Determination of Formic Acid Vapour Using Piezoelectric Crystals With 4-Ethyl-3-thiosemicarbazide and 2,6-Diacetylpyridine Coatings

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Two sensors have been suggested for formic acid vapour. These sensors are based on piezoelectric crystals coated, by immersion, with films of 4-ethyl-3-thiosemicarbazide and 2,6-diacetylpyridine. The sensors have been perfected using a new static system comprising an oscillator mounted on a die-plate and placed inside a testing chamber which, by means of a series of auxiliary devices, can reproduce and control environmental conditions. The sensors show their sensitivity to formic acid for at least 60 d. Selectivity is adequate with both coatings. The sensors begin to respond to formic acid vapour immediately, reaching a stable frequency after 5 min; average recovery times are about 28 min. For the 4-ethyl-3-thiosemicarbazide sensor, the sensitivity is 29.7 Hz mg^{-1} l (for an amount of coating corresponding to Δf_0 = 475 Hz) with a correlation coefficient of 0.9997 and a detection limit of 0.17 mg l^{-1}. For the 2,6-diacetylpyridine sensor, the values are 10.9 Hz mg^{-1} l^{-1}, 0.987 and 0.33 mg l^{-1} respectively (Δf_0 = 824 Hz). The sensors could be used to detect formic acid vapour in the atmosphere and in working environments if a suitable preconcentration device were connected. The advantages over existing techniques, *i.e.*, gas chromatography and pulsed ultraviolet photoacoustic spectroscopy, should be evident from their simplicity, reduced cost and capacity for use *in situ*.

Keywords: *Formic acid determination; piezoelectric crystal; sensor; 4-ethyl-3-thiosemicarbazide; 2,6-diacetylpyridine*

There is increasing interest in the development of detection systems for toxic gases, and piezoelectric (PZ) crystals are playing a remarkable role in this field. This is due to their special characteristics, which facilitate the construction of portable, simple and cheap detection units. The first work on the application of PZ crystals for gas detection was by King.[1] Later a PZ crystal detector for hydrocarbons in the atmosphere was developed.[2] The atmosphere is the medium in which research in this field has been most widely applied. Guilbault and co-workers[3–10] discovered several applications of coated PZ crystals for the detection of some gases in the atmosphere. Ho *et al.*[11] constructed a portable detector to measure toluene in the environment. Fraser *et al.*[12] developed a multi-sensor system to measure pollution in the air. Alder *et al.*[13] tested many metallic salts as coatings for PZ crystals for detecting hydrocyanic acid in the atmosphere. Mierzwinski and Witkiewicz[14] examined the use of PZ crystals as air pollution detectors, and Alder and McCallum[15] and McCallum[16] also carried out some remarkable investigations on the applications of PZ crystals to sensors.

Formic acid is very toxic when inhaled or swallowed, and is present, mainly as vapour,[17] in significant amounts in the atmosphere and in acid rain, where it accounts for 0.1–19% of the acidity.[18] It also has numerous industrial applications. Therefore, it is extremely important to have sensor systems for its detection.

The existing detection methods use either gas chromatography[18] or gas chromatography with a preconcentration stage on a column with adsorbent;[19] determination has also been described using pulsed ultraviolet photoacoustic spectroscopy.[20] These techniques give a high level of sensitivity but they involve the use of sophisticated instruments.

Only two processes using sensors to detect formic acid have been described and both detect formic acid in solution. One uses an optical fibre sensor for continuous measurement in biological systems.[21] The Naval Research Laboratory optical waveguide sensor works by the attachment of a colorimetric redox dye indicator film to the outer surface of a hollow cylindrical waveguide, which, when immersed-in an aqueous solution, can reversibly detect various reducing species, reaching a sensitivity to formic acid of 7.5 mmol l^{-1} (345 mg l^{-1}). The other sensor described in the literature is based on the property of certain bacteria which produce hydrogen from formic acid, formic acid can be detected using *Clostridium butyricum* and a fuel type electrode[22] consisting of a platinum anode and a silver peroxide cathode that can be used for measuring hydrogen. The minimum concentration for determination is 10 mg l^{-1}.

In the literature, we found no sensor for the determination of formic acid in its vapour form. This paper describes for the first time two sensors for formic acid vapours, based on AT-cut PZ crystals, coated with 4-ethyl-3-thiosemicarbazide and 2,6-diacetylpyridine films. These sensors combine good selectivity and much greater sensitivity than those suggested for formic acid in solution, although not sufficient for application to the atmosphere or working environments, threshold limit value–time weighted average (TLV–TWA) 0.009 mg l^{-1}.[23] Sensitivity might be improved by the addition of an initial preconcentration stage, *cf.* the method of Ali *et al.* for determination of gaseous ammonia using a coated quartz PZ crystal.[24]

To study and perfect the new sensors we used our own design system[25] which is capable of working statically, this is more easily adaptable to measurement *in situ*, unlike other techniques proposed with other sensors, which work dynamically.

Experimental

Reagents

Formic acid, diphenylamine, 4-ethyl-3-thiosemicarbazide, 2,6-diacetylpyridine, phenylhydrazine, 2,2-bipyridine and reagents used in the study of interferences, were of analytical-reagent grade. The nitrogen was of type N-50 from SEO (Spanish Oxygen Company).

Materials and Equipment

The oscillator circuits employed were made of common commercial electronic components (resistors, capacitors, transistors). The 8.9 MHz, AT-cut (Universal Sensors) PZ crystals, were mounted on HC-25/U type bearings and the rest of the equipment consisted of control and measurement instruments described previously.[25] The sensor unit is placed inside a testing chamber, which is capable of reproducing normal atmospheric conditions.

Procedures

Preparation of the coated crystal

The crystal was cleaned by submerging it in ethanol. It was dried in warm air then placed in the testing chamber under vacuum for 5 min, dry nitrogen was injected and after 30 min the frequency was measured. The crystal was removed from the chamber and coated by immersion for 5 s or more according to the amount of coating desired, in a solution of the appropriate reagent (0.190 g of diphenylamine in 10 ml of ethanol; 0.100 g of 4-ethyl-3-thiosemicarbazide in 10 ml of ethanol; 0.100 g of 2,6-diacetylpyridine in 10 ml of acetone; 0.085 g of phenylhydrazine in 9 ml of ethanol; and 0.100 g of 2,2-bipyridine in 10 ml of ethanol). The coated crystals, dried as described, are protected for storage with a metallic capsule and placed in a vacuum desiccator.

Measurement of the response to formic acid

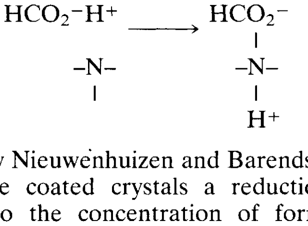
In a nitrogen or air atmosphere (in the testing chamber) and in the absence of formic acid vapour the stabilized frequency of the coated crystal was measured and noted. The chamber was evacuated and the formic acid injected. The nitrogen or air atmosphere was re-established (at the same pressure and temperature) and the frequency again measured and noted. The difference, Δf, between this measurement and the previous one was calculated. The sensor was restored to its original condition by evacuation and nitrogen admission after this second measurement.

The concentration of formic acid vapour was calculated from the previously constructed calibration graph of Δf *versus* the concentration of formic acid.

Results and Discussion

Selection of Coatings

The acid nature of the sample for analysis led us to select basic coatings. Furthermore, in the search for selective chemical sorption processes we considered compounds containing nitrogen atoms, which will probably give the following:



$$\begin{array}{ccc} HCO_2^-H^+ & \longrightarrow & HCO_2^- \\ & & | \\ -N- & & -N- \\ | & & | \\ & & H^+ \end{array}$$

as described by Nieuwenhuizen and Barendsz.[26]

With all the coated crystals a reduction in frequency proportional to the concentration of formic acid in the chamber was noted but the reduction varied markedly for different coatings. For a fixed amount, 3.31 mg l^{-1}, of formic acid in the chamber, the differences in frequency (Hz) of the coated crystals, in the absence and presence of formic acid were: diphenylamine, 8; phenylhydrazine, 2; 2,2′-bipyridine, 7; 4-ethyl-3-thiosemicarbazide, 60; and 2,6-diacetylpyridine, 40.

On the basis of these results the 4-ethyl-3-thiosemicarbazide and 2,6-diacetylpyridine were chosen as coatings.

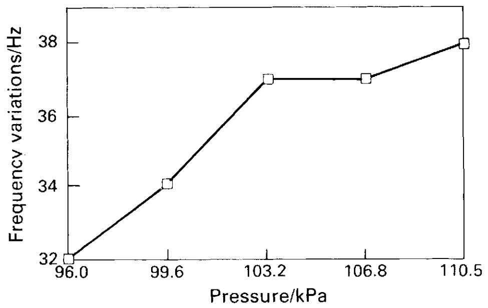


Fig. 1 Effect of pressure on the 4-ethyl-3-thiosemicarbazide sensor

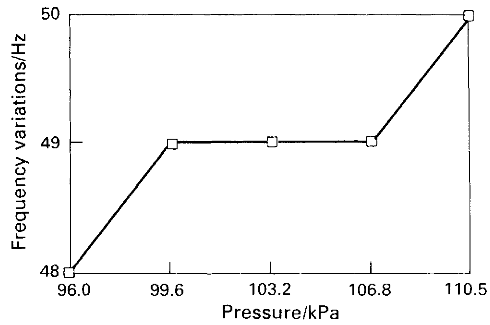


Fig. 2 Effect or pressure on the 2,6-diacetylpyridine sensor

Variation of Response With the Amount of Coating and With Time

The Δf_0 value is dependent on the amount of coating. Crystals were prepared with three different amounts of coating substance. The values of Δf_0 are listed in Table 1.

However, it was found that the frequencies of the coated crystals shift with time. Using the crystals mentioned above, Δf_0 was measured daily for 60 d and the results are also shown in Table 1.

Generally, Δf_0 decreased with time owing to a slow loss of coating but after 30–40 d Δf_0 may increase owing to crystal contamination. This small frequency variation was taken into account when measuring Δf_0 at a particular time.

Variation in the Measuring Conditions

The testing chamber reproduces environmental conditions and enables a study of the influence of variations in pressure, temperature or relative humidity on the sensor response to formic acid to be made. The frequencies of the coated crystals (for a given Δf_0) were first measured without and then with a known amount of formic acid. The atmospheric parameter was then varied and the corresponding frequencies recorded.

Pressure

Experiments were carried out at a constant temperature of 27 °C. The chamber was evacuated and dry nitrogen at different pressures was injected with a fixed amount (10 µl) of formic acid. Figs. 1 and 2 show that between 96 and 110.5 kPa, in the presence of formic acid, the frequency variation is 0.413 Hz kPa^{-1} (0.675 Hz kPa^{-1} between 96 and 103 kPa) for the 4-ethyl-3-thiosemicarbazide coated crystal (Δf_0 = 185 Hz), but it is only 0.15 Hz kPa^{-1} (0.30 Hz kPa^{-1} between 96 and 103 kPa) for the 2,6-diacetylpyridine coated crystal (Δf_0 = 1077 Hz). In the absence of formic acid and under the same conditions, the differences in frequency are almost unchanged, especially for the 2,6-diacetylpyridine coating.

Crystal response under a dry air atmosphere has also been studied. The results are very similar to those obtained under the nitrogen atmosphere.

Temperature

Experiments were carried out under a nitrogen atmosphere at a constant pressure of 105 kPa, injecting a volume of 10 μl of formic acid (3.31 mg l^{-1}) and measuring the recovery times of the sensor. It was found that the effect of temperature, both on frequency and recovery time, is dependent on the PZ crystal coating.

For 4-ethyl-3-thiosemicarbazide (crystal with Δf_0 = 185 Hz), crystal frequency both in the absence and presence of formic acid, decreases when the temperature increases, which appears illogical. Although the frequencies differ in both situations, Δf decreases as the temperature rises, as shown in Table 2, which means that the sorption onto the coated crystal is reduced. When the temperature rises, the recovery time also increases at first, and then decreases.

For 2,6-diacetylpyridine (crystal with Δf_0 = 1077 Hz), and in the absence of formic acid, the crystal frequency fluctuates as the temperature rises, but on average remains approximately constant. However, in the presence of formic acid, the frequency increases as the temperature rises, suggesting a decrease in sorption, which is confirmed by the decrease in Δf. When the temperature rises, the recovery time initially stays constant, then increases and finally decreases abruptly so that at 40 °C it is reduced by one half.

Table 1 Variation of Δf_0 with time

Time elapsed/d	Δf_0/Hz 4-Ethyl-3-thiosemicarbazide			2,6-Diacetylpyridine		
1*	1551	771	308	1113	890	682
2	1542	682	252	1051	890	699
5	1237	614	181	1017	859	697
10	1181	—	—	1008	—	—
20	1121	—	—	1048	830	—
30	1107	443	186	1073	—	622
40	1104	430	190	1113	863	556
60	1200	—	—	1766	—	—

* Just coated crystals.

Table 2 Temperature influence on frequencies of formic acid sensors

	2,6-Diacetylpyridine		4-Ethyl-3-thiosemicarbazide	
T/°C	Δf/Hz	t_R/min	Δf/Hz	t_R/min
15	91	30	40	20
20	78	30	38	25
25	50	35	31	30
30	54	35	26	35
35	41	20	30	20
40	45	15	29	11

Table 3 Influence of concentration of formic acid on frequency and recovery time

	2,6-Diacetylpyridine				4-Ethyl-3-thiosemicarbazide			
	Δf_0 = 824 Hz		Δf_0 = 687 Hz		Δf_0 = 475 Hz		Δf_0 = 185 Hz	
mg l^{-1}	Δf*	t_R†	Δf	t_R	Δf	t_R	Δf	t_R
0.17	0	0	0	0	4	3	3	3
0.33	8	5	4	5	6	3	7	3
3.31	37	21	23	20	96	20	39	20
8.28	43	24	32	26	114	26	53	26
16.55	47	26	44	27	130	30	68	30
24.82	56	35	58	35	146	35	96	35
33.10	72	35	76	35	179	35	122	35

* Δf/Hz.
† t_R/min.

Humidity

In view of the great influence of water on the frequency of some coated crystals,[25] a study on the effect of relative humidity (RH) on the oscillation frequency of the sensors tested was carried out. A test-chamber temperature of 25 °C with a vacuum to cause the water to evaporate was used and 5, 10 and 50 μl of water (equivalent respectively to 10, 20 and 100% relative humidity) with 10 μl of formic acid was injected. Dry air was injected into the chamber until a pressure of 100.8 kPa was reached; the oscillation frequencies of the crystal were measured, and compared with those measured in the absence of formic acid.

The frequency of the PZ crystal with a 4-ethyl-3-thiosemicarbazide coating (Δf_0 = 1177 Hz) shows a slight but uniform reduction between 0 and 100% relative humidity (RH), amounting to 0.2 Hz (unit of RH)$^{-1}$, both in the absence and presence of formic acid. The difference in frequencies is constant over that range, thus it was concluded that the humidity does not interfere in the determination of formic acid unless the RH variation is very large.

The results of the tests for the 2,6-diacetylpyridine coated crystal (Δf_0 = 1042 Hz) were similar to those described above, although Δf first decreases when the RH rises to 20% and then from 20 to 100% RH, shows a slight increase.

Influence of the Concentration of Formic Acid

Calibration of the sensors in the presence of formic acid was carried out in a dry air atmosphere (0% RH) at 25 °C and a pressure of 101.3 kPa. For each concentration of formic acid we measured the frequencies, both in the presence and in the absence of the acid. The difference between the frequencies, Δf, was plotted against the formic acid concentration.

Table 3 shows the results obtained for the crystals coated with 4-ethyl-3-thiosemicarbazide and with 2,6-diacetylpyridine. It can be seen that the relationship between the frequency variations Δf (in the presence and absence of the sample) and the concentration of formic acid, reveals two trends: one between 0.17 and 3.31 mg l^{-1} and the other between 3.31 and 33.1 mg l^{-1}. The calibration equations for the coated crystals are given in Table 4.

Greater sensitivity was obtained with the 4-ethyl-3-thiosemicarbazide coating for Δf_0 = 475 Hz, being 29.7 Hz mg^{-1} l. The detection limit (defined as the concentration of sample that produces a three times greater variation in frequency than that produced in the absence of the sample) was 0.17 mg l^{-1}.

Recovery Time (t_R) and Variation of Response With Time

The time taken for the sensor to recover its original frequency after exposure to formic acid was studied. For the 4-ethyl-3-thiosemicarbazide coated sensor, the average t_R was 29 min and for the 2,6-diacetylpyridine coated crystal, 28 min. Nevertheless, as shown in Table 3, the recovery time is dependent on the formic acid concentration.

Table 4 Calibration equations for the coated crystals over two formic acid concentration ranges

	$[HCO_2H]$ = 0.17–3.31/mg l^{-1}			$[HCO_2H]$ = 3.31–33.1/mg l^{-1}		
Coating	Δf_0/Hz	Δf	*r*	Δf_0/Hz	Δf	*r*
4-Ethyl-3-thiosemicarbazide	475	$29.7[HCO_2H] - 2.4$	0.9997	475	$2.6[HCO_2H] + 88.3$	0.9890
	185	$11.1[HCO_2H] + 2.2$	0.9984	185	$2.8[HCO_2H] + 28.2$	0.9947
2,6-Diacetylpyridine	824	$10.9[HCO_2H] + 1.2$	0.9870	824	$1.10[HCO_2H] + 32.2$	0.9730
	687	$6.9[HCO_2H] + 0.24$	0.9930	687	$1.74[HCO_2H] + 16.7$	0.9772

Table 5 Statistical analysis of repeatability data

Coating	Δf_o/Hz	$(\Delta f)_m$/Hz	$\delta_{\Delta f}$/Hz	$(\delta_{\Delta f})_m$/Hz	Δf/Hz	ε (%)	t_R/min
4-Ethyl-3-thiosemicarbanide	185	37.25	1.85	0.56	37.25 ± 1.24	±3.3	20.90 ± 2.50
2,6-Diacetylpyridine	824	37.10	1.75	0.53	37.10 ± 1.21	±3.3	19.54 ± 2.29

Table 6 Study of interferences

Interferent	Concentration/mg l^{-1}	Δf_D*/Hz	Δf_E†/Hz
Chloroform	61	14	14
Diethyl ether	29	0	19
Benzene	36	6	2
Acetone	32	12	12
Acrolein	34	0	0
Formaldehyde	16	15	17
Diisopropyl ether	29	9	0
Isobutyl methyl ketone	32	0	0
Isopentyl alcohol	50	10	11
Acetonitrile	31	4	5
Carbon tetrachloride	63	8	9
Chlorobenzene	45	11	7
Toluene	36	0	0
Acetic acid	43	22	24
Hexane	27	8	4
Butyl acetate	35	13	21
Dichloromethane	54	0	15
Propan-2-ol	32	0	0
Tributyl phosphate	40	0	0
Hydrochloric acid	17	31	50
Ethanol	32	7	9

* Decrease in frequency for 4-ethyl-3-smithiocarbazide, Δf_0 = 830 Hz.

† Decrease in frequency for 2,6-diacetylpyridine, Δf_0 = 460 Hz.

Repeatability

In order to determine the repeatability, eleven measurements were carried out under identical reaction chamber conditions with a formic acid concentration of 3.31 mg l^{-1}. Statistical treatments (95% probability level) for both sensors are listed in Table 5.

Interferences

First, the frequency was measured with a known amount of formic acid (10 μl, equivalent to 3.31 mg l^{-1} within the chamber) and then the frequency was measured with the same amount of formic acid and a 5–20 times greater volume of the interfering substance.

The responses of crystals coated with 4-ethyl-3-thiosemicarbazide and 2,6-diacetylpyridine to 21 interfering species were studied. Conditions of steady pressure (99.6 kPa) and temperature (28 °C) were maintained. The concentration of interferents (mg l^{-1}) and the decrease in frequency and for 4-ethyl-3-thiosemicarbazide (Δf_E) and 2,6-diacetylpyridine (Δf_D), respectively, are listed in Table 6.

From the results it can be concluded that for both coatings the greatest interferences are caused by species of an acid nature (*e.g.*, hydrochloric acid, acetic acid). Formaldehyde also showed significant interference.

The authors acknowledge their gratitude to CICYT (Project AMB92-0863) for financial support.

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Paper 2/02278H
Received May 1, 1992
Accepted November 2, 1992