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THE DETECTION OF AMMONIA AND NITROGEN DIOXIDE AT THE PARTS PER BILLION LEVEL WITH COATED PIEZOELECTRIC CRYSTAL DETECTORS

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In recent years coated piezoelectric quartz crystals have been developed as selective and sensitive air pollution sensors. The pioneering work of Sauerbrey[1] on the theoretical aspects and of King[2–4] on the practical applications of piezoelectric quartz crystals opened a new line for the detection and measurement of gases and vapors. The principle of detection by a piezoelectric quartz crystal is that the frequency of vibration of an oscillating crystal can be decreased by the presence of a foreign material on its surface. A gaseous pollutant is selectively absorbed by the coating on the crystal surface, thereby increasing the weight on the crystal and decreasing the frequency of vibration. The decrease in frequency is a measure of the amount of gas absorbed. King[4] and Karasek and Tiernay[5] used coated quartz crystals as sensitive g.c. detectors. Frechette and Fasching[6] have used a coated crystal as a sensor for sulfur dioxide pollution in a static system. The ability of coated piezoelectric quartz crystals to detect pollutants at the parts per billion level was shown by Karmarkar and Guilbault[7] in which sulfur dioxide was detected as low as 1 p.p.b. by using a sensitive cell design and selective and sensitive amine coatings.

This paper describes new coatings for the piezoelectric crystals in the detection of ammonia and nitrogen dioxide in the parts per billion range. The i.r. spectra of the gas–solid reaction, and the results of a study of interference from other pollutants, are also presented.

EXPERIMENTAL

Apparatus

Figure 1 shows the experimental set-up with a piezoelectric crystal detector in a flow system. The cell design is based on a design described by the authors earlier[7], and is the most sensitive one for a flow system. The cell is made from a flattened pyrex tube (1.6 cm o.d.). A pyrex 14/20 ground joint is connected to the flattened tube which facilitates the change or removal of the crystal from the detector cell, if necessary. The crystal is situated in the flattened position of the cell, the parallel walls of which are separated by a distance of 0.6 cm. The parallel cell walls are 2 cm long and 1.2 cm wide making the effective cell volume about 1.5 cm^3 ($2 \times 1.2 \times 0.6$ cm^3). The column effluent is equally divided by two 0.5-cm (o.d.) pyrex tubes. These tubes are connected through the two parallel walls in such a way that their tapered ends (0.2 cm o.d.) reach as close to the center of the opposite faces of the crystal as possible. This arrangement ensures the maximum

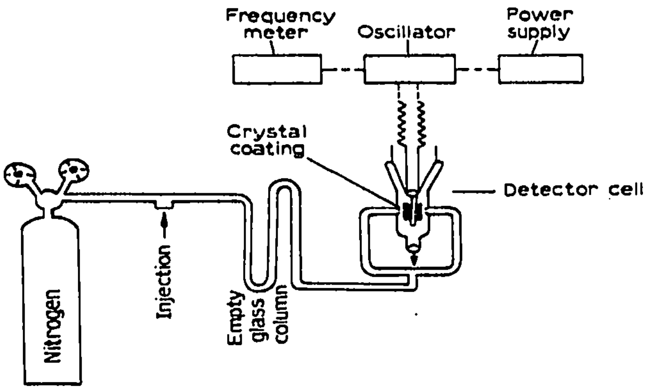


Fig. 1. Experimental set-up with a piezoelectric crystal detector.

amount of the sample gas reacting with the coating at any moment, and therefore the sensitivity is greatly increased. The gas escapes through an exit tube (0.7 cm o.d.) connected at the bottom of the cell. Dry nitrogen at a rate of 20 cm^3 min^{-1} is used as carrier gas which passes through an empty 30 cm long and 0.7 o.d. pyrex column. The crystals used in this study were 9 MHz AT cut quartz crystals with silver-plated metal electrodes on both sides and were obtained from Jan Crystals, Florida. A low-frequency OX transitor oscillator was built from an oscillator kit (International Crystal Co., Oklahoma). Two tungsten–nickel (W–Ni) leads connected the crystal to the oscillator. The oscillator was powered by a Heathkit 1–30 V d.c. variable power supply (Model 1P-28). Even though the applied voltage had no effect on the sensitivity of the crystal under these conditions, it was always kept constant at 9 V. A Systron-Donner frequency meter, Model 8050, with a range of 0–30 MHz and a resolution of 0.1 Hz, was used for a digital read-out of frequency.

Reagents

Ucon 75-H-90,000 and Ucon-LB-300X (Union Carbide Corp., from Analabs, Inc., Connecticut) were used as coatings. NH_3, NO_2, SO_2, H_2S, NO, CO, and CO_2 (Matheson Co., Inc.) were used from lecture bottles. Benzene, acetone, methanol and chloroform were of Technical grade.

Method of application of coatings

The Ucon compounds are dissolved in proper solvent (*e.g.*, chloroform) and the solutions are applied on the entire surface of the electrode on both sides with a tiny brush. The organic solvent evaporates quickly leaving the Ucon compounds on the crystal. The amount of Ucon-75-H-90,000 coating used was equivalent to a decrease of 7000 Hz and that of Ucon-LB-300X corresponded to a decrease of 9000 Hz in the basic frequency (9 MHz) of the crystal. These coated crystals are then exposed to a 1 : 3 mixture of nitrogen dioxide and nitrogen in a small pyrex chamber for about 5 min; nitrogen dioxide reacts with the coatings and this causes a further decrease of frequency of about 3000 Hz and 4000 Hz respectively for the two coatings.

Test gas dilution

The test gases are diluted with nitrogen by the syringe method earlier described by the authors[7] and also by Karasek and Tiernay[5]. Pure test gas (1 ml) is sucked in a 10-ml syringe. Then the syringe is filled to capacity with dry nitrogen. The desired dilution of the test gas is obtained by repeating the above procedure for the required number of times. A 5-ml test mixture is always injected to observe the response, except when 1 ml of ammonia mixture is injected as for the curve C of Fig. 6.

I.r. measurements

Pyrex glass cells with KBr windows were built in order to obtain i.r. spectra of pure Ucon substrate films and of the compounds formed on exposure to nitrogen dioxide of the Ucon substrates. Figure 2 shows the i.r. cell used. A small amount of Ucon solution is placed on the KBr windows; as the solvent evaporates a thin film of Ucon is formed on the KBr surface. The cell is evacuated by a rotary pump. A 1:3 nitrogen dioxide–nitrogen mixture is then injected into the cell, sufficient time is allowed for the reaction to occur, and the cell is again evacuated. This ensures removal of all unreacted nitrogen dioxide. I.r. specta are taken on the Perkin-Elmer 257 Grating IR spectrometer.

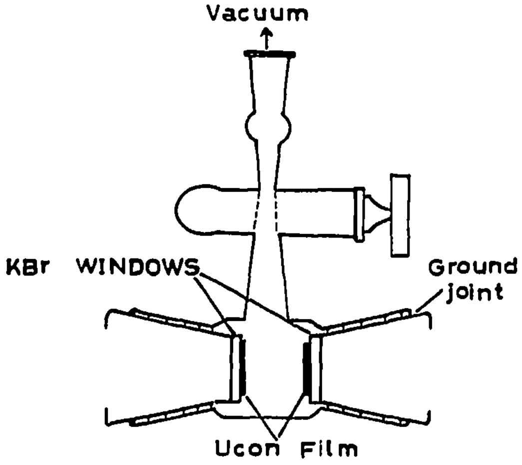


Fig. 2. Pyrex infrared cell with KBr windows.

RESULTS AND DISCUSSION

Both Ucon-75-H-90,000 and Ucon-LBL-300X coatings showed sensitivity to ammonia and nitrogen dioxide only after an exposure to nitrogen dioxide for about 5 min. This suggests that nitrogen dioxide reacts with Ucon coatings and new compounds are formed on the crystal. These new compounds act as sensitive coatings for ammonia and nitrogen dioxide. Ucon fluids and lubricants are polyalkylene glycols with less known structures. The fact that new compounds are formed on reacting with nitrogen dioxide is evident from the appearance of new bands and some band shifts observed in the i.r. spectra of these substances. Figures 3 and 4 show the i.r. spectra of Ucons before and after reaction with nitrogen dioxide.

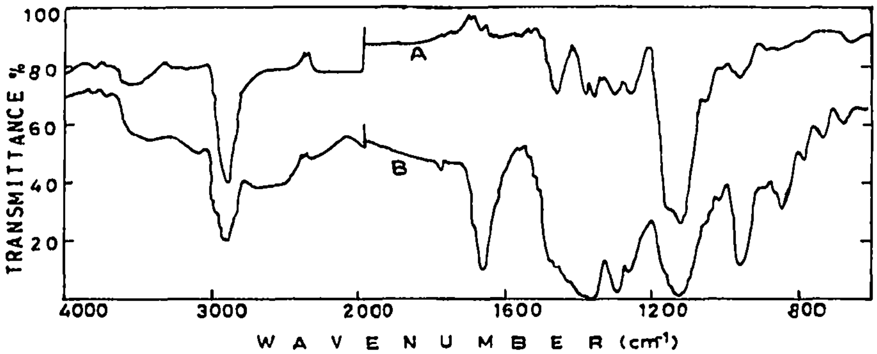


Fig. 3. (A) I.r. spectrum of pure Ucon-75-H-90,000; (B) I.r. spectrum of Ucon-75-H-90,000 exposed to NO_2.

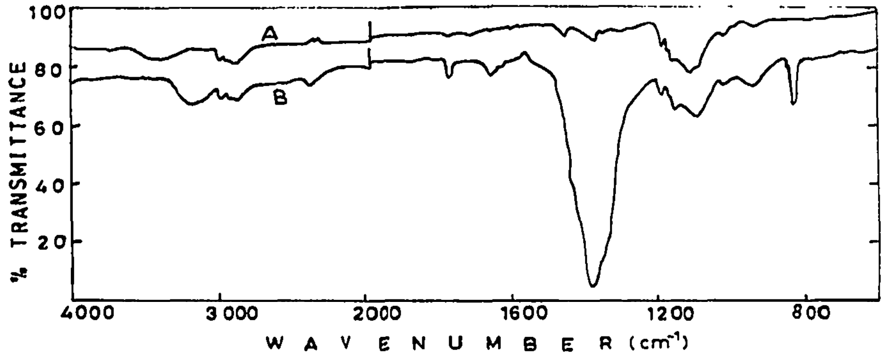
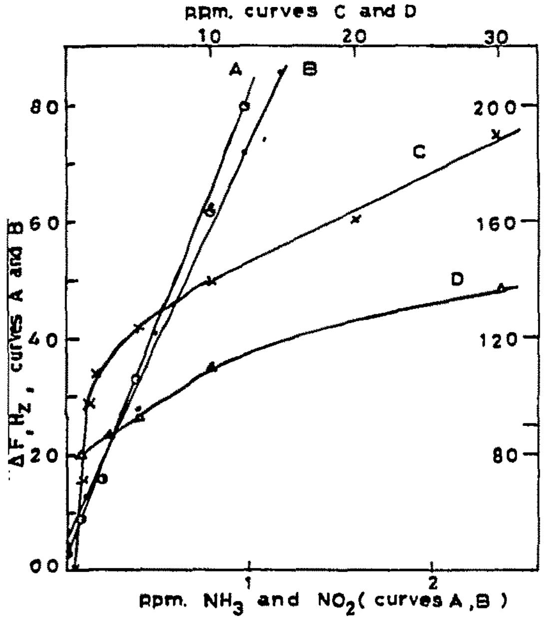


Fig. 4. (A) I.r. spectrum of pure Ucon-LB-300X; (B) I.r. spectrum of Ucon-LB-300X exposed to NO_2.

It is known that Ucon-75-H-90,000 is made by reacting ethylene oxide, propylene oxide and ethylene glycol, but its real structure is not known. Under these circumstances, it is reasonable to suggest that in Fig. 3 the new bands at 1650 cm^{-1} and between 800 cm^{-1} and 700 cm^{-1} show the presence of covalent nitrite[8], R–O–NO. The broad band between 1500 cm^{-1} and 1320 cm^{-1} may represent a nitroso (R–NO) compound. Similarly, in Fig. 4, the new band at 1380 cm^{-1} represents a nitroso (R–NO) compound. The band at 1380 cm^{-1} together with another new band at 830 cm^{-1} might even show the presence of ionic nitrate. But this seems rather less probable.

Figures 5 and 6 show calibration plots for ammonia and nitrogen dioxide on the two Ucon substrates exposed to pure nitrogen dioxide. The responses are fairly linear between 1 p.p.b. and 1 p.p.m. on both coatings. At about 1 p.p.m. the curves seem to bend but become linear again, and remain so for a quite large concentration range. The position of bending depends on the amount of mixture injected. For example, when 1 ml of ammonia mixture was injected instead of 5 ml, a curve linear between 1 p.p.m. and 50 p.p.m., and a sort of bending above 50 p.p.m. resulted (Fig. 6, Curve C). It seems possible that concentrations lower



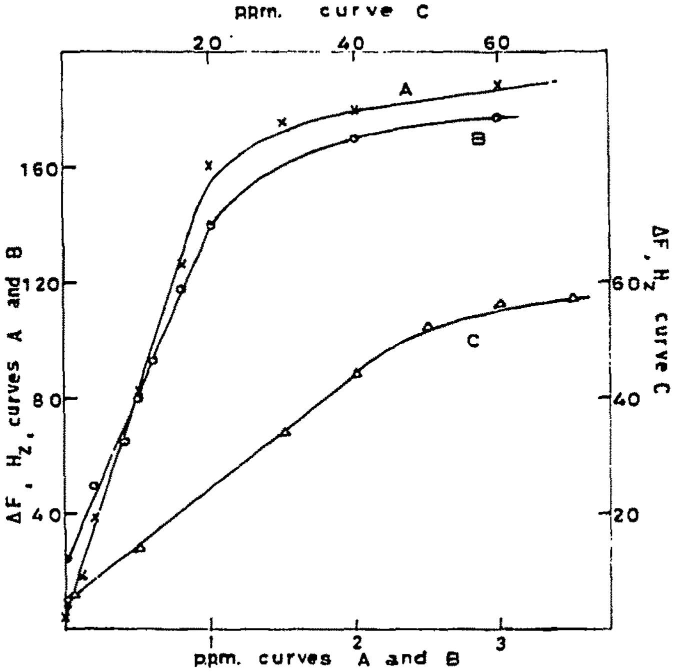


Fig. 5. Calibration plots for NH_3 and NO_2 on Ucon-75-H-90,000 substrate exposed to NO_2: Curves A and D for NH_3; B and C for NO_2.

Fig. 6. Calibration plots for NH_3 and NO_2 on Ucon-LB-300X substrate exposed to NO_2: Curve A for NO_2: curves B and C for NH_3.

than 1 p.p.b. could be detected if 10-ml or 15-ml mixtures were injected instead. The response is fast, and reversibility is observed at low concentrations of pollutants. At concentrations above 1 p.p.m., however, a long time (about 20–30 min) is required to observe reversibility.

Interferences and drawbacks

The most important drawback with the piezoelectric crystal detectors is that they give response for atmospheric moisture. The present detectors gave a response of about 300 Hz for 5 ml of laboratory air, but no response for dry laboratory air. Under varying conditions of humidity, it may be difficult to differentiate between moisture response and a pollutant response. This problem may be solved by using a drier to remove moisture or by using two crystals simultaneously; one measuring pollutant plus moisture, and the other measuring only moisture. The actual concentration of the pollutant can then be obtained from the difference between the two responses. The work on the latter procedure is in progress. Another shortcoming noted about Ucon coating is that the crystal loses all activity if kept exposed to air for long times (1 h). But this also is not serious since the activity can easily be restored by re-exposing the crystal to a nitrogen dioxide–nitrogen mixture for 5 min. The process of this reaction seems critical since in some cases irreversible

TABLE I

INTERFERENCE STUDY

Coating	*Gas and interfering concentrations*								
	CO (p.p.m.)	*CO_2 (p.p.m.)*	*NO (p.p.m.)*	*SO_2 (p.p.m.)*	*H_2S (p.p.m.)*	*Acetone (p.p.m.)*	*Methanol (p.p.m.)*	*Chloroform (p.p.m.)*	*Benzene (p.p.m.)*
Ucon-75-H-90,000 exposed to NO_2	No interf.	No interf.	1000	5000	10000	2000	1000	500	600
Ucon-LB-300X exposed to NO_2	No interf.	No interf.	1000	10000	20000	2000	1000	600	600

responses with Ucon-75-H-90,000 coatings were observed.

It was observed that oganic pollutants produce larger interferences than the inorganic ones. Table I contains the results of the interference study. The interfering concentrations are those which produce response roughly equivalent to a response for 1 p.p.b. of either nitrogen dioxide or ammonia. Since the concentrations of all the interfering substances are much higher than that ever found in air, no interference is expected. Thus, the systems described may prove valuable for the sensitive and specific detection of nitrogen dioxide and ammonia.

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SUMMARY

Ucon-75-H-90,000 and Ucon-LB-300X are the new substrates used on the piezoelectric crystal detectors. On exposure to nitrogen dioxide these substrates form new compounds on the crystal which are sensitive to nitrogen dioxide and ammonia. With these coatings it is possible to detect nitrogen dioxide and ammonia in the parts per billion range. Some problems are caused by atmospheric moisture and high concentrations of organic pollutants.

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