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DESIGN, CONSTRUCTION AND TESTING OF A SYSTEM FOR DETECTION OF TOXIC GASES BASED ON PIEZOELECTRIC CRYSTALS

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Summary—A system for static operation of toxic gas sensors based on piezoelectric crystals was constructed as a preliminary step in the development of this type of sensor.

The sensing part of the setup consists of a twin oscillating circuit assembled from commercially available electronic parts mounted on a motherboard. The oscillating circuits can accommodate two piezoelectric crystals, of which one or both can be coated with different materials, or a single one, as required. The sensing assembly (crystals plus oscillating circuits) is placed in a customized test chamber that allows one to control and reproduce its internal environment.

Once assembled and fine-tuned, the proposed setup was used to test a commercially available piezoelectric crystal for sensing formaldehyde in order to expand available information on this type of sensor.

The gradual deterioration of our environment is a matter of growing social concern. Industrial and commercial activities occasionally produce vast amounts of toxic gases, which ultimately end in the atmosphere, where they pose serious hazards to workers at the facilities concerned and living beings in general. This has aroused interest in the development of sensing systems for detecting the presence of toxic gases in the environment and measuring their concentrations in order to enforce protective and control measures. In this context, piezoelectric crystals (PZ), notwithstanding their still relatively scant current use among chemical sensors, are being given highly significant applications on account of their major assets, which enable development of straightforward, inexpensive portable measuring systems. The earliest application of PZ crystals to gas detection was reported by King,[1] who later developed a PZ crystal detector for atmospheric hydrocarbons.[2] Guilbault *et al.*[3–10] used coated PZ crystals to detect various atmospheric gases. Many applications of PZ crystals for this purpose are described in an excellent review by McCallum.[11]

Most PZ crystal assemblies are designed for dynamic operation with flowing gases,[3,4,7,12,15] however, gases in a variety of environments (*e.g.* the atmosphere, garages, warehouses, ship holds, workshops) are in a more or less static condition. In this work, a system for testing PZ crystal-based sensors to be used under static conditions was designed as a preliminary step to the future development of several such sensors. While the sensors will be less sensitive in static operation, they will provide more realistic conclusions and lend themselves more readily and economically to the development of portable devices for on-site control of toxic gases.

Once fine-tuned, the proposed setup was used to test a commercially available piezoelectric crystal for formaldehyde, available information of which was significantly expanded as a result.

EXPERIMENTAL

Reagents

Both formaldehyde and the reagents used in the interference study were P.A. grade chemicals. Type N-50 nitrogen was supplied by Sociedad Española del Oxígeno (SEO).

Apparatus

The oscillating circuits were assembled from commercially available electronic parts (resistors, capacitors and transistors). The piezoelectric crystals, which were mounted on HC-6/U boards, were supplied by Universal Sensors

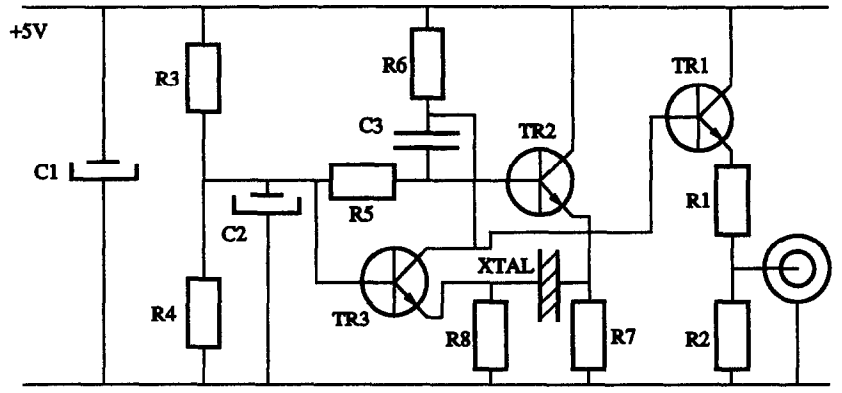

Fig. 1. Scheme of the oscillating circuit.

(New Orleans, U.S.A.); one, uncoated, featured an AT cut of 9 MHz, while the other, coated with enzymes for detection of formaldehyde, had an AT cut of 10 MHz. The experimental setup included a Grelco Dl-3010 power supply, a Bremi BRI-913 frequency counter with 1 Hz resolution, a Schaevtiz P-5041-B-2546 pressure transducer, a Promax PD-618 digital multimeter, a Bremi BRI-8025 printer, a Leybold-Trivac D-8-B 8-1 vacuum pump providing 7.4×10^5 mm Hg vacuum, and a Selecta Tectron S 473.100 thermostatic bath furnished with PVC tubes for wrapping the chamber.

System for static measurements in polluted environments

The sensing part of the setup consisted of a twin oscillating circuit mounted on a copper and fibreglass motherboard with a stainless steel frame. The oscillators were of modified Colpitts type and designed according to a scheme previously reported by Beitnes and Shoreder.[16] Each oscillating circuit can accommodate a differently coated PZ crystal for simultaneously measuring the response to the same gas or, alternatively, one of them can use an uncoated PZ crystal both as reference and to offset any frequency variations potentially arising from temperature changes. In order to control the frequencies of both crystals almost simultaneously, a duplexer connecting the signal outputs of the crystals with the frequency counter and allowing the frequency of either crystal or their ratio to be read at any time was developed. The system can also be used with a single crystal by disconnecting the other, as was the case in this work. The whole circuit used is depicted in Fig. 1.

The sensing assembly (crystals plus oscillating circuits) was placed in a customized test chamber that allowed its atmosphere to be controlled and reproduced. Essentially, the chamber consisted of a glass vessel of 2.427 l drained volume (after accommodating the different devices). It included two side valves for incoming and outgoing gases, a nozzle furnished with a septum for injection of samples, an auxiliary socket for a thermometer and a tight-fitting lid through which electrical power was supplied and frequency readings were made. The seal also supported the electronic circuits, the pressure transducer and a customized fan composed of a moving, magnetic part (mounted on the lid) and a fixed, also magnetic part, including the transformer and regulator, placed outside the chamber. The fan was operated by magnetic induction and was used to homogenize the gases inside the chamber prior to measurements.

Figure 2 shows a block diagram of the whole assembly.

Fine-tuning of the setup

Tuning the proposed setup entailed checking whether it was suitable for measuring toxic gases and vapours. This in turn involved checking if the chamber was tight and resistant, and

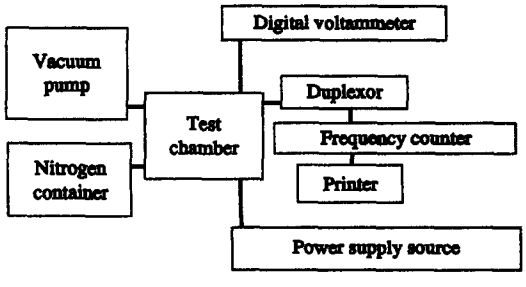

Fig. 2. Block diagram of the experimental setup.

whether its internal pressure and temperature could be accurately measured.

Tightness and resistance. After 10 min of continuous functioning of the aspiration pump, the chamber was found to maintain vacuum for over 1 h. By using a nitrogen cylinder, the chamber was found to withstand 1140 mm Hg—no higher pressures were assayed as they are unlikely to be encountered under ordinary measurement conditions.

Pressure control. The pressure inside the chamber was controlled with the aid of a nitrogen or dry-air cylinder and a gauge. The gauge used was of analogical type, with a mV reading scale, so a calibration was needed in order to convert readouts into mm of Hg. Between 800 and 1200 mV, the two were related by the following expression:

$$mm_{Hg} = 0.274 \times mV + 501,$$

with $r = 0.999$.

Temperature control. By using a thermostatic bath, a cryostatic bath and PVC tubing coiled around the chamber and carrying thermostatted warm water, the temperature inside the chamber was regulated to within ± 0.5°C.

Procedure

The system response to a given gas or vapour was studied by measuring the stabilized frequency of the pertinent sensing crystal in the absence of analyte under nitrogen at near-atmospheric pressure (inside the test chamber). The chamber was evacuated by means of the vacuum pump and a known amount of analyte was injected into it. The chamber was then filled with nitrogen at the same pressure and temperature as before and a new frequency reading was made in order to calculate the difference between the two measurements, Δf. The initial sensor frequency was restored by alternate evacuation and admission of nitrogen. Liquid samples were inserted by injection with a syringe, the chamber being previously evacuated in order to facilitate volatilization.

The influence of pressure, temperature and relative humidity variations was studied similarly: the sensing crystal frequency was measured in the absence and presence of a known amount of analyte under given atmospheric conditions, and either the pressure, temperature or humidity was changed, the other two being kept constant, in order to measure a new frequency.

The effect of potential interferences was studied by first measuring the crystal frequency at a given, near-atmospheric pressure, with no analyte in the chamber. Then, the chamber was evacuated, the analyte injected, the original pressure restored with nitrogen and the frequency measured again. The entire measurement process was conducted at a constant temperature.

RESULTS AND DISCUSSION

Testing of a commercially available PZ crystal for formaldehyde

The functioning of the proposed setup was tested by carrying out a critical study of the performance of the commercially available Universal Sensors crystal for formaldehyde. Preliminary tests, in which the sample humidity was not controlled, showed the temperature to have a marked influence on the crystal oscillation frequency, which increased with increasing temperature, both in the presence and in the absence of formaldehyde, but rather erratically. The frequency also decreased inconsistently with increase in the HCHO concentration.

The study performed at the time the formaldehyde sensor was developed[17] was done at a relative humidity of 50% and excluded the potential influence of the sample water contents. In this work we investigated the influence of 25 species on the crystal oscillation frequency and found water (in addition to formic acid, chloroform, acetone, hydrochloric acid and acetic acid) to be among those that diminished such a frequency to the greatest extent. Accordingly, the original experiments were repeated in a dry nitrogen atmosphere in order to avoid the effect of water.

Influence of pressure

At a constant temperature of 26°C, the crystal frequency was found to vary with the pressure inside the chamber. Experiments were conducted both in the absence of formaldehyde and in the presence of a 1.6 mg/l concentration of the analyte in the chamber; the *in vacuo* vibrational frequency of the crystal was found to be 9,969,760 Hz. The Δf values obtained were very small in both cases, namely *ca* 0.07 Hz/mm Hg between 665 and 883 mm Hg. The differences were much smaller than those obtained in a dry atmosphere.

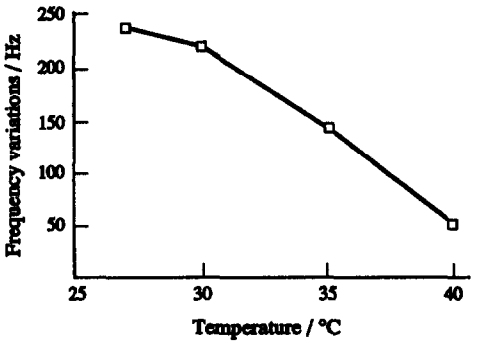

Fig. 3. Influence of temperature on the PZ crystal frequency.

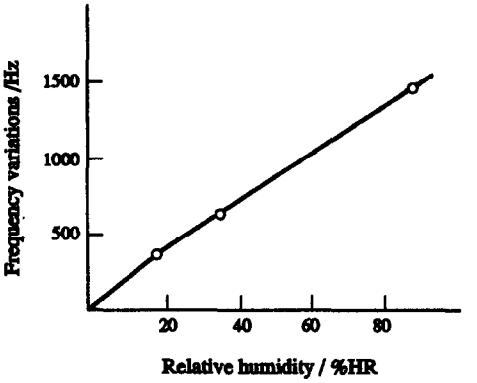

Fig. 5. Influence of the relative humidity on the sensor response.

Influence of temperature

Experiments were also performed in the presence and absence of 1.6 mg/l HCHO in the chamber. The results obtained are shown in Fig. 3. As can be seen, Δf decreased with increasing temperature, which suggests a decrease in the degree of adsorption on the crystal.

Sensor calibration

By using a dry nitrogen atmosphere at 774.5 mm Hg and a constant temperature of 27°C, variable concentrations of HCHO between 0.8 and 4.0 mg/l were injected into the chamber. The results thus obtained are shown in Fig. 4. As can be seen, the crystal frequency decreased with increasing HCHO concentration. The difference Δf between the frequencies measured in the absence and presence of HCHO increased roughly linearly with the formaldehyde concentration according to the following expression

$$\Delta f = 25.01 \times [\text{HCHO}] + 135.04$$

with $r = 0.971$ and the HCHO concentration in mg/l.

Apparently, the formaldehyde crystal ages with usage (*i.e.* with the number of adsorption/desorption cycles), which may account for the fact that the sensitivity obtained in this work was below the manufacturer's certified value. On the other hand, such a decreased sensitivity could also be the result of using the sensor under static rather than dynamic conditions.

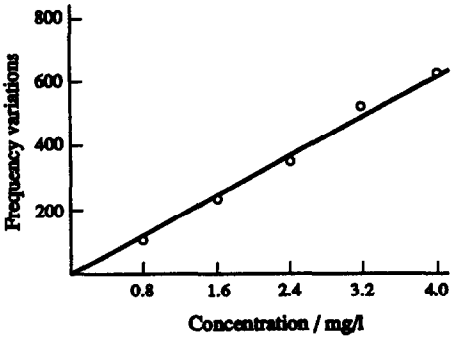

Fig. 4. Calibration of the formaldehyde crystal sensor.

Sensor regeneration

In order to remove formaldehyde deposited on the crystal, the chamber was evacuated for 20–30 min at HCHO concentrations between 0.2 and 3.4 mg/l, and for 45–90 min at higher analyte concentrations.

Influence of H_2O

Under a nitrogen atmosphere at 780 mm Hg and 25°C, the frequency of the PZ crystal was measured for a fixed HCHO concentration of 1.6 mg/l and variable amounts of water equivalent to 20 100% relative humidity. As can be seen in Fig. 5, water caused a serious interference, so the formaldehyde sensor should only be used in its absence or at an accurately known, constant relative humidity.

Study of interferences

Because of the seriously adverse effect of water, the study of interferences was repeated in a dry nitrogen atmosphere at 788 mm Hg and 26°C. For this purpose, the frequency of the formaldehyde crystal was first measured *in vacuo*, then in the nitrogen atmosphere alone and, finally, in the presence of 1.6 mg/l HCHO and 100 μl of interferent. All readings were made 5 min after injection. The results obtained are listed in Table 1. Interferences were much less serious than under conditions of uncontrolled humidity.

On the other hand, since the sensor was operated in an adsorption/desorption cycle that

Table 1. Study of interferences

Interferent	Concentration mg/l	Δf*/Hz	Δf†/Hz
Chloroform	61	7483	1354
Ethyl ether	29	4743	165
Benzene	36	1259	0
Acetone	32	9635	2160
Acrolein	34	1519	230
Isobutylmethylketone	32	829	84
Isoamyl alcohol	50	936	255
Acetonitrile	31	1127	133
Carbon tetrachloride	63	715	8
N,N-Dimethylformamide	43	4347	1315
Chlorobenzene	45	339	130
Toluene	36	0	0
Triethanolamine	46	0	0
Acetic acid	43	12796	2932
N-Hexane	27	0	0
N-Butyl acetate	35	287	0
Formic acid	33	—	6253
Methylene chloride	54	0	0
Propan-2-ol	32	843	352
Tributyl phosphate	40	72	0
Ethyl acetate	36	246	0
Formamide	48	246	1146
Hydrochloric acid	17	4931	1856
Ethanol	32	0	80

*T = 22–24°C.
†T = 40°C.

was probably markedly influenced by the temperature, no literature reference to its potential effect was available, the effect of interferents was also studied at 40°C (see Table 1). The frequency decrease at this higher temperature was much smaller for all species studied, formaldehyde included, for which the response dropped by *ca.* 10%. This resulted in diminished sensitivity but substantially augmented selectivity: a number of species such as benzene, carbon tetrachloride, toluene, triethanolamine, ethyl acetate and *n*-butyl acetate, which posed serious interferences at 26°C, had virtually no effect at 40°C.

The sensor responsiveness to interferents was found to change with time. Thus, in an atmosphere containing 1.6 mg/l HCHO and 43 mg/l *N,N*-dimethylformamide at 30°C, the frequency diminished gradually for over 260 min, even though 50% of the overall decrease occurred within the first 10 min.

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