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A COATED PIEZOELECTRIC CRYSTAL SENSOR FOR ACETIC ACID VAPOUR DETERMINATION

J. A. Munoz Leyva,* J. L. Hidalgo Hidalgo de Cisneros and
D. Garcia Gomez de Barreda
Department of Analytical Chemistry, Apdo, 40, 11510 Puerto Real, Cádiz, University of Cádiz, Spain

Summary—A novel sensor for acetic acid vapour determination is proposed. This sensor is based on a piezoelectric crystal covered with a film of diethylenetriamine. For the sensor development a system of our own design—consisting of testing chamber, oscillator circuit and measure instruments—has been employed. The sensor shows its activity to the acetic acid vapours for more than 60 days. The selectivity is adequate although some vapours interfere: hydrochloric acid, formic acid, formaldehyde, tributyl phosphate, chloroform, chlorobenzene, acetone and isobutylmethylketone. The sensor described can be applied to detect acetic acid vapours in the presence of other vapours: acetonitrile, acrolein, benzene, *n*-hexane, ethanol, propanol, *n*-butyl acetate, isopropyl ether, isoamyl alcohol, ethyl ether, methylene chloride, carbon tetrachloride and toluene. The major advantages of the proposed sensor over other existing techniques are its simplicity, reduced cost and capacity for use *in situ*.

Piezoelectric crystals, due to their special characteristics,[1] are very appropriate for the construction of portable, simple and cheap detection units. In recent years coated piezoelectric crystal sensors have attracted increasing interest for monitoring traces of toxic gases in the atmosphere as well as in the air of working environments.[2–15]

Acetic acid is a corrosive acid which has numerous industrial applications and hence it is present, mainly as vapour, in some industrial atmospheres. On the other hand, it is the principal constituent of the volatile acidity of wines[16] and its content in vinegars is not smaller than 50–60 g/l.[17] The Threshold Limit Value - Time Weighted Average (TLV-TWA) for the acetic vapours is 10 ppm (25 mg/m^3).[18] So for all these reasons, it is very important to have sensor systems to detect acetic acid.

The existing methods for detecting acetic acid vapours use gas chromatography with a preconcentration stage on a column with adsorbent;[19,20] determination has also been described using pulsed UV photoacoustic spectroscopy.[21] With these techniques a high level of sensitivity is achieved, but they involve the use of sophisticated instruments.

As for using sensors to detect acetic acid, only one process has been described and it is used to detect the acid in solution. The sensor described in the literature is based on the property of certain bacteria which produce oxygen from acetic acid, so the acid can be detected using immobilized *Trichosporon brassicae* on a Teflon membrane electrode and an amperometric oxygen electrode. The minimum concentration for determination is 5 mg/l.[22]

In the literature which we reviewed, we found no sensors for the determination of acetic acid in its vapour form. This paper describes for the first time one sensor for acetic acid vapours, based on AT-cut piezoelectric crystals coated with diethylenetriamine films. This sensor combines a good selectivity and an acceptable sensitivity.

For studying and perfecting the new sensor we used our own design system,[23] which is capable of working statically, and is thus easily adaptable to measurement *in situ*, unlike other techniques proposed with other sensors, which work dynamically.

EXPERIMENTAL

Reagents

All reagents, those used as coatings and those used in the interference study, were of analytical reagent grade. The nitrogen was type N-50 from S.E.O. (Spanish Oxygen Company).

Materials and equipment

The 8.9 MHz At-cut PZ crystals (Universal Sensors) were mounted on HC-25/U type bear-

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*Author for correspondence.

ings. The oscillator circuits employed were made of common commercial electronic components (resistors, capacitors, transistors). The sensor unit was placed inside a testing chamber which was capable of reproducing atmospheric conditions. The rest of the equipment consisted of control and measurement instruments. The complete installation, of our own design, has been reported elsewhere.[23]

Procedures

Preparation of the coated crystal. The crystal, cleaned with ethanol, was dried in warm air and placed in the testing chamber under vacuum for 5 min, whereupon dry nitrogen was injected. After 30 min, the frequency was measured and noted, the crystal removed from the chamber and then coated by immersion for 5 sec or more (or by several immersions)—according to the amount of coating desired—in a solution of 0.100 g of diethylenetriamine in 10 ml of ethanol. The crystal was dried again and the frequency measured and noted. For storage the coated crystals were each protected with a metallic capsule and introduced in a vacuum dessicator.

Measurement of the response to acetic acid. The stabilized frequency of the coated crystals in an air or nitrogen atmosphere (in the testing chamber) was measured and noted. The chamber was evacuated and the acetic acid injected. The initial conditions (pressure and temperature) were re-established and the frequency again measured and noted, calculating the difference, Δf, between this measurement and the previous one. The sensor was restored to its original condition by vacuum and nitrogen after this second measurement. The time necessary for this restoration is defined as recovery time (T_R). In this manner, the measurements are all independent.

The concentration of acetic acid vapours was calculated from the previously constructed calibration graphs.

RESULTS AND DISCUSSION

Selection of coatings

The acidic nature of the sample for analysis led us to select basic coatings. With all the coatings tested, a reduction in frequency was noted in the coated crystal, but the magnitudes of variation were very different. For a fixed amount of 4.33 mg/l. of acetic acid in the chamber, the differences in frequency in Hz, Δf, of the crystal, in the absence and presence of the sample being analysed, were as follows:

Diphenylamine, 6 Hz
Thiosemicarbazide, 9 Hz
Diethylenetriamine, 32 Hz
Phenylhydrazine, 10 Hz
2,4-dinitrophenylhydrazine, 8 Hz
1,10-phenanthroline, 19-Hz
2,2′-bipyridine, 5 Hz
4-ethyl-3-thiosemicarbazide, 16 Hz
4-phenylthiosemicarbazide, 1 Hz
2,6-diacetylpyridine, 20 Hz.

On the basis of these results, diethylenetriamine was chosen as the coating. The fact that the aliphatic amine responds most sensitively to acetic acid suggests that interaction between the ethyl group of the acetic acid and the amine could help to attract acetic acid into the coating.

Variation of response with the amount of coating and with time

The decrease in the frequency of the coated crystal with respect to that of the non-coated crystal, Δf_O, is dependent on the coating amount: the greater the coating the greater the Δf_O value. We prepared coated crystals with two different quantities of diethylenetriamine, obtaining the decreasing frequencies (Δf_O) shown in Table 1.

On the other hand, we found that the frequencies of the coated crystals shift with time. Using the above mentioned crystals, we measured Δf_O of the coated crystals over 60 days and the results are also shown in Table 1.

The Δf_O values first decrease quickly and then slowly, indicating a loss of coating. After 19 days, Δf_O begins to increase slowly, probably

Table 1. Variation of Δf_O with time

Time elapsed (days)	Δf_O(Hz)	Δf_O(Hz)
1*	5786	2242
2	2589	1368
3	1292	432
4	1217	—
5	—	322
8	1204	—
9	1151	—
11	1382	266
15	1416	235
20	1440	266
25	1512	275
35	1559	278
40	1687	280
50	1720	—
60	1764	—

*Coated crystals only.

Table 2. Influence of pressure

Pressure (*mm Hg*)	Δf_O(Hz)*	Δf_O)Hz)†	Δf_O(Hz)
720	8,995,877	8,995,848	29
747	8,995,876	8,995,847	29
775	8,995,875	8,995,846	29
802	8,995,874	8,995,845	29
829	8,995,873	8,995,844	29

*In the absence of acetic acid.
†In the presence of acetic acid.

owing to progressive contamination of the crystals. Nevertheless, after 60 days the crystals are even sensitive to acetic acid vapours.

The frequency variations we observed have been borne in mind when realizing the experiments measuring Δf_O at that time.

Variation in the measuring conditions

In order to study the alterations when the operating conditions are modified, we utilized a testing chamber which reproduces environmental conditions and enables us to study the influence on the sensor response to acetic acid vapours in several atmospheric conditions (pressure, temperature or relative humidity). For each value studied we measured the frequencies of the coated crystals (for a given Δf_O) first in the absence and then in the presence of a definite quantity of acetic acid, calculating the difference between them (Δf). Subsequently, the magnitude should be varied in both cases in the same way.

The influence of pressure

Experiments were carried out at a constant temperature of 27°, making a vacuum in the chamber and injecting dry nitrogen at different pressures with a fixed amount (10 μl) of acetic acid each time. The variation of frequency in the range from 720 to 829 mm Hg—in the absence as well as in the presence of acetic acid—is only 4 Hz, whereas Δf for crystals with and without acetic acid at the same pressure is constant in the range studied (Table 2).

The crystal response in a dry air atmosphere (obtained by passing laboratory air through silica gel) has also been studied, and was the same as in the case of a nitrogen atmosphere.

The influence of temperature

Experiments were carried out in a nitrogen atmosphere at a constant pressure of 787 mm Hg (crystal with $\Delta f_O = 1435$ Hz), injecting in each case a volume of 10 μl of acetic acid (4.33 mg/l.), and measuring the Δf and the recovering times of the sensor. The results are shown in Fig. 1. An increase of 0.33 Hz/° is observed within the range 15–30°, and a decrease of 0.2 Hz/° between 30 and 35°.

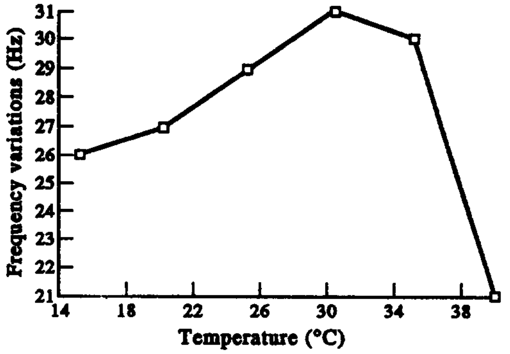

Fig. 1. Effect of temperature on the sensor frequencies.

The influence of humidity

Since the presence of water had a great influence on the frequency of some coated crystals,[23] we carried out a study on the effect of relative humidity (RH) on the oscillation frequency of the sensors tested (crystal with $\Delta f_O = 1375$ Hz). To do this, we used a test chamber temperature of 25°, with a vacuum to cause the water to evaporate, and injected 5, 10 and 50 μl of water (equivalent respectively, to 10, 20 and 100% RH) and 10 μl of acetic acid each time. Then we injected dry nitrogen into the chamber until a pressure of 750 mm Hz was reached, measuring the oscillation frequencies of the crystal at that time, and comparing these with those measured in the absence of acetic acid.

The frequency of the PZ crystal with a diethylenetriamine coating shows a reduction of 2.8 Hz/% RH between 0 and 10% RH, whereas it is only 0.28 Hz/% RH between 10 and 100% RH (Fig. 2). The difference in frequencies in-

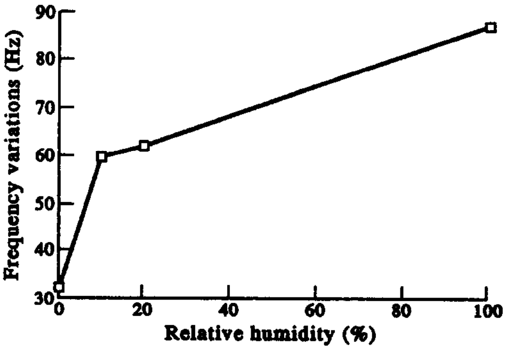

Fig. 2. Effect of relative humidity on the sensor frequencies.

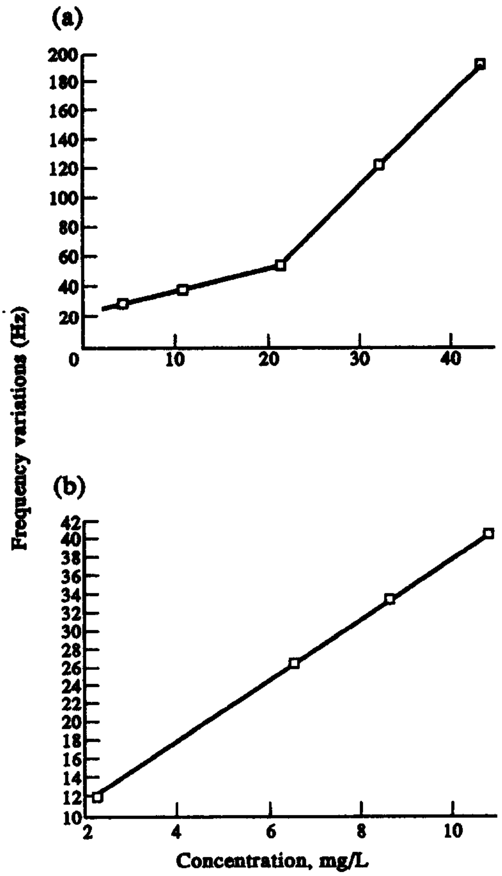

Fig. 3. Influence of acetic acid concentration: (a) $\Delta f_O = 1490$ Hz; (b) $\Delta f_O = 652$ Hz.

creases over the complete range, so we have to conclude that the humidity content interferes in the determination of acetic acid, but this interference is eliminated by passing the sample through silica gel.

Influence of acetic acid concentration

The calibration of the sensors in the presence of acetic acid was done in a dry air atmosphere (0% RH) at 25° and a pressure of 760 mm Hg. For each concentration of acetic acid we measured the frequencies, both in the presence and the absence of the acid, and calculated the difference between them (Δf).

We tested two crystals with different quantities of coating and with values of Δf_O at the time of the experiments of 1490 and 652 Hz for the larger and smaller quantities of diethylenetriamine, respectively.

Figure 3 shows the results obtained for the coated crystals. The calibration equations for the crystals coated with diethylenetriamine were as follows:

$$(\Delta f_O = 1490\ \text{Hz})\ \Delta f = 1.63\ [\mathrm{CH_3COOH}] + 22.3,\quad r = 0.9981\ (4.33\text{–}21.7\ \text{mg/l.})$$

$$(\Delta f_O = 1490\ \text{Hz})\ \Delta f = 6.28\ [\mathrm{CH_3COOH}] - 79.0,\quad r = 0.9997\ (21.65\text{–}43.3\ \text{mg/l.})$$

$$(\Delta f_O = 652\ \text{Hz})\ \Delta f = 1.31\ [\mathrm{CH_3COOH}] + 8.00,\quad r = 0.9944\ (0.43\text{–}32.5\ \text{mg/l.}).$$

Greater sensitivity was obtained for $\Delta f_O = 1490$ Hz, *i.e.*6.3 Hz/mg/l. The detection limit—defined as the concentration of sample for analysis which produces a three-fold greater variation than the sensor in the absence of the sample—was 0.22 mg/l.

When we used coated crystals alone the sensitivity was much greater than that above (Δf_O: 5786 Hz; sensitivity: 46.9 Hz/mg/l.); nevertheless, it varies quickly with time. For this reason in this paper coated crystals alone are not used.

Recovery time (T_R and variation of response with time

Once the sensor had been exposed to the action of acetic acid, we studied the time it took to recover its original frequency for a content of acetic acid in the chamber of 4.33 mg/l. The average recovery time was found to be 14 min. Nevertheless, the recovery time is dependent on the acetic acid concentration.

Repeatability

In order to determine the repeatability, we carried out 11 measurements in the optimized conditions, in each case by injecting acetic acid

Table 3. Study of interferences

Interferences	Conc. (*mg/l.*)	Δf
Carbon tetrachloride	63	3
Acetonitrile	31	0
Ethanol	32	0
2-Propanol	32	0
n-Hexane	27	0
Benzene	36	0
Isopropyl ether	29	0
Isoamyl alcohol	50	1
Ethyl ether	29	2
n-Butyl acetate	35	0
Methylene chloride	54	3
Toluene		0
Chlorobenzene	45	14
Isobutylmethylketone	32	9
Acrolein	34	0
Acetone	32	60
Chloroform	61	147
Tributyl phosphate	40	220
Hydrochloric acid	17	952
Formaldehyde	16	94
Formic acid	33	499

Acetic acid concentration = 4.33 mg/l.

into the chamber so that its concentration was 4.33 mg/l. Statistical treatments (95% probability level) for the greater amount of coatings used gave us the following data:

PZ coated with diethylenetriamine ($\Delta f_{\mathrm{O}} = 1440$ Hz),

$$\Delta f_{\mathrm{m}} = 29.63 \text{ Hz}, \ \delta_{\Delta f} = 1.43, \ (\delta_{\Delta f})_{\mathrm{m}} = 0.45,$$

$$\Delta f = 29.63 \pm 1.01, \ \epsilon = \pm 5.4\%,$$

$$T_{\mathrm{R}} = 14.36 \pm 1.48 \text{ min.}$$

Study of interferences

First, we measured the frequency with a given amount of acetic acid (10 μl, equivalent to 4.33 mg/l. within the chamber) and then the frequency with the same amount of acetic acid and a volume of the interfering substance 5–20 times greater.

We studied the responses of crystals coated with diethylenetriamine to 21 interfering species. In each case we worked under conditions of constant pressure (750 mm Hg) and temperature (25°). Table 3 shows the concentration of the interferents (mg/l.) and the decrease in frequency Δf.

From the results it can be concluded that the greatest interferences are caused by species of an acidic nature (hydrochloric acid, formic acid), with the effect of tributyl phosphate, chloroform, formaldehyde and acetone being significant as well.

The following do not have any effect on the sensors: acetonitrile, ethanol, 2-propanol, toluene, acrolein, *n*-hexane, benzene, isopropyl ether and *n*-butyl acetate. The rest of the specimens studied interfere to a lesser extent.

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