Piezoelectric Detectors for Organophosphorus Compounds and Pesticides

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A quartz piezoelectric crystal coated with a substrate has been used for the detection of small mass changes caused by the selective adsorption of organophosphorus compounds and pesticides. Incorporation of the crystal into a variable oscillator circuit and measurement of the change in frequency of the crystal due to the increase in mass allows a highly sensitive indication of the amount of organophosphorus compound present in the atmosphere down to the part per million level. Instrumentation is relatively inexpensive and can be easily used in the field. Analysis is nondestructive and requires very little time. AT cut quartz crystals with fundamental frequencies of 9.0 MHz were coated with various inorganic substrates and these were evaluated as to selectivity and sensitivity with respect to organophosphorus pollutants. Other parameters that affect the efficiency of the detector were also studied and evaluated. The detector has potential use as both an air pollution sensor and a specific gas chromatography detector.

AIR POLLUTION is an ever-growing problem in our environment today, and the need for monitoring devices that are small, simple, and rugged and yet sensitive and selective is urgent. King (*1–4*) has shown that the piezoelectric detector is such a device. This detector consists of a vibrating quartz crystal that is coated with a substrate that is capable of interacting selectively with a component of interest in a static system or flowing gas stream. The frequency of vibration of the crystal is dependent on the weight of the coating and the weight of the vapor adsorbed onto the coating. The concentration of the pollutant in the atmosphere is therefore measured by detecting changes in the frequency of the coated piezoelectric crystal detector.

Organophosphorus Pollutants. Great concern has arisen in recent years concerning the effects of pesticides on the environment (*5*). Chemical pesticides hold a unique position among the environmental pollutants since distribution in the environment is the way that they are used. Adding to this is the fact that pesticides are fashioned and valued for their deadly effect and persistence.

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, a phosphoryl-containing organophosphorus compound, diisopropyl methylphosphonate (DIMP), was chosen as the model compound to be used in this study. The major part of the study was done with the model compound instead of regular pesticides because of its relatively low toxicity and similar complexing ability and reactions.

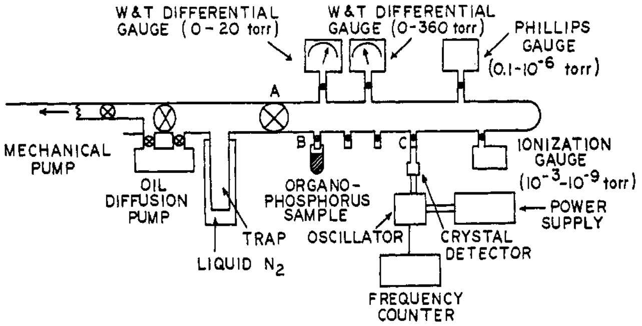

Figure 1. Experimental apparatus

Extensive study has been made within the past 10 years concerning the interaction of organophosphorus compounds with metal salts. Most is known and most work has been done with phosphine oxide ligands (*6–10*), whereas the phosphate esters have been studied primarily as extractants for various metal ions from solution (*11–13*). Less is known about the intermediate phosphoryl compounds, the phosphonate and phosphinate esters (*14–17*). Because of the strong interactions of organophosphorus ligands with transition metal, lanthanide, and actinide salts, as evidenced by infrared shifts of the phosphoryl stretching frequencies, these substrates were chosen as coatings for this study.

Piezoelectric Sorption Detectors. In 1959, Sauerbrey (*18, 19*) developed a relationship between the weight of metal films deposited on quartz crystals and the change in frequency. The relationship which he derived is:

$$\Delta F = -2.3 \times 10^6 \; F^2 \frac{\Delta mf}{A} \qquad (1)$$

where

ΔF = the change in frequency due to the coating (Hz)

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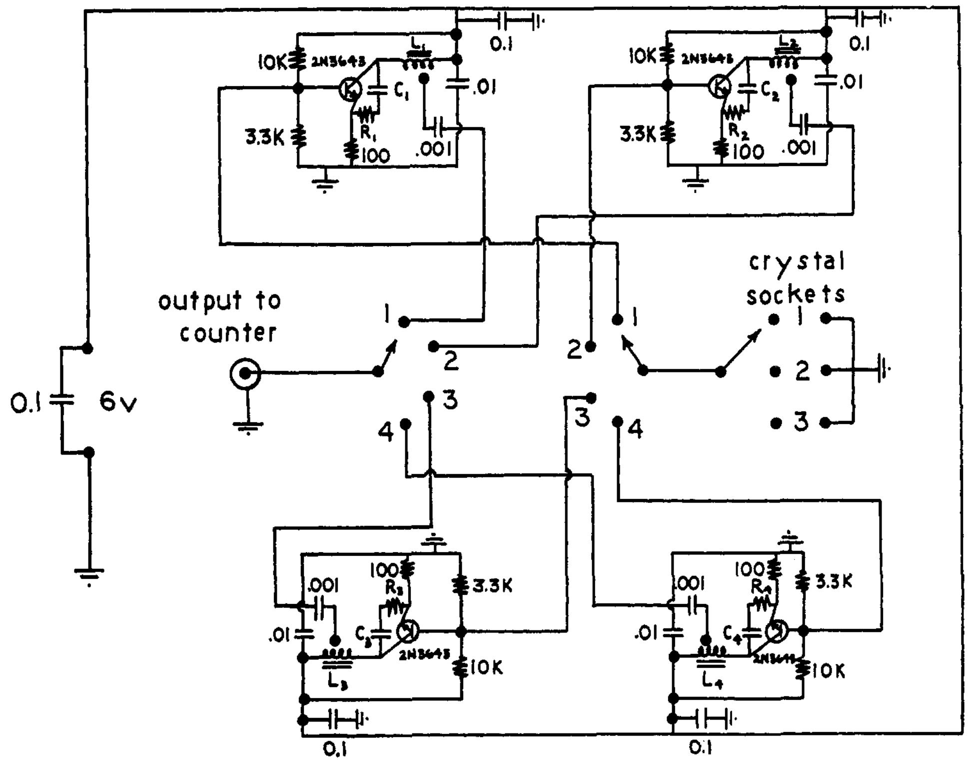

Figure 2. Variable oscillator schematic

Oscillator	Frequency range (kHz)	C (pF)	R (Ω)
No. 1	3000–6000	100	82
No. 2	6000–10,000	100	82
No. 3	10,000–20,000	...	...
No. 4	20,000–45,000	6.8	jumper

All resistance values are given in ohms, and all capacitance values, other than those listed above, in microfarads

F = the fundamental frequency of the piezoelectric crystal (MHz)
Δmf = the mass of the coating deposited (grams)
A = area coated (cm^2)

This equation predicts that a commercially available 9 MHz crystal would have a mass sensitivity of about 400 Hz per microgram. 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} gram (*20*).

In 1964, King (*1*, *2*) used the idea of a coated piezoelectric crystal to construct a sensitive and selective detector for gas chromatography. King coated the crystals with substrates used in gas chromatographic columns. Since these substrates had proved useful in partitioning various gases on a column, King proposed that they would be capable of interaction with the same components of a gas stream while on the crystal surface. The frequency of the crystal depended on the mass of the coating which in turn depended on the mass of the vapor taken up by the coating. Using Equation 1, King estimated that detection limits of 10^{-12} gram could be realized. Furthermore, this detection limit was independent of carrier gas provided the carrier gas did not partition in the substrate. King called his device the "piezoelectric sorption detector," since the interaction "is probably a combination of adsorption and absorption."

The most useful feature of the "sorption" detector is the ability to detect gases selectively. By applying polar substrates, such as polyethylene glycol, selective detection of polar compounds was possible. On the other hand, a nonselective hydrocarbon detector was devised by coating the crystal with squalene. In another study, Hartigan (*21*) investigated the use of a coated piezoelectric crystal as a sulfur dioxide detector and used this device for amine classification.

In 1969, King (*3*) reviewed his work and described the utility of the moisture analyzer in detecting air pollutants by selective combustion of hydrocarbons to carbon dioxide and water. The high sensitivity, selectivity, and ruggedness of the sorption detector make it an ideal candidate for certain air pollution applications. If hydrocarbons, moisture, hydrogen sulfide, etc. can be continuously and sensitively monitored by using coated piezoelectric detectors, then why not other species? If appears that the sorption detector will play an important role in the future of air pollution control and monitoring.

EXPERIMENTAL

Equipment and Chemicals. A diagram of the experimental apparatus used is shown in Figure 1. The piezoelectric crystal was connected directly to a high-vacuum line equipped with the appropriate pumps and pressure gauges. The

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crystal was driven by a variable oscillator whose schematic is shown in Figure 2. The oscillator was powered by a Heathkit variable power supply (Model 1P-28) set at 5.6 volts. The frequency of the vibrating crystal was monitored by using a digital read-out frequency counter (Systron-Donner, Model 8050) which has a read-out capability of 9 digits with a precision of ±1 in the last digit and an accuracy of 0.1 cycle.

The variable oscillator shown in Figure 2 was built using four OX oscillator kits (International Crystal Mfg. Co., Oklahoma City, Okla.) in order to extend the range of operation and makes it possible to oscillate crystals with resonant frequencies from 3.0 to 45 MHz.

The piezoelectric crystals used were 9 MHz quartz crystals with a plated metal electrode, AT cut in a HC 6/U holder (Piezoelectric Crystal Co., Carlisle, Pa.). The inorganic substrates used were CP and not further purified. The solvents used were kept anhydrous. The organophosphorus compounds were degassed and further purified using the freeze-thaw method on the vacuum line.

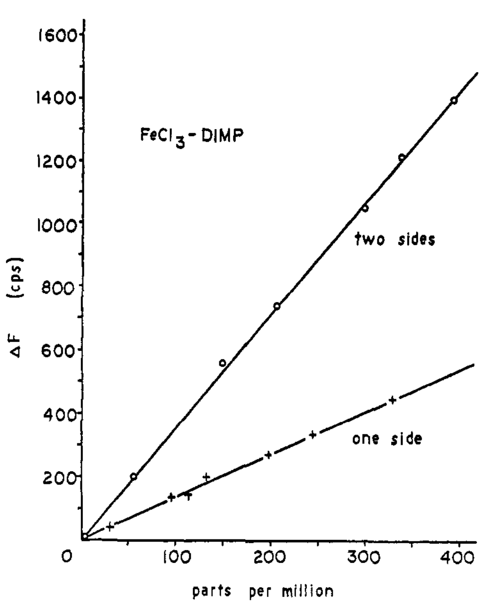

Figure 3. Comparison of sensitivities of one *vs.* two sides of the crystal coated

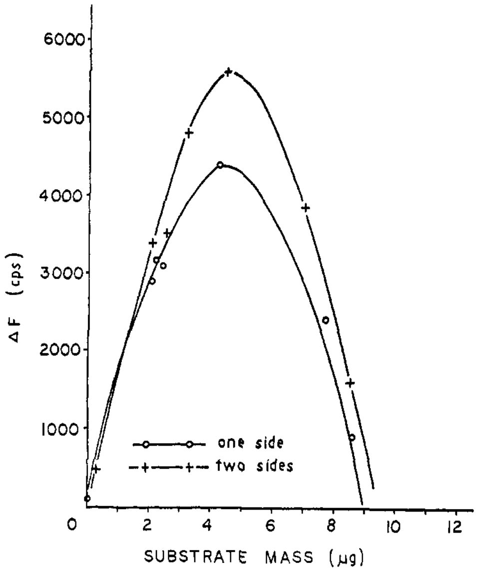

Figure 4. Optimization of coatings

Table I. Cut-Off Frequency for 9 MHz Crystals

	One side	Two sides
ΔF at cut-off (cps)	242,065	321,747
Mass of substrate at cut-off (μg)	605.16	804.37

Operating Procedure. The piezoelectric crystal was coated by spraying a solution of the inorganic salt in a suitable solvent onto the crystal surface. The crystal was then sealed into the crystal housing using Apiezon Q wax (J. G. Biddle Co., Plymouth Meeting, Pa.) and connected to the vacuum system. The entire system was then evacuated to 10^{-3} Torr to remove any volatile materials and traces of solvent that might be present. Evacuation was continued until minimal drift in the crystal frequency occurred which indicates that the mass of the crystal and substrate was stable. At this point the organophosphorus compound was introduced by closing the main stopcock (A) which seals the system and opening the stopcock to the sample (B). A specific amount of sample was introduced and monitored by the pressure of the system. Stopcock (C) to the crystal detector was then opened. The frequency was monitored as a function of time and also until a change no longer occurred. This change in frequency is a direct measure of the amount of organophosphorus sample that was adsorbed onto the substrate surface.

RESULTS

Stability Studies. Studies were conducted in order to determine the most optimum conditions to work under. The results of these studies indicate that the greatest stability occurs when the instrumentation is left on continually, and all of the components, including the crystal, are shielded properly. Normal variations of room temperature presented no problem.

Cut-Off Studies. The next set of preliminary experiments performed was the determination of cut-off or overload frequencies of the piezoelectric crystals. This was done by coating the crystals and monitoring the frequency *vs.* mass of the coating. The frequency of the crystal decreases with increasing mass according to the Sauerbrey equation until the crystal is overloaded and then ceases to resonate. This cut-off point is important in determining the optimum amount of substrate to be applied to the crystal. A slightly larger amount of substrate can be added before cut-off occurs if the crystal is coated on two sides instead of one. This is also much better because the surface area exposed is doubled which should theoretically increase the sensitivity by two. The results of the cut-off frequency study for 9 MHz crystals are summarized in Table I.

Optimization of Coatings. The next experiments performed were done in order to determine the optimum amount of substrate to be used. This was accomplished by exposing a standard sample of the gas to coatings of various mass and comparing the frequency change. The results ot this study are shown in Figure 3.

When a fresh coating of ferric chloride was used as the substrate, and the same experiment repeated several times, it was noticed that the response increased each time for the first few trials and then leveled off and was reproducible. Also, upon evacuation, the original base-line frequency was never obtained. The value was always lower indicating a gain in mass of the crystal. This was not unexpected. From previous chemisorption studies of these same complexes

Table II. Response of Paraoxon Detector to Various Interferences

Interference	Frequency change (cps) due to 100 ppb of interference
Dry air	0
Lab air	1
NO_2	3
CO_2	2
H_2O	0
SO_2	8
Paraoxon	44

(*22–25*), it is known that the complexes formed when diisopropyl methylphosphonate (DIMP) is adsorbed onto a ferric chloride surface are chemisorption and not physisorption in nature. This means that the surface bonds formed are comparatively strong and the gas cannot be desorbed by high vacuum. This explains the data mentioned above. During the first few trials, chemisorption complexation occurred at the surface until all of the surface sites were filled. On top of the monolayer of chemisorption complex, further adsorption of the DIMP occurred which is physisorption in nature. This explains the fact that once a chemisorption layer is formed, the physisorbed ligand can be removed reproducibly. In fact, the substrate that we are using on the detector is the complex, $Fe(DIMP)_xCl_3$, and not $FeCl_3$. The process occurring, after the complex is formed, is a completely reversible physisorption of the organophosphorus compounds. The masses shown in Figure 4 are of the $FeCl_3$ coatings before complexation occurred.

Figure 4 shows that for ferric chloride an increase in sensitivity occurs when two sides of the crystal are coated as compared to only one side. This is better illustrated in Figure 3 which shows plots of concentration *vs.* response of one and two sides coated. The overloading effect is very important and the coatings should be applied to obtain maximum surface area and minimum weight. Once the entire surface has been covered, additional substrate will only decrease the sensitivity. Since coating the crystal on both sides increases the sensitivity, all subsequent measurements and detectors were made of crystals coated on two sides.

Response *vs.* Chemisorption. As mentioned previously, the chemisorption of DIMP onto various metal halide surfaces has been studied and certain metal halides form stronger complexes than others as evidenced by the shift in the infrared-active P–O stretching band. Although the interaction might be stronger, as shown by a large band shift, this does not necessarily mean that the coating would be best for the piezoelectric detector because this does not tell anything about the kinetics of the reaction. The assumption that the stronger interaction will show faster kinetics is not necessarily a valid one. The next experiments performed were to evaluate several different substrates and to compare their sensitivity to the strengths of interaction obtained from the chemisorption studies. The results of this study are shown in Figure 5. Qualitatively, it can be seen from this study that the stronger the surface interaction, the more sensitive the substrate is, as shown by comparing the slopes of the concentration curves (Figure 5). For the most sensitive substrate ($Fe(DIMP)_xCl_3$), a sensitivity of below 10 ppm (1 ppm = 1 μg of the material in the gaseous state in 1 cubic meter of volume) was attained. This compares very favorably with air pollution detection methods that are currently in use.

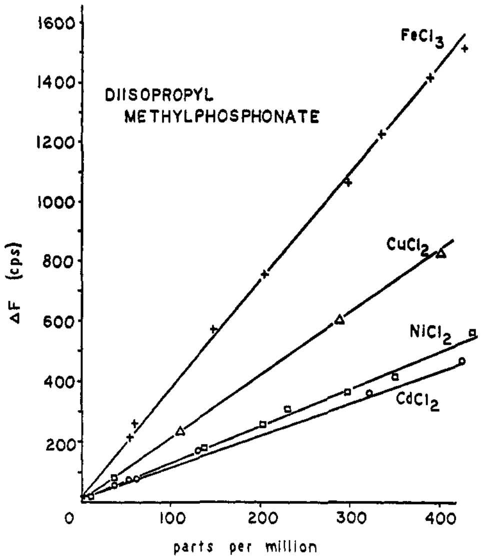

Figure 5. Response of detectors using various substrates to DIMP

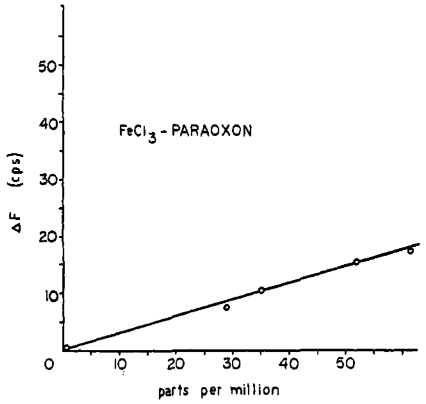

Figure 6. Paraoxon detector

Detection of Organophosphorus Pesticides. The next step of this project was to apply the most sensitive detector developed for DIMP to the direct determination of organophosphorus pesticides. It was assumed that the $FeCl_3$–DIMP complex which was used as the substrate in the determination of low concentrations of DIMP would also be useful in the detection of other organophosphorus compounds of similar structure. The first actual pesticide that was tried was paraoxon (*O*,*O*-diethyl-*o*-*p*-nitrophenyl phosphate). The response of the DIMP detector to paraoxon was extremely small. The reason for this, we believe, is that steric factors of the substrate in physisorption processes are much more important than originally thought. If the structure of the substrate is similar to that of the adsorbent, or is capable of weak interactions with the adsorbent, then this is a good surface for physisorption. Evidently, the difference in the structures of DIMP and paraoxon are too great to use the DIMP complex as the substrate for the detection of paraoxon. To test this hypothesis, a detector was built using a $FeCl_3$–paraoxon complex as the substrate on the piezoelec-

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tric crystal for the determination of paraoxon. The results of this work are shown in Figure 6. The sensitivity is not so great as the DIMP system, but nevertheless a lower concentration limit of 10 ppm can be attained.

Interferences. Before considering using this detector for the detection of pesticides in the atmosphere, other common atmospheric constituents and pollutants must be tested as possible interferences. The results of this study are summarized in Table II. The only gas that presents even a slight interference is SO_2, and this could be removed if need be, or tested separately and the frequency change due to it subtracted from the total. Because of the specificity of the substrates used, interferences should present no problem unless a reaction with the substrate should occur. In this case, the interference would have to be removed prior to sampling.

CONCLUSIONS

By complexing the organophosphorus pesticide to be determined with an inorganic salt, and then using this complex as a substrate on a piezoelectric crystal detector, good specificity and sensitivity can be attained. Direct monitoring of concentrations below 10 ppm can be accomplished in less than 15 minutes. Many different organophosphorus pesticides can be determined by building detectors with various substrates.

RECEIVED for review January 12, 1972. Accepted April 18, 1972. The financial support of the Army Research Office (Grant No. DA-ARO-D-31-124-70-G69) and the National Institutes of Health (Grant No. 8-R01-OH-00345-02) is gratefully acknowledged.

Apparatus for Automated Gel Permeation Cleanup for Pesticide Residue Analysis

Applications to Fish Lipids

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The gel permeation cleanup procedure for fish and other tissue extracts in pesticide residue analysis, previously reported by Stalling, Tindle, and Johnson, has been automated. The automated system allows unattended operation while processing up to 23 samples with the system as described. Reproducibility of recoveries were quite good (coefficient of variation 5%) and cross-contamination was estimated at less than 1% The chromatography system was constructed from commercially available components so that other investigators may easily duplicate the device without the necessity for fabrication of special components.

SEPARATION OF LIPIDS from pesticides is often the most time consuming process in the analysis of sample extracts for pesticide residues. Most previously reported techniques for achieving these separations can be grouped into four categories: adsorption chromatography (Florisil), liquid/liquid partition (acetonitrile/hexane), forced volatilization (sweep co-distillation), and low-temperature precipitation of the lipids. None of these techniques is readily amenable to automation. Stalling, Tindle, and Johnson (*1*) reported a cleanup technique which may be readily automated. The advantages of an automated pesticide cleanup procedure include improved analytical precision and accuracy, decreased manipulative sample losses, and a significant saving of labor.

Automated chromatography is widely accepted in amino acid analysis by ion exchange chromatography. In addition to commercial equipment to perform these analyses, noncommercial equipment for various types of automated aqueous chromatography systems has been reported.

Roubal and Tappel (*2*) reported an automated gel permeation system for the separation and molecular weight determination of proteins. This system, however, was automated only in the sense that a commercial pump system and associated apparatus was used to quantitatively determine the protein fractions eluting from the gel permeation column. Sample loading was performed manually, and eluted samples were not collected.

Hicks and Nalevac (*3*) made a device for the sequential addition of aqueous buffer solutions to a gel permeation column. This system used a "column follower" to sense when the solution level reached the top of the gel bed. When this occurred, the conductance between the electrodes of the column follower decreased, causing a stepper relay to advance and open a solenoid valve to admit the next solution. Again, there were no provisions for automatic sample introduction or collection.

Dus, Lindroth, Pabst, and Smith (*4*) automated amino acid analysis by use of rotary valves to select buffers and to direct the selected buffer to one of six ion exchange columns. Samples were loaded in the tubes which connected the six output ports of the second rotary valve to the corresponding columns. A cam-type programmer was used to operate this analytical system but there were no provisions for sample collection.

Many other authors have reported automation techniques for use with chromatography columns. These include Tschida and Markowitz (*5*) who added automatic regeneration

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