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Analysis of Environmental Pollutants Using a Piezoelectric Crystal Detector†

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Piezoelectric crystal detectors possess a good potential as sensors in Analytical Chemistry. Their specificity is excellent, provided a highly selective adsorbent layer is placed on the surface of the crystal. Sensitivity is also good, down to parts per trillion levels of atmospheric pollutants are detectable, with a large linear range up to parts per million.

Specific detectors have been developed for organophosphorus compounds, toluene in printing plants, dynamite and explosives, CO, SO₂, NO_x, NH₃, HCl and organochlorine compounds. Results on some of these detectors is presented herein.

KEY WORDS: Piezoelectric crystals, specific detectors, atmospheric pollutants, organophosphorus compounds, toluene, carbon monoxide, explosives, ammonia, hydrogen chloride.

INTRODUCTION

The concept of piezoelectricity was first discovered in 1880 by Pierre and Jacques Curie,¹ who observed that a pressure exerted on a small piece of quartz caused an electrical potential between deformed surfaces, and also that the application of a voltage to a quartz crystal effected physical distortions. A crystal, activated by a concise electrical charge, vibrates mechanically for a short time until a physical equilibrium is attained.

For piezoelectric crystal detectors, alpha quartz is most widely used. Its properties of water insolubility and resistance to temperatures up to 579° with no loss of piezoelectric properties make it particularly desirable. The

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frequency of the quartz crystal is dependent upon the physical dimensions of the quartz plate and upon the thickness of the electrodes placed on it. For use as a piezoelectric crystal detector, only AT or BT cut quartz plates are useful.² These crystals are two high-frequency mode plates which vibrate in a shear mode about an axis parallel to the major surface; these plates have low or zero temperature coefficients at the temperature of use, and have surfaces that are antimodal in displacement. The temperature coefficients are a critical function of the angle of cut. The AT cut is superior in temperature coefficient and in mass sensitivity. The 9 MHz crystals used most frequently are 10 to 16 mm discs, squares and/or rectangles which are approximately 0.19 mm thick. The metal electrodes are 3,000 to 10,000 Å thick, 3 to 8 mm in diameter and are made of gold, nickel, silver or aluminum. The resonant frequency of a crystal is normally obtained using a frequency meter attached to the output of an oscillator circuit.

Sauerbrey^{3,4} has developed a relationship between the weight of metal films deposited on quartz crystals and the change in frequency; this relationship was derived for quartz (AT-cut) crystals vibrating in the thickness shear mode:

$$\Delta F = -2.3 \cdot 10^6 F^2 \frac{\Delta Ms}{A}$$

where ΔF = the change in frequency due to the coating [Hz]

F = the frequency of the quartz plate [MHz]

ΔMs = Mass of deposited coating (grams)

A = area coated (cm²).

This equation predicts that a commercially available 9 MHz crystal would have a mass sensitivity of about 400 Hz/μg or a 15 MHz crystal a sensitivity of 2600 Hz/μg. It is therefore apparent that the vibrating quartz crystal can be an extremely sensitive weight indicator. The detection limit is estimated to be about 10⁻¹² grams.⁵

Piezoelectric devices have been used for many years for controlling frequency in the communications field, as selective filters in electronic networks and recently for the detection and determination of micro concentrations of substances. In this article some of the applications of piezoelectric crystal detectors in environmental analytical chemistry will be discussed.

EXPERIMENTAL

Apparatus

A typical experimental set-up with the piezoelectric quartz crystal detector is shown schematically in Figure 1. The cell design is the most sensitive one for use in a flow system. The piezoelectric crystals used are 9-MHz quartz crystals with silver-plated metal electrodes on both sides. The crystals are AT-cut mounted in HC 25/U holders (JAN Crystals Mfg.

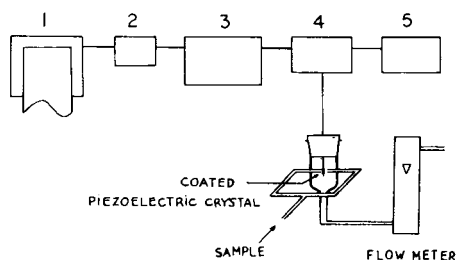


FIGURE 1 Experimental apparatus: (1) Recorder, (2) digital to analog converter, (3) frequency counter, (4) oscillator, (5) power supply.

Co.). The instrumentation consisted of a low frequency OX transistor oscillator (International Crystal Mfg. Co., Oklahoma City) powered by a regulated power supply (Heath Kit model 1P-28). The applied voltage was kept constant at 9 V-dc. The frequency output from the oscillator was measured by a frequency counter (Health-Schlumberger model SM-4100), which was modified by a digital-to-analog converter, so that the frequency could be recorded. The frequency (peak maximum) could be read on either the frequency counter or the recorder.

Air as the carrier gas is supplied by a vibrating diaphragm air pump. An empty gas chromatographic column of stainless steel can be placed between the pump and cell in order to minimize a change in flow rate. The flow rate of air is maintained at 30 ± 2 ml min.

For field measurements of environmental pollutants an apparatus shown in Figure 1 is inadequate. A self-contained small, portable detector was designed using the basic components shown in Figure 1, but with a 6 V battery, a mini pump and digital readout.⁶

PIEZOELECTRIC CRYSTAL DETECTOR FOR DETECTION AND DETERMINATION OF AIR POLLUTANTS

Detector for sulfur dioxide

Oil refineries, pulp mills, and effluents from a number of other industrial stacks constitute a prime source of SO_2 discharge into the atmosphere. Burning of high sulfur fuels in automobiles is another cause of pollution at ground level. Therefore, an ever-increasing demand has arisen for new, simple and inexpensive methods for measurement and control of sulfur dioxide pollution.

There have been several research reports describing the use of coated piezoelectric quartz crystals as highly sensitive detectors for SO_2 . Many coating materials have been investigated for SO_2 .

Trace amounts of SO_2 can be detected using a new detector cell design with triethanolamine and quadrol as coating materials.⁷ One important feature of this design is that the column effluent is split into two equal streams which directly and simultaneously fall on the opposite faces of a coated crystal. This arrangement is expected to improve the sensitivity since the amount of the sample gas reacting with the coating at any moment is appreciably increased.

Effects of changes of temperature were investigated in several experiments. Guilbault *et al.*⁸ pointed out that the frequency for the crystals increased with increases in temperature, especially from 100 to 200°C. From 25° to 40° the effect of the temperature is very small, an increase of about 40 Hz. These experiments show that temperature must remain constant during the reading, but a change of 10°C is not critical.

Triethanolamine was used as coating material by Cheney *et al.*^{9,10} who measured the temperature dependence of an uncoated 9 MHz crystal and found 71 Hz of change when the temperature increased from 10°C to 35°C. Adsorption and desorption of the SO_2 on the coating material at different temperatures were also investigated.

The method of coating the crystal with various substrates has been shown to be very important. Several different techniques were evaluated for application of the substrate to the piezoelectric crystal; dropping, dipping and spraying methods. Earp¹¹ had shown in a previous study that the sensitivity of the sorption detector is inversely proportional to the area coated and to the distance from the center of the crystal. As the area of coating on the electrode surface decreased, the sensitivity increases to a maximum and then decreases again due to less surface area being available for sorption. It is essential, therefore, that the coating be placed on the crystal in the exact same manner each time. In the drop method, the substrate is dissolved in a volatile solvent and then a drop of this

solution is placed at the center of the crystal electrode using a micro-syringe or glass bar; the solvent is then allowed to evaporate. In the dip method, the crystal is dipped into a solution of the substrate in a volatile solvent and then allowed to dry. In the spray method the crystal is coated by spraying a solution of the different compounds (contained in a suitable solvent) onto a crystal surface. The critical factor involved in coating the crystal is not so much the amount of coating as it is the ability to reproduce the coating operation, as proposed by Hartigan.¹²

Cheney *et al.*¹³ used cotton swabs to coat a crystal with the substrate ethylenedinitrotetraethanol for detection of SO₂. The technique of coating the crystal was checked for repeatability of both coating amount and sensitivity. A greater sensitivity to SO₂ was obtained using a 9 MHz crystal coated in the center (340 Hz) than a totally coated crystal (260 Hz). The authors also found that the frequency change due to a varying coating is predictable and consistent for a center-coated crystal, but not for a fully coated crystal.

Considerable interferences were caused by NO₂ and moisture in the assay of SO₂ using all coatings. An accurate quantitative determination cannot be obtained for SO₂ in the presence of NO₂ using coated piezoelectric crystals. Guilbault *et al.*¹⁴ showed that a hydrophobic membrane filter (pore size 0.45 μm) was successful in greatly reducing the response of a quadrol coated crystal to atmospheric moisture. Each additional filter layer further reduced the effect of moisture response, and with 4 layers the response for moisture was completely suppressed.

The use of piezoelectric crystals for detection of SO₂ in stack-gas and automobile exhaust analysis has been described.¹⁵

Ammonia detectors

The detection of NH₃ in the ppb range was effected using coated piezoelectric crystal detectors. When Ucon 75-H-90,000 and Ucon-LB-300X were used as coatings,¹⁶ good sensitivity to ammonia was obtained, and nitrogen dioxide reacts only after a 5 minute exposure of the coating to nitrogen dioxide. The nitrogen dioxide reacted with the Ucon coatings, and new compounds were formed on the crystal; a great sensitivity for both ammonia and nitrogen dioxide resulted. The formation of new compounds was evident from the appearance of new bands and the shift of some bands observed in the infrared spectra of these substances. Some problems were caused by atmospheric moisture, and by high concentrations of organic compounds, which dissolve the coatings.

Several coating materials (Capiscum annum pods, ascorbic acid, and ascorbic acid with silver nitrate) were applied as coatings for the selective detection of ammonia in the atmosphere.¹⁷ These specific coatings were

not dependent on activation, and could be used at ambient conditions. The ascorbic acid and an extract of *Capiscum annum* react reversibly with ammonia; this type of coated crystal can be used to detect ammonia over a wide concentration range. In order to determine the type of reaction which occurs between ammonia and the coating substrates, infrared spectra were obtained under various conditions. These spectra suggested that the reaction of ammonia with ascorbic acid is a simple acid-base reaction, and this was assumed to be the mechanism of the *Capiscum*-ammonia reaction also. The nature of the increased sensitivity caused by silver nitrate is not known; however, it undoubtedly results from some type of interaction between ascorbic acid and silver. This interaction is probably an oxidation of ascorbic acid by silver ion, which is in turn reduced.

Hlavay and Guilbault¹⁸ described two new coatings for the detection of ammonia in ambient air: L-glutamic acid-HCl and pyridoxine-HCl. These two coatings give greater sensitivity and better selectivity than with previously described substrate coatings. The response time for both coatings is less than 7 minutes, and complete reversibility of response is observed in 5 minutes. No significant interferences were found from other gas. The effect of moisture on the coating material was eliminated by using a gas chromatographic precolumn packed with silica gel. With these coatings, ammonia was detected at less than ppb concentrations.

The reaction between L-glutamic acid HCl and ammonia was investigated by IR methods. According to the IR spectra a reaction between the carboxyl group and ammonia could have occurred, yielding the ammonium salt of the carboxylic acid. With pyridoxine·HCl and ammonia the IR spectra provides evidence that the reaction between the hydroxyl group and ammonia has occurred, yielding the ammonium salt of pyridoxine.

Detector for hydrogen sulfide

Hydrogen sulfide is a dangerous gas which has presented a safety problem in a number of American industries. This is especially true since hydrogen sulfide at a dangerous level is not noticed by workers and levels can increase suddenly. A method for selective detection of hydrogen sulfide in the atmosphere has been developed.¹⁹ This method is based on the adsorption of hydrogen sulfide on the surface of a quartz crystal coated using an acetone extract of various soots resulting from the burning of several organochlorine compounds. The extract of a soot prepared from chlorobenzoic acid provided the best substrate material, and the method is most useful in the concentration range 1 to 60 ppm. Since the OSHA limit

is 20 ppm as a ceiling value, this detector provides measurement within range of interest.

Other coating materials, such as lead acetate, metallic silver, metallic copper and anthraquinone-disulfonic acid for detection of hydrogen sulfide with coated piezoelectric crystals were proposed by King.²⁰

Detector for organophosphorus compounds and pesticides

In recent years great concern has arisen concerning the effect of using pesticides in the environment. Some pesticides are powerful cholinesterase inhibitors and as such are toxic to wildlife and humans, as well as to pests. The organophosphorus insecticides are all structurally related and undergo similar reactions. Since almost all of the organophosphorus pesticides contain either phosphoryl or thiophosphoryl groups, and the thiophosphoryl pesticides readily undergo oxidation reactions to produce phosphoryl containing compounds, diisopropylmethyl phosphonate (DIMP) was chosen as a model compound in studies by Guilbault and Scheide.²¹

Applying different inorganic salts (FeCl_3 , CuCl_2 , NiCl_2 , CdCl_2) as coatings for the crystal, the detection of DIMP in the ppm range was effected. It was established that the FeCl_3 -DIMP complex, which was used as the substrate in the determination of low concentrations of DIMP, could not be used in detection of other organophosphorous compounds of similar structure.^{22,23} Therefore, a detector was built using the FeCl_3 -paraoxon complex as the substrate on the piezoelectric crystal for the specific determination of paraoxon.

A special instrument was developed from a modified design of Karasek's apparatus²⁴ in the Shackelford-Guilbault experiments.²³ The instrument consisted of two modified Clapp oscillators, the signals from which were mixed, and the resultant frequency difference fed through a pump diode circuit to either an ammeter or a recorder. A cobalt-isonitrosobenzoylacetone (IBA-diethyl-p-nitrophenylphosphonate-Paraoxon) complex was evaluated for use as a substrate on the quartz crystal. Three different compounds; parathion, DDVP (dimethyl-dichlorovinyl phosphate) and DIMP, were studied; parathion showed the strongest interaction with the coating used. The recovery time for the crystal when parathion was the pesticide detected, was longer than that for DDVP in the ppb range, but recovery to the original frequency was complete. Various interferences were also investigated, and water vapor was compensated for by use of a mixer circuit in the instrument.

Several experiments were done in order to determine the most optimum condition for detection of pesticides with a coated crystal.²¹ Among these the cut-off points and the optimization of coatings were investigated in

detail. The cut-off is important in determining the optimum amount of substrate to be applied to the crystal. The frequency of oscillation of a crystal decreases with increasing mass according to the Sauerbrey equation, until the crystal is overloaded and ceases to resonate. It was established that a slightly larger amount of substrate can be added before cut-off occurs, if the crystal was coated on two sides instead of one.

Guilbault and Tomita²⁵ found a piezoelectric quartz coated with 3-PAD, Triton X-100 and NaOH, to be an excellent detector for assay of organophosphorus compounds, possessing properties of high sensitivity, excellent selectivity, fast response and long life time.

Several coatings were screened for response to organophosphorus compounds; 2- and 3-PAD (pyridinium aldoxime dodecyl), 2-PAM (pyridinium aldoxime methyl), histidine hydrochloride and succinyl choline salts were the most reactive and selective. Of these, 3-PAD was the best coating for compounds with the G agent structure, and histidine hydrochloride for compounds of the malathion type.

Detector for toluene in the atmosphere of printing plants

A coated piezoelectric quartz crystal for detection and assay of toluene in the working place has been developed by Guilbault *et al.*⁶ Carbowax 550 was used as a coating substrate, and toluene vapor can be detected in the linear range 30 to 300 ppm with a reproducibility better than 4%. The response time was 30 sec, and a complete reversibility was obtained in less than 40 sec. No interferences were observed at a 5% Volume/Volume level. The lifetime of the detector is more than two months. Also a portable monitoring device for toluene, which is 20 cm × 14.7 cm × 9 cm in dimension and less than 3 lbs in weight, has been developed.

Detector for mononitrotoluene

Two new coating materials were evaluated as to selectivity and sensitivity for the detection of mononitrotoluene (MNT), which can serve as a reliable indication of the presence of its less volatile parent (trinitrotoluene, TNT): Ucon XMP-1018 and Carbowax 1000. These two coatings were very sensitive to MNT vapor. Carbowax 1000 was selective to MNT, while Ucon XMP-1018 suffers interference from organic vapors such as toluene. With Carbowax 1000, no interference was observed from any of the inorganic gases and organic vapors which were tested, except some perfumes. Some kinds of perfumes, which were saturated at room temperature or higher, gave a response on the coatings. However, the interferences due to perfumes could be considered negligible when the

concentrations of these vapors were one-tenth saturation. Since concentration of all perfumes in air can be usually considered less than one-tenth of sample saturated at room temperature, these compounds would not interfere in the assay of MNT.²⁶

The coating was also shown to be active toward atmospheric humidity. This problem could be corrected by using air as the carrier gas.

Other parameters that affect the efficiency of the detector were also studied and evaluated. The flow rate of the carrier gas was observed to affect the sensitivity of detection. As the flow rate is increased, the change in frequency decreased, because the adsorption of the MNT vapor becomes incomplete on the surface of the coatings. On the other hand, the sensitivity also becomes lower with decrease in flow rate, because MNT vapor diffuses in the tube between the injection port and the crystal, resulting in a spread of the signal peak. The optimum flow rate of carrier gas observed is 30 ml/min. The temperature of the measuring cell has an effect on the sensitivity, which decreased with increasing cell temperature. However, the cell temperature also affected the response time of the detector. The response becomes faster as the cell temperature is increased. At a 70°C cell temperature, the response time observed was only a few seconds and a complete reversibility of response was obtained in less than 20 seconds, while at room temperature the response time was about 20 seconds or more and a complete reversibility was more than 2 minutes. For rapid analysis, 50°C is the optimum cell temperature, with respect to both the sensitivity and response time. Under these optimum conditions, the change in frequency ranged from 200 Hz for 10 ppm MNT to 20 Hz for 10 ppb when 2 ml samples were injected. The coatings are very stable because the coated crystal gave almost the same sensitivity even after a month. The detector has potential use as a simple device for assay of explosives.

Carbon monoxide detector

A piezoelectric crystal detector for carbon monoxide has been developed using mercuric oxide, which reacts with CO to produce Hg°. The Hg° produced is then detected by using a gold coated piezoelectric crystal.

The optimum temperature for the reaction: $\text{HgO} + \text{CO} \rightarrow \text{Hg}^\circ + \text{CO}_2$ has been found to be 210°C. HgO decomposes at 500°C; however, at this temperature (210°C), some HgO will be decomposed and gives a slightly changing background of the baseline. By using a reference cell, this background is completely eliminated. In the reference cell, the CO sample will first pass through Ag₂O and is quantitatively oxidized before it reaches HgO. Therefore, only the Hg background is measured in the reference cell.

The gold coated piezoelectric crystal adsorbs Hg° at room temperature. Reversibility is achieved by desorption at 150°C . A straight line calibration plot, i.e. ΔF vs concentration, has been obtained in the ppm range of 1–400 ppm with a 10 ml sample. By varying the sample size, a 10 fold or 100 fold increase in sensitivity in the linear range can be achieved.²⁷

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