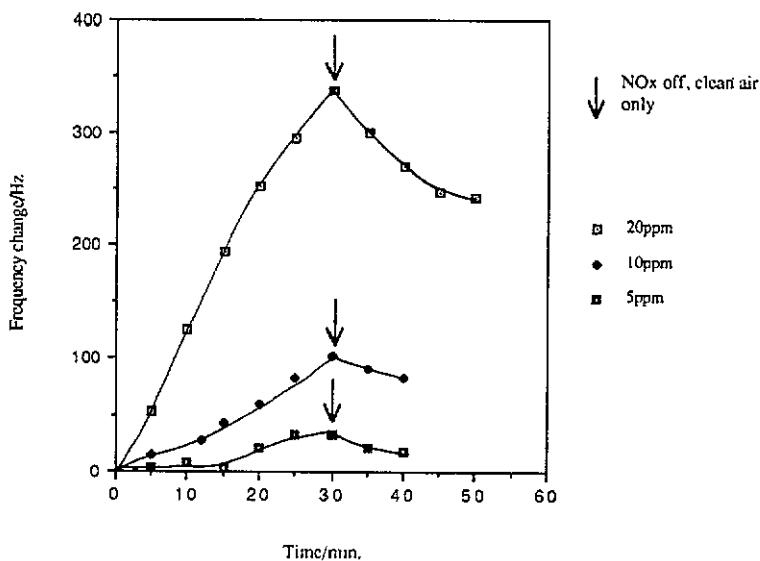


Figure 6. Response of SAW device coated with five layers of PPPcVO (50 mol% in cadmium stearate) to 5, 10 and 20 ppm NO<sub>x</sub>.

than the thin films for the same concentration of NO<sub>x</sub> (figure 8), their responses were not as reproducible.

The reversibility was generally poor, for example PPPcVO samples showed reversal of only 12–48% over 20–23 min. This lack of reversibility may be due, partly, to the presence of cadmium stearate which was found, by SAW experiments and XPS, to adsorb and retain NO<sub>x</sub>.

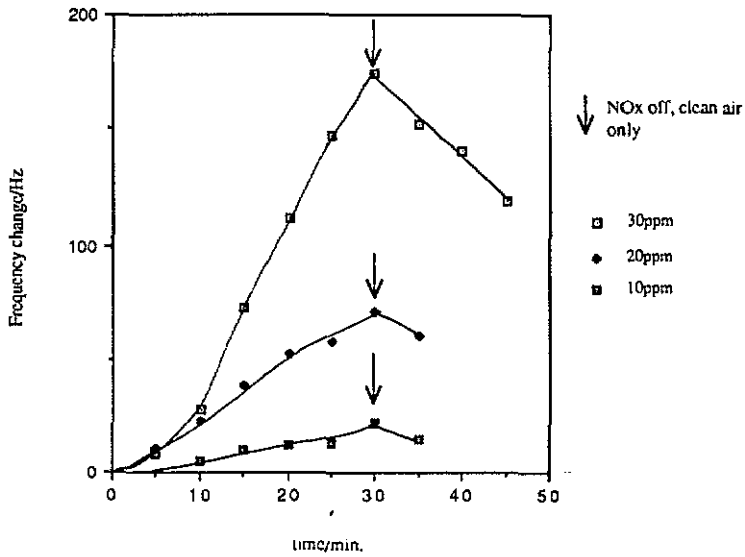


Figure 7. Response of SAW device coated with two layers of CPTAAcO to 10, 20 and 30 ppm NOx.

Table 1. Results for SAW devices coated with LB films of Pcs and TAAs exposed to NOx.

Sample	NOx conc (ppm)	Frequency change over 20 min (Hz)	Reversal (%)
TMCO <sub>2</sub> TAA 20 layers 50 mol%	20	64	7
	30	152	18
	40	350	12
	50	349	30
	60	187	64
CPTAAcO 2 layers	10	12	32
	20	52	13
	30	112	32
CPTAAcO 5 layers	10	120	—
	20	113	—
	30	112	—
CPTAAcO 10 layers	5	72	—
	10	102	—
	20	485	—
CPTAAcO 20 layers	10	405	—
PPPCVO 20 layers 50 mol%	20	167	>100
	30	195	40
	40	707	46
PPPCVO 5 layers	50	870	48
	5	22	45
	10	60	19
PPPCVO 10 layers 50 mol%	20	252	36
	10	495	36
	5	132	18
NPPCCu 10 layers 20 mol%	10	175	—

#### 4. Surface plasmon resonance (SPR)

Silver is commonly used as the metal film for SPR because of its sharp resonance, but it is less suitable than gold for gas sensing because of its greater surface reactivity. This is shown in figure 9 where exposure of the silver film to NO<sub>x</sub> in dry air produced an immediate increase in the reflectivity and prolonged exposure to 100–200 ppm of NO<sub>x</sub> resulted in a permanent yellow/brown discoloration of the silver. Coating the silver surface with up to 23 LB layers of cadmium stearate did not prevent the metal/gas interaction occurring. The interaction of NO<sub>x</sub> with gold was less significant; at 200 ppm NO<sub>x</sub>, the maximum reflectivity change was 8%.

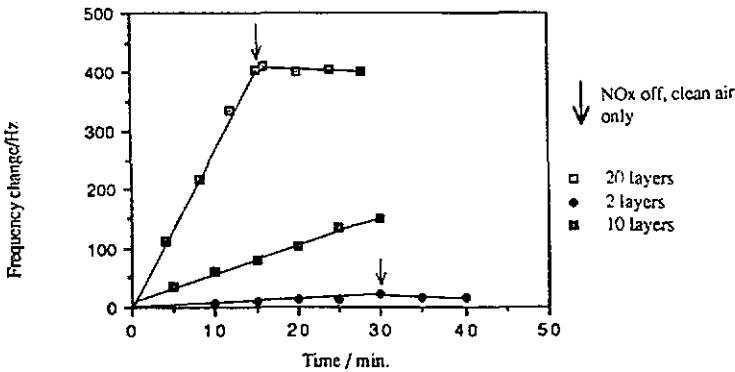


Figure 8. Thickness dependence of the response of CPTAAcO on SAW device to 10 ppm NO<sub>x</sub>.

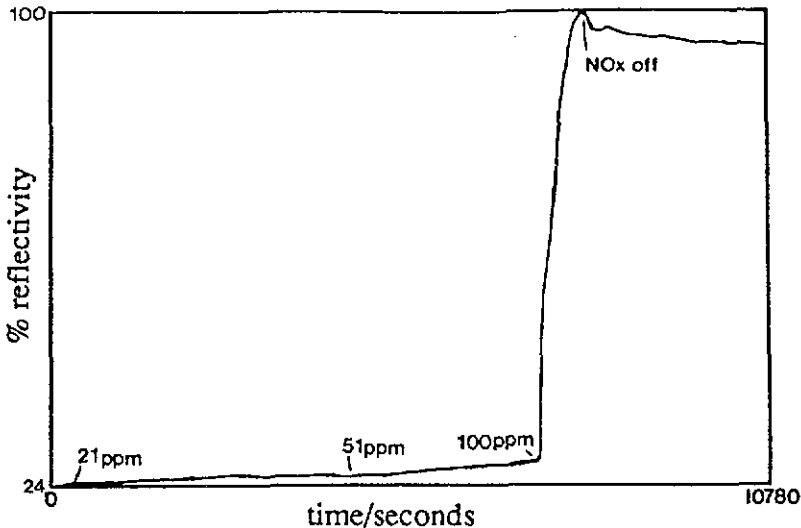


Figure 9. SPR response of silver film to NO<sub>x</sub>.

The increased broadening and shift in the position of the resonance on increasing film thickness was demonstrated by depositing LB layers of cadmium stearate



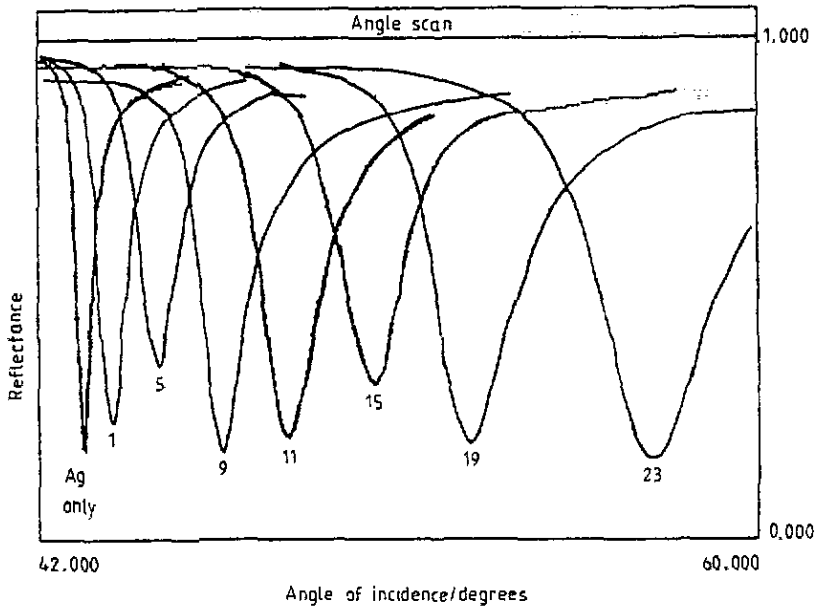


Figure 10. Angle shift and increase in breadth of resonance minimum with increasing thickness cadmium stearate film.

(figure 10). Thus, the thickness of the overlay needed to be controlled to maintain a sharp resonance. LB films were ideal for this purpose.

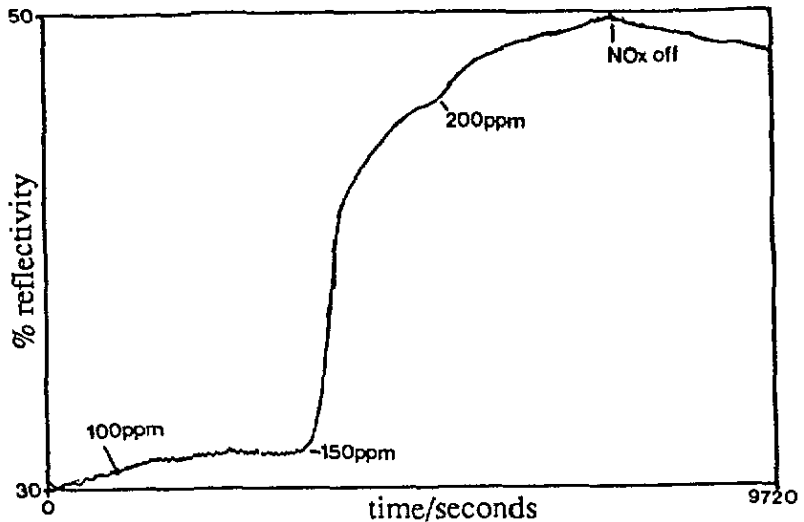


Figure 11. Change in reflectance for  $\text{TMCO}_2/\text{TAA}$  film exposed to  $\text{NO}_x$ .

The lowest concentration detected was 50 ppm  $\text{NO}_x$  by  $\text{TMCO}_2/\text{TAA}$ , a monolayer film on cadmium stearate, which also exhibited the largest reflectance change overall (figure 11). A mixed film of  $\text{TMCO}_2/\text{TAA}/\text{stearate}$  at 50 mol%, however, showed only a small change in reflectivity.  $\text{PPPCu}$ , both as a monolayer and as multilayer mixed films, showed significant changes in reflectance in response to 100–200 ppm  $\text{NO}_x$  (figure 12).

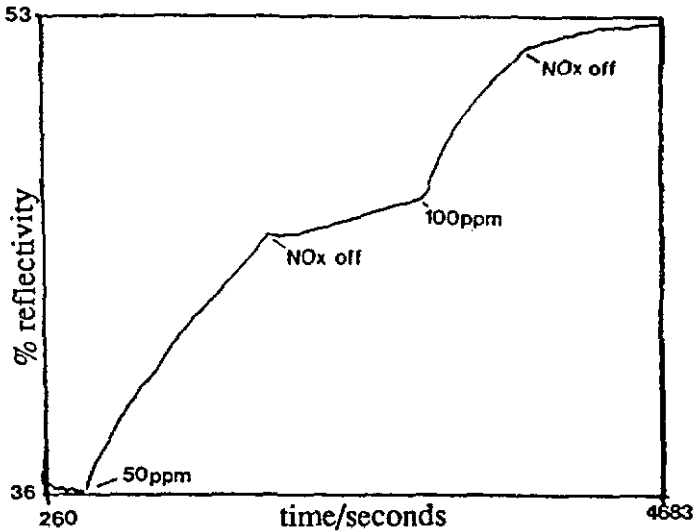


Figure 12. Change in reflectance for PPPCu film (1 layer) exposed to NOX.

## 5. Conclusions

The adsorption of fairly low concentrations of NOX onto LB films of Pcs and TAAs was easily monitored using both acousto-electrical and SPR sensors. TAAs were demonstrated to be as good in sensor performance as the more widely investigated Pcs [6, 7].

The SAW device experiments indicated possible advantages in using very thin LB films of 2-5 layers. Although thicker films produced larger responses, the thin films showed faster equilibrium attainment and simpler adsorption kinetics. For SPR, thin films were required to maintain a sharp resonance curve.

For materials such as Pcs and TAAs to have practical applications in sensor devices, a detailed knowledge of their interaction with a gas together with accurate control of their film morphology is required. The LB film technique permits precise control over film deposition. Therefore, if the structure of LB films could be thoroughly elucidated, the LB technique could be a valuable tool in future gas adsorption studies.

## Acknowledgments

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