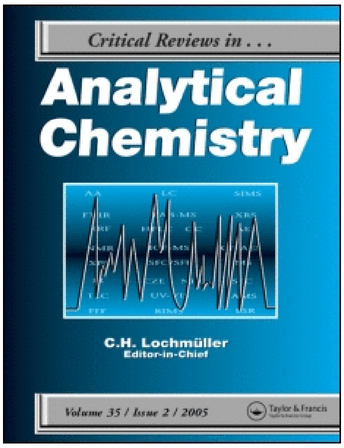

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ANALYTICAL USES OF PIEZOELECTRIC CRYSTALS: A REVIEW

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I. INTRODUCTION

Piezoelectricity was first discovered in 1880 by the brothers Pierre and Jacques Curie.[1] They observed that when pressure is applied to the surface of a quartz crystal an electrical potential forms between the deformed surfaces, and they also found that the application of a voltage to a quartz crystal effected physical distortions. The crystal, when activated by a concise electrical charge, will vibrate mechanically for a short period until physical equilibrium is established.

Alpha quartz is most often used for piezoelectric crystal detectors (Figure 1). The properties that make it most suitable for this application are its water insolubility and resistance to temperatures up to 579°C with no loss of piezoelectric properties. The resonant frequency of the quartz crystal depends on the physical dimensions of the quartz plate and the thickness of the electrode deposited. For use as a piezoelectric detector, only AT- or BT-cut quartz plates are useful.[2] AT and BT refer to the orientation of the plate with respect to the crystal structure. These plates are the only two high-frequency mode cuts that vibrate in the thickness shear mode about an axis parallel to the major surface. They have low or zero temperature coefficients at room temperature and have surfaces that are antimodal in displacement. The temperature coefficient is a critical function of the angle of cut. The AT-cut crystal is more stable than most other piezoelectric cuts and has a temperature coefficient of about 1 ppm per degree centigrade over a temperature range of 10 to 50°C.[3] The crystals most frequently used are 9 MHz quartz of 10 to 16 mm disks, squares and/or rectangles that are approximately 0.15 mm thick. The metal electrodes are 3000 to 10,000 Å thick, 3 to 8 mm in diameter, and can be made of gold, silver, aluminum, or nickel. The resonant frequency of a plated crystal can be obtained using a frequency counter attached to the output of an oscillator circuit.

The thoretical foundation for the use of quartz crystals as a microbalance or detector can be traced to Lord Rayleigh, who showed that small changes in the inertia of a mechanically vibrating system perturbed the resonant frequency of the system.[4] Onoe first considered the problem of a quartz crystal coated with a surface film in 1957.[5] In that same year, Sauerbrey[7] suggested the use of the piezoelectric crystal as a sensing device for the measurement of the thickness of thin films. He showed that the shift in resonant frequency of the crystal was proportional to the mass deposited to within ± 2%.

In 1959, Sauerbrey[7,8] developed an empirical equation for AT-cut crystals vibrating in the thickness shear mode that describes the relationship between the mass of thin metal films deposited on quartz crystals and the corresponding change in resonant frequency of the crystal:

$$\Delta f = -2.3 \times 10^6 F^2 \Delta m/A \qquad (1)$$

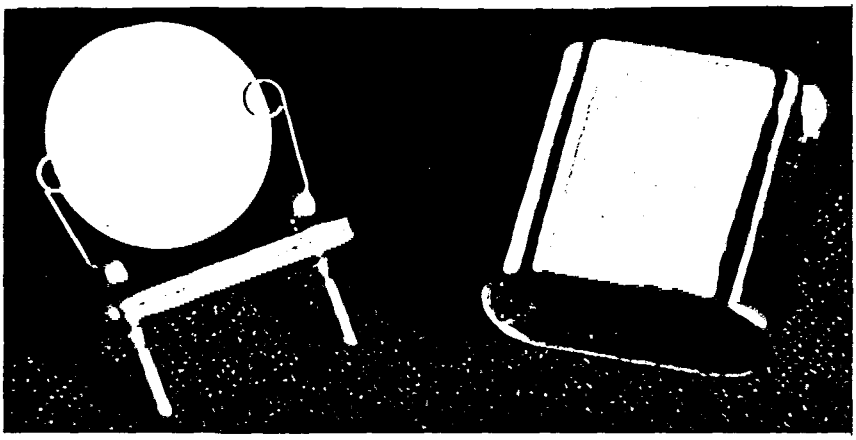

FIGURE 1. 9-MHz piezoelectric quartz crystal.

where Δf is the change in frequency due to a coating (Hz), F is the resonant frequency of the piezoelectric crystal before coating (MHz), Δm is the mass of the deposited coating (g), and A is the area coated (cm^2).

This equation predicts that a commercially available 9 MHz piezoelectric crystal would have a mass sensitivity of about 400 Hz/μg or a 15 MHz crystal would have a sensitivity of 2600 Hz/μg. From this, it can be seen that a vibrating quartz crystal can be an extremely sensitive weight indicator. The limit of detection is estimated to be about 10^{-12} g.[9]

Metals and a number of other solids have been found to change the resonant frequency of a crystal when deposited without affecting the ability of the crystal to oscillate. However, when liquids are deposited on the surface of the crystal, the ability to oscillate is often impaired due to the dissipation of energy in the liquid from the vibrating crystal. When a gas is allowed to absorb onto a suitable coating, the amplitude of vibration of the crystal changes in porportion to the concentration of the gas.

II. GENERAL EXPERIMENTAL APPARATUS

A typical experimental setup used for the evaluation of piezoelectric detectors is shown schematically in Figure 2. The cell is designed with optimum sensitivity for use in a flow system. The piezoelectric crystals are usually AT-cut mounted in HC 25/μ holders with a 9 MHz resonant frequency. The electrodes are usually constructed of silver or gold. Instrumentation consists of a low-frequency OX oscillator powered by a regulated power supply set at 9 V. The frequency output form the oscillator is monitored with a frequency counter, coupled with a digital-to-analog frequency converter, so that the frequency changes may be recorded. The frequency can be read from either the counter or recorder.

The carrier gas can be supplied from compressed cylinders or, for air, by a vibrating diaphragm pump. The optimum flow rate must be determined for each coating and application and it is usually around 100 mℓ/min.

For field measurements, this type of apparatus is inappropriate. A self-contained, small, portable detector was designed using the basic components shown in Figure 2, but with a 6 V battery, a mini pump, and digital readout.[10] Such a unit is shown in Figure 3.

III. "SORPTION DETECTOR"

The first use of the frequency-mass relationship for detector development was in 1962 by Slutsky and Wade,[11] who conducted limited experiments on the adsorption of gases onto

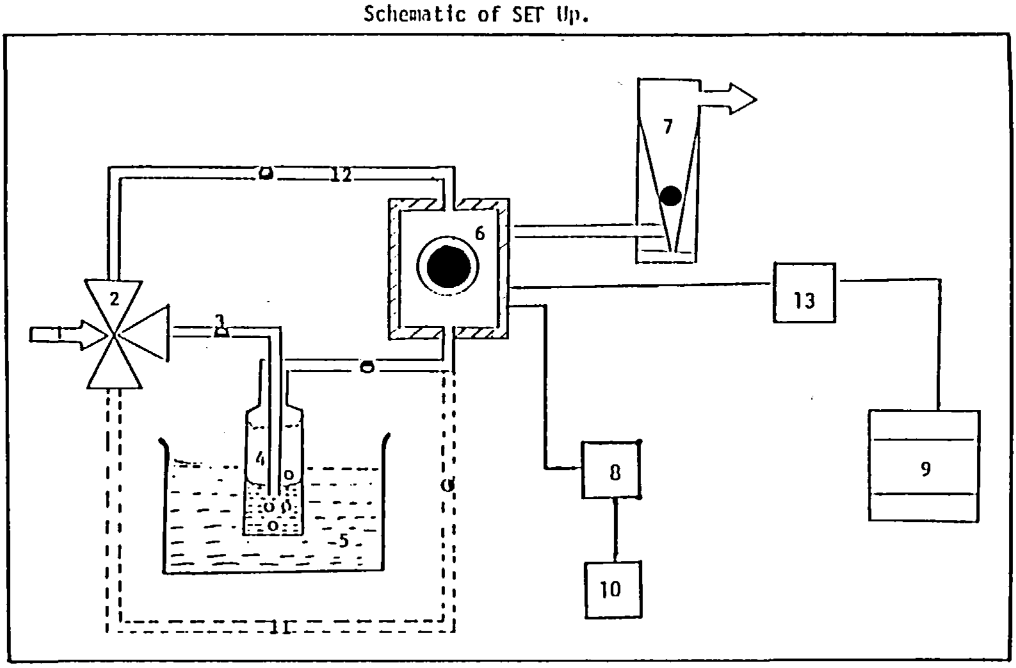

FIGURE 2. Typical experimental setup.

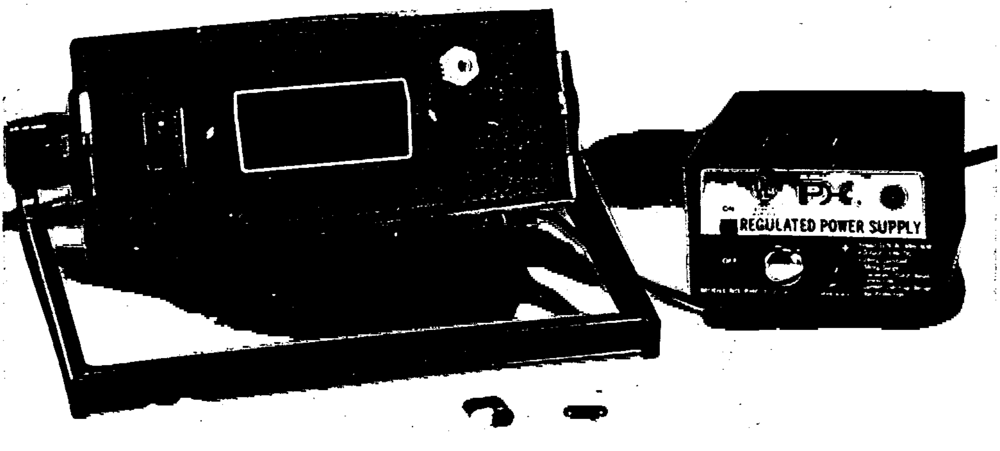

FIGURE 3. Commercial PZ 101 unit. (Courtesy of Universal Sensors, P. O. Box 736, New Orleans, La.)

quartz crystals. It was not until 1964 that the use of coated piezoelectric crystals for vapor detection was actually applied. King[12,13] used a piezoelectric crystal coated with different substrates used in gas chromatographic columns to detect effluent gases from a gas chromatograph. Since the frequency of a vibrating crystal can be easily measured to within ± 1.0 Hz, any frequency change greater than this can be detected. Since the chromatographic substrates had proved useful in partitioning various gases on a column, King proposed that they would also be capable of interaction with the same components of a gas stream while on the surface of the crystal. The frequency of the crystal depends on the mass of the deposited coating, which in turn depends on the mass of the vapor adsorbed by the coating. Using Equation 1, King estimated a limit of detection of 10^{-12} g could be realized. Furthermore, this detection limit was completely independent of the carrier gas provided it 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 high sensitivity and ruggedness of the piezoelectric crystal detector makes it ideal for use in analytical chemistry.

IV. WATER VAPOR DETECTOR

King has developed a coated crystal analyzer that is sensitive to as little as 0.1 ppm water.[13-15] The adsorption isotherms of many materials are readily available, hence, the performance of the sorption detector can be easily predicted. The relative adsorption of water on crystals coated with molecular sieves, hygroscopic polymers, silica gels, and polar liquids was investigated. The crystals with liquid coatings were rapid and linear response detectors, but the solid absorbents served as outstanding coatings for the assay of water vapor at very low concentrations.

The response of uncoated gold-, nickel-, and aluminum-plated crystals to water vapor was investigated.[14] Assuming a 1 cm^2 electrode surface area, a gold electrode collected a 10 Å layer of water at 50% relative humidity. This response was probably a result of surface adsorption, since the crystals had been washed in methanol prior to the test. Compared to the amount of water adsorbed on a coated crystal, the uncoated crystals adsorbed only a very small amount of water vapor. The coatings placed on the crystal correllated to frequency changes of 5 to 50 kHz, thus a 1% adsorption will amount to frequency changes from 50 to 500 Hz.

Deliquescent salts, when used as coatings for piezoelectric crystals, behave very differently from other coatings for water vapor. The response of the detector is rapid at normal conditions, but at low temperatures and humidities the response may be very slow due to a lack of driving force for the reaction, slower diffusion, and the existence of a solid-state reaction. A crystal coated with 50 nmol of lithium chloride, for example, had a time constant of 18 min at -32°C and less than 1 sec at room temperature.

The adsorption isotherms of melt salts are well known, but the hysteresis effects are not. A coated piezoelectric crystal proved to be a very sensitive and a rapid way to study this. As was established, hysteresis does not occur in LiCl or $CaCl_2$ over an 11% change in relative humidity.[14] When the liquid hydrate is formed, the hysteresis loop is then closed.

Water vapor detectors can be constructed from a wide variety of materials and each has its own range of usefulness.[16] A selective water detector using a hygroscopic polymer-coated crystal has been commercially available since 1964.[15] This instrument is able to detect water vapor at parts-per-million concentrations in 30 sec with very high selectivity and a long lifetime. Gjessing et al.[17] developed a radio sound humidity element consisting of an SiOx film evaporated onto a piezoelectric crystal. No hysteresis was found between 15 and 95% relative humidity.

A number of studies have demonstrated conclusively that the piezoelectric crystal detector can be used to measure moisture in the atmosphere of Mars. The atmospheric environment on the surface of Mars differs dramatically from that of the Earth. Recent Mariner flybys have shown that the Martian atmosphere contains 80% carbon dioxide, as compared to only 0.03% on Earth, and the total pressure of the Martian atmosphere is approximately 6 to 8 mbar. Evidence suggests that atmospheric water vapor pressure may range from 50 to 0.9 mm on Mars.[18] In order to accurately measure water vapor concentrations under such adverse conditions, a King piezoelectric sorption hygrometer, with several different polymer-coated sensors, was used.[19,20] Since the quartz crystal detector is extremely sensitive to mass changes, and the water vapor is detected by measuring changes in mass of the sorbent coating, and since windblown Martian dust could accumulate on the crystal, thus interfering with the water vapor measurements, an electronic method for removing dust particles from the crystal was incorporated into the final design. Water was quantitatively determined at different experimental conditions (temperature, pressure, etc.).

V. GAS CHROMATOGRAPHY DETECTOR

The detector used most often with gas chromatography is the thermal conductivity detector or the more sensitive flame ionization detector. Recently, more sophisticated detection methods have been developed using electron capture and mass spectrometry.

A relatively inexpensive gas chromatography system, utilizing a piezoelectric crystal detector, has been developed by King[12,13] and Karasek et al.[21-23] The same partitioning liquid used in the gas chromatography columns was used to coat the quartz crystal. The separated compounds are detected as they leave the column by passage over the surface of the coated crystal, where they partition into the coating, causing a change in the resonant frequency of the piezoelectric crystal. The change in frequency is converted to a voltage, where it is used as a detector response. The piezoelectric detector can operate at room temperature or higher, using air, nitrogen, or helium as the carrier gas.

Although the chromatograph using a piezoelectric detector has a limited range, it can be applied to a large number of compounds present in the boiling range up to 200°C. The response of a coated piezoelectric crystal to a compound eluted from a gas chromatographic column is described by the following equation:[22]

$$A = CW/\gamma P^{\circ} F \tag{2}$$

where A is the area of the response curve, W is the total weight of the eluent, γ is the activity coefficient of the eluent in the coating of the crystal, P° is the vapor pressure of the eluent at the operating temperature, F is the carrier gas flow rate, and C is a constant that is characteristic of the detector temperature, the piezoelectric crystal, and the liquid phase coating on the crystal. This equation illustrates the many solvent characteristics of the piezoelectric crystal detector when it is used in conjunction with the gas chomatograph.

The temperature of the detector is a very important parameter when using piezoelectric crystals. When used at above ambient temperatures, essentially the same characteristics, such as sensitivity and linearity, are observed as when used at room temperature. However, the relative partitioning coefficients of the gas components will vary with temperature so that there is a difference in separation between compounds detected at high temperatures. The absolute detector response for a given compound will decrease with increasing temperature. This effect is not as pronounced as is predicted from the theoretical considerations. For optimum detector conditions, the column and detector temperatures should be kept as low as possible, yet sufficiently high to elute the compound of interest in a reasonable amount of time.[22]

All chromatographic partitioning solvents have a definite vapor pressure, hence the lifetime of the coated crystals depends on the solvent used and one whether a carrier contains the substrate vapor from the column. Polymer- and adsorbent-coated crystals appear to have extremely long lifetimes. Water-analyzer crystals have been in service for 5 years. If an accident occurs and a crystal detector is fouled, it can be reconditioned by washing in an appropriate solvent or by placing a new coating on the crystal. In practice, the detector lifetime does not become an important consideration in instrument performance.

Janghorbani et al.[24] described the response characteristics of a coated piezoelectric crystal in terms of a partition detector for vapors dissolved in a gas stream. In the development of the partition detector theory, these authors assume the detector is connected to the outlet of a gas chromatographic column. The peak area response is related to an "imaginary plug" of the sample gas mixture. The equation they derived describes the behavior of crystal partition detectors employed in gas or liquid chromatography under the conditions of approximate equilibrium:

$$A_y = mK_{y,x}\, V_x\, W_T/F \tag{3}$$

where A_y is the area under the peak due to component Y, m is the constant describing the frequency change (Δf) of the crystal due to an incremental mass addition (ΔW) to the surface ($\Delta f = m\Delta W$), and $K_{y,x}$ is the partition coefficient of gas Y in liquid x, describing the ratio:

$$W_{y,x}/W_y = K_{y,x}$$

where $W_{y,x}$ is the mass of gas Y in a unit volume of crystal coating material, x, at equilibrium and W_y, is the mass of gas Y in a unit volume of gas phase. V_x is the volume of the liquid coating x that is present on the effective surface area of the crystal. W_T is the mass of the gas contained within the detector volume when it is at equilibrium with the liquid coating and F is the flow rate of the gas phase. Excellent linear relationships between A_y and an injected volume of octane, hexane, and pentane were reported when a squalene-coated crystal was used as the detector.

Other theoretical predictions presented in the paper include response time and the effect of temperature on sensitivity. It was predicted that subsecond response times were possible when using very small detector volumes.

Edmonds and West[25] described unique response characteristics of a coated piezoelectric crystal in terms of a partition detector for traces of atmospheric gases. Theoretical response curves for the leading edge of the response vs. the time curve were derived. The effects of variable parameters, such as detector cell volume, gas flow rate, analyte concentration, and distribution and size of detector coating, were investigated, as well as the intrinsic properties of the coating material. It was found that the behavior of model systems, set up arbitrarily for traces of toluene and chloroform, were in good agreement with their predictions.

VI. LIQUID CHROMATOGRAPHY DETECTORS

Based on the oscillating piezoelectric crystal, a universal mass detector for liquid chromatography was developed by Schulz and King.[26] In this system, effluent from a liquid chromatograph was sprayed on the crystal surface. After the solvent evaporates, the mass of the residual solute is determined from the change in crystal frequency. The liquid stream sampling and solute deposition can occur at rapid intervals. Spraying, drying, and measuring were all accomplished in 10 sec, and the sensitivity is similar to that obtained using common liquid-liquid chromatographic detectors. In the piezoelectric system, the effluent was directed to the crystal detector from a differential refractometer on a gel permeation chromatograph. To test the system, butyl rubber and a mixture of polystyrenes were run through the chromatograph. The differential distribution curves of polymer mass vs. retention volume compared closely to the results obtained using the differential refractometer detector. The piezoelectric crystal detector was found to be equal, and in some ways superior, to the refractometer detector.

These advantages, as summarized by Schulz and King,[26] are as follows: nondestructive; high sensitivity; large dynamic measuring range; mass detector; universal detector; independent of temperature, pressure, or flow rate variations of the chromatograph; volatile impurities do not interfere; any solvent or solvent mixture may be used; and digital response compatable with digital processing equipment.

Bastiaans and Konash[27] incorporated a piezoelectric crystal detector directly into the liquid phase for the detection of effluents. Adsorption measurements are more difficult to obtain in the liquid phase due to a greater energy loss at the liquid-crystal interface, thus making crystal oscillation more difficult to maintain. The frequency of the piezoelectric crystal is dependent on the density of the liquid phase at the surface of the crystal, thus density changes from solvent gradients and solute cause a drift in the resonant frequency of the crystal. Compensation for the liquid density changes were made by using a reference and a coated sample crystal. Only one face of each crystal comes in contact with the liquid phase in order to establish stable oscillation. By using a reference crystal, the effects of density gradients, temperature, and flow rate are eliminated. Long chain hydrocarbons were coated onto the sample crystal to control the surface adsorption properties of the crystal in the presence of the effluent. Using these coatings, only small nonpolar molecules were detectable, but with improved surface modification techniques more sensitive detection may be possible.

Much better results have been obtained with piezoelectric crystals when they are used in photoacoustic detectors for liquid chromatography. The principle of photoacoustic detection is that when a solute is dissolved in a solvent and then irradiated by an appropriate source, the adsorption of light causes the solution to expand. The expansion against the face of a piezoelectric crystal causes a change in its resonant frequency. The photoacoustic detection of compounds in a static solution can be an extremely sensitive technique, especially when a laser is used to irradiate the sample. It is for this reason that the use of this type of detection system in liquid chromatography has been investigated.

Oda and Sawada[28] developed a laser-activated photoacoustic detector for high-performance liquid chromatography (HPLC). The flow cell developed for this detector has an internal voume of only 20 $\mu\ell$. Initially, pressure fluctuations caused by the pulsating flow from the pump seriously affected the measurement of the photoacoustic signal. This effect was reduced, however, by increasing the modulation frequency of the laser. The system was evaluated using three isomeric forms of chloro-4-(dimethylamino)azobenzene. The response of the detector was linear over the range of 0.31 to 2.6 ng. The detection limit was found to be 0.21 ng of the injected sample. The photoacoustic-piezoelectric system was reported to be about 25 times more sensitive to a comparable UV system.

Photoacoustic detection offers low selectivity; however, the information obtained from this system has been found to compliment fluorescent detectors when the two methods are used simultaneously. The sensitivity of this system is very high and it is predicted that with the development of inexpensive tunable lasers the range of application will be considerably extended.

VII. THE QUARTZ CRYSTAL MICROBALANCE

The advantages of microweighing with a quartz crystal over conventional techniques are a detection sensitivity of less than 1 ng/cm^2, as well as a rapid response time when performing experiments. The high sensitivity permits observing the initial stages of reaction to less than 0.01 monolayers of an adsorbate or of reaction products. The piezoelectric quartz crystal has been used selectively for the quantitative measurement of thin films deposited on its surface.[29-31]

In an oxidation study of uninhibited styrene-butadiene rubber (SBR), King[14] was able to attain the results within only a few minutes when using a piezoelectric crystal. Commercial SBR was dissolved in hexane and a coating mass corresponding to 5.3 kHz was applied to the surface of a 10 MHz crystal, which was then purged with nitrogen at 150°C. At time zero, pure oxygen was replaced with nitrogen. At the beginning of the experiment the frequency can either increase or decrease, depending on whether oxygen uptake is slower or faster than the competitive cracking and volatilization reactions. Because the film was thin, and the technique sensitive, it was possible to observe the very initial phases of oxidation. This technique permits a rapid quantitative study of inhibition, effect of light, polymer type and blends thereof.

Another interesting application described by Haller and White[32] is the use of a piezoelectric crystal for the study of the polymerization of butadiene. Fisher and King[33] reported on the oxidation of an elastomer, and King and Corbett[34] studied the oxidation and volatilization of asphalts.

VIII. PIEZOELECTRIC CRYSTAL FOR POLYMER RESEARCH

Vapor solubilities of a wide variety of plastics and elastomers have been measured using polymer-coated piezoelectric crystals. The equilibrium between the vapor and rubber coatings is virtually instantaneous, mainly because the film is so thin. The data obtained from this technique are highly precise, thus allowing the observation of subtle changes in the polymer coating. King[14] carried out studies of a film of butyl rubber coated on a crystal exposed to vapors of hexane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, and chloroform.

King et al.[35] developed a differential thermal analysis (DTA) probe using a piezoelectric crystal for the analysis of waxes, polymers, inorganic salts, metals, and a wide variety of other materials. The calorimetric data generated from this technique were superior to any previously described DTA system. Differential scanning calorimetry (DSC) was also possible by adding a thin film resistance heater under each thermocouple. The density-temperature profiles of normal paraffins were investigated by Vand using a similar technique.[36]

A piezoelectric crystal thermogravimetric analyzer (TG), developed by Henderson et al.,[37] allows for the analysis of microgram samples at rates up to 100°C/min. The samples are first dissolved in an appropriate solvent and then deposited on the crystal; TG curves of samples as small as 200 ng were obtained with the instrument described. The theoretical minimum sample possible to analyze was predicted to be at least two orders of magnitude less. This device has the potential to be applied to the study of the volatilization of thin films and coatings. Studies of the flammability of polymers as thin films would be possible rather than the studies of bulk properties required by current TG instrumentation. In addition, this instrument could find application in the study of the kinetics of a wide range of surface phenomena by introducing reactive gases or agents into the purge gas.

IX. PARTICULATE MASS CONCENTRATION DETECTION

With respect to both health and safety, the detection, quantification, and identification of aerosol components and suspended particles in air is of great importance. The first to use piezoelectric crystals for this purpose was Chuan.[38] Using an adhesive-coated 10 MHz crystal, the mass of airborn "micro-grit" aluminum oxide particles was measured. The device was reported to yield particulate mass concentrations as low as 1 g/m^3. Individual particulates could be resolved to a mass of 10^{-11} g. Adhesion of smaller particles was made possible by integrating the observed frequency changes.

A portable, direct reading instrument for measuring particulate mass concentrations from 0.05 to 5 mg/m^3 was later developed by Chuan.[39] The detector is insensitive to water and pollutant vapors normally encountered in the atmosphere. Examples of measurements of spatial and temporal variations in particulate mass concentration caused by specific short-term effects in a workshop over a 25-hr period were presented.

Olin et al.[40,41] incorporated electrostatic precipitation into a piezoelectric system for the deposition of airborne particles onto the electrode surface of a quartz crystal. The aerosol concentration could be measured with a 5% accuracy in 10 sec. Automobile emissions, cigarette smoke, and laboratory aerosols were all examined with this instrument. The reported mass sensitivities for cigarette smoke were 15.5 and 179 Hz/μg for a 1.5 and 5.0 MHz AT-cut crystal. The average aerosol concentration ranged between 7 and 14 μg/m³. Both crystals ceased to oscillate when the mass loading exceeded 400 g, corresponding to approximately a 6 kHz change in frequency for the 1.5 MHz crystal and a 60 kHz change for the 5.0 MHz crystal.

The size and concentration of particles produced in a cloud generated by an underground nuclear explosion were measured using a piezoelectric device designed by Chabre.[42] The lowest measurable signals were obtained from 5-μm particles having a mass on the order of 3×10^{-10} g and ejected at a velocity of approximately 210 m/sec.

Carpenter and Brenchley[43] produced an instrument for the determination of the particle size distribution of aerosols. Inertial impaction was used to deposit the particles on a 10 MHz crystal at a flow rate of 500 mℓ/min, a mass sensitivity of between 140 ± 20 and 2303 ± 599 Hz/μg was obtained.

Daley and Lundgren[44] evaluated the performance of piezoelectric crystals for the determination of aerosol mass concentrations. The effects of five influencing parameters were studied, i.e., temperature, humidity, particle collection characteristics, response linearity, and mass sensitivity. Neither airstream temperature nor humidity fluctuations were compensated for by the addition of a reference crystal. The temperature-induced error was minimized by lowering the rate of inlet temperature fluctuations. The observed linear response limits ranged from 0.2 to 6 μg/mm² for the various aerosol and instrumental designs investigated. It was found that the mass sensitivity was a function of the deposit size and location. Sensitivity decreased for a particle size beginning at about a 2 m diameter, reaching zero at 20 m. Sensitivity in this range could be increased by using a more viscous coating. The humidity response characteristics of a coated piezoelectric crystal were also extensively investigated.

Piezoelectric crystals used for the detection of airborne particles offer the advantages of high sensitivity, with responses that are in good agreement with theoretical predictions, thus eliminating the need for mass calibrations. This technique has a wide frequency and mass response range and is compatable with available filtration and precipitation methods. The low-cost availability of the components of the mass detection systems make this technique particularly attractive. Soiled sensors may be easily disposed of and replaced within inexpensive new sensors rather than having to clean them.

X. TRACE METAL ANALYSIS

A method for the determination of trace metals in solution was devised by Mieure and Jones,[45-47] using piezoelectric crystals in an electrogravimetric assay. AT-cut quartz crystals were used as the cathode in an electrochemical cell. A current was passed through the cell for a known period of time and the crystal then removed, washed, and dried. The change in frequency as a result of metal deposition was used to determine the concentration. Cadmium solutions over a range of concentration from 5.0×10^{-4} *M* to 5.0×10^{-8} *M* were examined. The accuracy of the method for cadmium varied from 0.42% at high concentrations to 8.7% at low concentrations.

In another electrogravimetric type assay, Nomura and Mimatsu[48] used piezoelectric crystals, coated with silver over the platinum-plate gold electrodes, to determine iodide in solution. In a sample solution of 10^{-3} *M* potassium chloride, iodide was electrodeposited at −0.05 V. The pH of the sample solution was adjusted to pH 9.8 with 10^{-3} *M* sodium tetraborate (III)-sodium hydroxide solution. In this system, a reagent blank is first passed through the detector cell until a constant frequency is obtained. Then, the sample solution containing the iodide was allowed to pass for 1 min (10^{-6} to 10^{-5} *M*) or 10 min (10^{-7} – 10^{-6} *M*). After each assay, the iodide may be cleaned off the crystal by electrolysis at −0.4 V.

Lead was successfully extracted from solution by Nomura et al.[49] using a platinum-coated piezoelectric crystal. In this procedure, the 8-quinolate chelate of lead was first extracted into chloroform. The platinum-coated crystal was then immersed into this solution and a potential applied. After 2 min, the frequency change of the crystal is recorded and the procedure is repeated with a reagent blank after the crystal has been washed and dried. Using this procedure, lead concentrations over the range 3×10^{-6} to 5×10^{-5} *M* in aqueous solution could be determined. Interferences from nickel, zinc, cadmium, silver, cobalt (II), and iron (III) could be masked by using L-ascorbic acid and cyanide.

In another report, Nomura and Maruyama[50] investigated the stability of metal ions in solution, as well as the selective determination of iron (III) as its phosphate. Using a standard piezoelectric crystal, the observed frequency change for metals in solution was found to be proportional to the specific conductivity for concentrations up to 2 m*M*, where deviations due to solution viscosity and density occur. At concentrations above 20 m*M*, abrupt frequency changes as a result of the solution short-circuiting the crystal were found to occur. It was under these conditions that the electrode position of metal ions such as Mn^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}, Cu^{+2}, Pb^{+2}, and Ag^{+2} took place. With aluminum and iron, the adsorption of some salt was attributed to the frequency change.

For the determination of iron (III) a modified crystal was used. One surface of the quartz plate was covered with a separate quartz plate, with the two separated by only "four slim hairs laid on each edge of the 'square' quartz plate." These plates were then fused with epoxy resin. The lead wires of the crystal holder were also coated with the resin in order to avoid electrolysis problems. The response of the modified crystal to lead (III) was found to be linear over the range 1×10^{-5} to 1×10^{-4} *M*. Interference studies carried out with a 5×10^{-5} *M*. iron (III) solution showed that tenfold molar amounts would be a problem if changes of greater than 15% were obtained. This occurred with lead, aluminum, bismuth, sulfide,.and thiosulfite.

XI. SPECIFIC GAS DETECTION SYSTEMS

A. Acetoin

Acetoin (3-hydroxy-2-butanone) is a degredation product of certain fungi in canned juice and of 2,3-butanediol, a fermentation product of bacteria. It is also formed by the action of yeast on diacetyl. Since acetoin is present in many types of fruits and in certain meats, Suleman and co-workers[51] developed an analytical method for the detection of acetoin using piezoelectric crystals. It is suggested that this sensor would be useful in the law enforcement area as a method for locating contraband food entering the U.S.

Tetrabutylphosphonium chloride was first dissolved in chloroform and then applied to the surface of a 9 MHz quartz crystal with a microsyringe. The crystal was then heated in an oven at 60°C for 2 hr to completely remove the solvent. The amount of coating applied was calculated to be approximately 10 µg. This coating was found to be sensitive to acetoin in the parts per billion range with the response being completely reversible. The linear range of response covers a concentration from 8 to 120 ppb. Complete responses were obtained in 30 sec. Interferences to various organic compounds were tested with only acetone and ethanol giving an interfering response at very high concentrations.

B. Ammonia

Ammonia is a common air contaminant resulting from the combustion of fuels, decay of vegetation, and decomposition of nitrogen-containing organic substances. Evidence has shown that ammonia, when present in the air at parts per billion concentrations, plays an important role in the formation and stabilization of ambient polluting aerosols that can potentially cause adverse health effects.

Guilbault and Karmarkar[52] were the first the attempt to utilize piezoelectric crystals as a sensor for ammonia. Using Ucon LB-300X (a type of polyalkene glycol) as the coating, detection in the parts-per-billion range was reported. The coating material required initial activation, however, by passing NO_2 over the coated crystal for 5 min. Infrared spectra of the exposed coating indicated the formation of a new compound on the crystal that contained covalent nitrite and possibly nitroso groups. Unfortunately, these coatings were sensitive to moisture.

Ascorbic acid, ascorbic acid-silver nitrate, and an extract of *Capsicum annuum* pods were also investigated as coatings for ammonia detection.[53] Extracts of the pods in alcohol, chloroform, and toluene were applied to a crystal and tested. The chloroform extract gave responses of −45 Hz for 10 ppm of ammonia and −15 Hz for 0.001 ppm. The alcohol extract gave responses of −120 and −50 Hz, respectively, while the toluene extract proved to be inactive. When silver nitrate was added to the alcohol extract, responses of −75 and −15 Hz, respectively, were obtained for samples of ammonia that were 1/10 the previously tested volume. It is suggested that the active component could have been ascorbic acid; therefore, this substance was tested as a coating. Responses of −160 Hz for 10 ppm and −70 Hz for 0.001 ppm, using a 1 mℓ sample, were obtained. The addition of silver nitrate to this coating then increased the responses to 320 and 100 Hz changes, respectively. A detection limit of 1 ppb of ammonia is possible when using this coating.

L-Glutamic acid hydrochloride and pyridoxine hydrochloride were reported to have greater sensitivity and better selectivity than the ascorbic acid-silver nitrate coating.[54] The response times for both of these coatings were less than 1 min and complete reversibility of the response occurred in 5 min. No significant interferences from other gases were reported. The effect of moisture on the coating material was eliminated by using a gas chromatographic precolumn packed with silica gel. The pyridoxine hydrochloride coating had a very high sensitivity to ammonia. At 1 ppm of ammonia, a response of −1190 Hz was recorded. At 0.01 ppb, the response was about −386 Hz, thus suggesting a detection limit in the parts per trillion range. A plot of the log (frequency change) vs. log (concentration) was linear over the range from 0.01 ppb to 1 ppm. The reaction between pyridoxine hydrochloride and ammonia was investigated by infrared spectroscopy. The spectra provided evidence that the reaction between the hydroxyl group and ammonia occurs, forming an ammonium salt of pyridoxine.

Edmonds et al.[55] reported the successful use of polyvinylpyrrolidone as a sensitive coating for the detection of ammonia. At 1 ppm of ammonia a response of approximately −700 Hz was reported. Moisture was monitored using a separate silver chloride-coated piezoelectric crystal and a resistive type humidity probe.

C. Aromatic Hydrocarbons

Karmarkar and Guilbault[56] reported a piezoelectric crystal coating for xylenes and other aromatic hydrocarbons in air. Aromatic hydrocarbons are very common in gasoline, and, naturally, are found in the exhausts of automobiles. A nujol mixture of *trans*-chlorocarbonyl-*bis*-(triphenylphosphine) irridium (I) [*trans*-$IrCl(CO)PPh_3)_2$] was used as the coating material. This material was found to be reactive to aromatic hydrocarbons but was not as sensitive to aliphatic compounds and ordinary olefins. Compounds such as xylenes, benzaldehyde, 1,3,5-trimethylbenzene, anisole, and *n*-butyl benzene could be detected at low concentrations (1 to 120 ppm) but compounds such as hexane, heptane, octane, and cyclohexane could be detected only at high concentrations. No interference from atmospheric moisture was reported.

Toluene in ambient air was detected using a piezoelectric crystal coated with Carbowax

550.[57] Toluene and other alkyl-benzenes are known to be photochemically reactive and can have harmful effects upon long-term exposure even at moderate levels. Toluene is used widely in a number of chemical industries and printing plants as a solvent, as well as in paints, lacquers, adhesives, and cleaners. Using the Carbowax 550 coating, toluene vapor was detected in the linear range of 30 to 300 ppm with a reproducibility of better than 4%. The response time was on the order of 30 sec with complete reversibility in less than 40 sec. No interferences were reported at a 5% v/v level. The lifetime of the sensor is more than 2 months.

A portable detector for toluene was later developed, having a mass of less than 7 kg and 20 cm × 14 cm × 9 cm in dimension.[58] This instrument was reported to be capable of monitoring 1 to 200 ppm concentrations of toluene. The device was tested at a printing plant located in the greater Copenhagen, Denmark area. The results were in agreement with two accepted methods using the HNU Photoionization Detector and the Drager tube. A 2% relative standard deviation was reported, with no interferences from organic or inorganic gases. Moisture was eliminated by using Nafion® tubing (DuPont, Type 811). The water was removed from the walls of the tubing by the use of a counter current flow of dry nitrogen sweeping the tubing or by the use of an appropriate desiccant.

D. Carbon Dioxide

The use of piezoelectric crystals for the detection of carbon dioxide in water was investigated by Fogleman and Shuman.[59] In this study, 9 and 15 MHz AT-cut crystals with gold electrodes, coated with didodecylamine (DDDA) and dioctadecylamine (DODA), were used to continuously monitor CO_2 concentrations. The crystal was separated from the water by a Teflon® membrane, a Polyvinyl-chloride membrane, or a Fluoropore filter. The DDDA coating was at least 33 times more sensitive to the water vapor than the dissolved carbon dioxide. An −84 Hz response was observed for 100% sulfur dioxide and at 100% R.H. (25 to 30°C), a response of −1770 Hz to water vapor was recorded after 90 min, and −2736 Hz in 6 hr. However, the exposure to water vapor had no effect on the sensitivity to carbon dioxide.

Jordan[60] developed a carbon dioxide sensor for monitoring levels in a closed exhalation anesthesia system. End-expired carbon dioxide is often monitored during the administration of anesthesia in order to evaluate the effective alveolar ventilation of the patient and to detect hyperventilations, hypoventilation, abnormal blood flow in the lung, and even to watch for disconnected ventilators. In this study, monoethanolamine (2-aminoethanol), often used as a scrubber for CO_2, was mixed with ethylenene glycol diglycidyl ether (EGDE) in a 2:1 ratio. An exothermic reaction occurs in which the amine attacks the epoxy groups of the EGDE, forming the final product (7,10-dioxa-3,4-diaza-1,5,12,16-hexadecatetrol). This product, when used as a coating, eliminated volatility problems encountered when using MEA alone, without significantly reducing the sensitivity to carbon dioxide. Using only 5.4 μg to coat both electrode sides of the crystal, a −391 Hz response was recorded for 10% carbon dioxide. The response increased as the percentage of relative humidity increased, but was linear over the entire range of relative humidity. At 90% R.H. a −898 Hz response to carbon dioxide was reported. The sensor could be calibrated over a range of humidity, for reproducible responses in less than 30 sec, and complete recovery in less than 60 sec. No interferences from nitrous oxide, halothane, or oxygen were reported when tested individually or together at normal anesthesia concentrations (approximately 10%).

E. Carbon Monoxide

Carbon monoxide is generated during the incomplete combustion of organics. Approximately 80% of the carbon monoxide present in urban atmospheres is believed to originate from automobile exhausts. Because the gas is colorless and odorless, with the same density as air, it is particularly insidious. Asphyxiation occurs by forming meta-stable compounds with the hemoglobin in blood.

A piezoelectric crystal detector for carbon monoxide has been developed by Ho et al.[61] that is based on the conversion of mercuric oxide by carbon monoxide to mercury vapor, which can be detected with a gold-plated electrode. In this system the sample gas is first mixed with mercuric oxide and heated to 210°C to produce mercury vapor. If no carbon monoxide is present in the sample, any response by the crystal will be due to the thermal decomposition of the mercuric oxide. By using a reference crystal this background can be eliminated. In the reference cell the sample passes first through silver oxide and any carbon monoxide is quantitatively oxidized before it reaches the mercuric oxide. Hence, the reference cell measures only the mercury background.

The elemental mercury produced is adsorbed by the gold-coated crystal at room temperature. The reaction is reversible when the crystal is heated to 150°C. Response is linear from 1 to 50 ppm with a sampling time of 2 sec. The detector is reported to be capable of monitoring carbon monoxide in the parts per million and parts per billion levels by simply varying the size of the sample. At very low concentrations, larger sample volumes are needed. Organics that may cause interferences are removed by either activated charcoal or a molecular sieve 5A. Inorganic interferences were eliminated by a molecular sieve precolumn. Water vapor was removed using calcium chloride and phosphorus (V) oxide without affecting the concentration of carbon monoxide in the sample gas. This system is most practical as a fixed-site monitor due to the power requirements for the heating element around the mercuric oxide cell.

F. Formaldehyde

In one of the first papers ever published on the use of enzymes for the assay of substrates in the gas phase, Guilbault[62] reported the selective detection of formaldehyde using an enzyme/cofactor mixture as a coating on a piezoelectric crystal. Formaldehyde dehydrogenase was mixed, together with the cofactors reduced glutathione and nicotinamide adenine dinucleotide. The enzyme catalyzes the oxidation of formaldehyde to formic acid in the presence of the cofactors. The formaldehyde samples were generated using the syringe dilution method with lab air (~50% r.h.). A linear response from 10 ppb to 10 ppm was reported, corresponding to frequency changes from 2 to 500 Hz, or about 200 Hz per decade of concentration. The reaction time is kept less than 1 min, so that a complex forms reversibly, but no products are formed. The coating is specific for formaldehyde with only very small responses to other aldehydes and alcohols (at least a 1000:1 selectivity ratio is observed). In a study of reproducibility, a 1 ppm sample of formaldehyde was determined 10 times with responses of -300 ± 6 Hz obtained. A σ of 1.5 and a coefficient of variation of 1.5% was reported.

G. Hydrocarbons and Halogenated Hydrocarbons

Edmonds and West[25] investigated the behavior of variously coated 9 MHz AT-cut crystals to chloroform and toluene with respect to detector cell volume, flow rate, analyte concentration, and size of detector coating. In this study, Pluronics 64 was found to be the most sensitive coating for hexane, *o*-xylene, and ethylbenzene. Carbowax 20 *M* was most sensitive for the detection of acetone, chloroform, and Squalene was most sensitive for cyclohexane.

King[13] used a coated piezoelectric crystal to detect water vapor generated by the selective combustion of methane and other hydrocarbons. Some differentiations between ethane and methane and the alkanes ethylene and propylene were reported by the use of a controlled combuster filament temperature. Hydrocarbon determinations could be made in 5 min, with a 10 ppb detection limit. Reactive hydrocarbons could be determined directly, while the other hydrocarbons, including methane, were determined by the difference after total combustion. Calibration of the instrument is achieved using the internal electrolysis of water.

Kindlund and Lundstrom[63] described an instrument developed by Engstrom Medical AB of Sweden and marketed as EMMA (Engstrom Multigas Monitor for Anesthesia). A DOW corning oil, DC 190, was used as a coating for a piezoelectric crystal to detect halothane ($CF_3CHClBr$). Two crystals are used, one coated, the other as an uncoated reference. The frequencies of the two crystals were mixed and the difference between the two are converted to a voltage and monitored by a strip recorder. In a later paper[64] these workers examined the effect of the thickness of the coating on the response to 0.5% halothane, the effect of temperature on the solubility of some common solvents over the range −30 to 50°C, and the interference effects of moisture. The DC 190 coating did not show selectivity for halogenated hydrocarbons but appeared to discriminate against water-soluble solvents, probably due to a difference in the number of adsorption sites or in the heat of adsorption.

In 1981, researchers at Harvard Medical School[65] published a report detailing the development of a detector for halothane, enflurane, and nitrous oxide using a piezoelectric crystal. Apiezon grease, silicon oil 200, and several Silastic adhesives were tested as coating. The Silastic Medical Grade Adhesive Type A was found to be the most sensitive coating to these gases. A significant response to water vapor was reported.

Most recently, Jordan[60] has reported the use of a polymer coating for the specific detection of halogenated hydrocarbons in a closed anesthesia system. A 31.10 g coating of poly(isobutyl acrylate) generated a −964 Hz response to only 5% halocarbon, with only very small differences in sensitivity to isoflurane, ethrane, and halothane. The average standard deviation for successive measurements was 2.70%. The response time was less than 10 sec at a flow rate of 3 ℓpm. No interferences from nitrous oxide, oxygen, carbon dioxide, or a mixture of the three were reported.

H. Hydrogen

The application of a piezoelectric quartz crystal for the detection and assay of hydrogen (deuterium) in an inert gas and for determining the deuterium content in a gaseous hydrogen-deuterium mixture was reported by Bucur.[66] The measuring ranges for hydrogen and deuterium in nitrogen gas were 0 to 16% and 0 to 25%, respectively, with a relative error of only 4%. The measuring range for the deuterium content in isotopic mixtures was between 4 and 96%, with a relative error of less than 2%. The working temperatures were 46 and 50°C, respectively. Deuterium in the mixture was determined by measuring the difference between a palladium film coating being saturated with hydrogen and the film exposed to the hydrogen-deuterium mixture. The extent of exchange between the two isotopes is proportional to the partial pressure of deuterium. A detection limit of 0.01% for hydrogen and 0.03% for deuterium was reported.

Another sensitive and selective hydrogen detector was made by evaporating platinum or palladium onto the surface of a piezoelectric crystal with heating to 150°C.[14] The special integral heater crystal is ideal for use as a reactive gas detector. These measurements are somewhat simpler since the reaction occurs only on the hot crystal, while the rest of the environment can remain at ambient conditions. Both of these coatings are easily sensitive to hydrogen in the parts per million range; however, high concentrations of hydrogen sulfide foul the catalyst and reduce the sensitivity of the sensor.

Hydrogen and hydrocarbons can be analyzed continuously by the DuPont 510® moisture analyzer, which uses two coated crystals. Less than 1 ppm analyte can be detected with this method. An integral part of the analyzer is a heatless dryer used to provide a dry reference air sample.[67]

I. Hydrogen Chloride Gas

Hydrogen chloride gas is a noxious byproduct of many industrial chloride processes, as well as a major exhaust product from the combustion of most solid-rocket boosters. Detection of this gas in the parts per billion and parts per million concentration ranges was successfully accomplished by Hlavay and Guilbault[68] using tertiary amines as coatings for the piezoelectric crystal. The sensitivity of triphenylamine (TPA) was studied as a coating for hydrogenchloride as a function of time.[69] TPA exhibits a strong affinity for HCl and it is believed that this reactivity may be attributed to the lone nitrogen pair of the TPA, which can easily and specifically bind the hydrogen chloride. Linear calibration curves were obtained between 10 to 100 ppb and 0.1 to 100 ppm. The responses reported for TPA were −154 Hz (100 ppm), −52 Hz (1 ppm), −40 Hz (0.1 ppm), −26 Hz (0.01 ppm), and −16 Hz (0.001 ppm). The response time is on the order of seconds with complete reversibility in less than 1 min. No serious organic or inorganic interferences were reported. A new coating technique was used for depositing trimethylamine hydrochloride (TMA-HCl) on a crystal for hydrogen chloride gas detection.[68] A small amount of the coating material was placed in a two-neck flask with the crystal positioned above the material. Using vacuum and heat, a vapor deposit of the TMA-HCl on the crystal surface was obtained. Reproducible coatings were possible with this technique, since the amount of coating material deposited can be controlled by varying the heating time and the temperature. The response of this coating to HCl gas was linear over the concentration range of 1 ppb to 100 ppm. The response time was on the order of seconds, with complete recovery in 30 sec. The responses reported for TMA-HCl were −400 Hz (100 ppm) and −180 Hz (0.001 ppm).

J. Hydrogen Sulfide

Hydrogen sulfide is an extremely toxic gas. Even at dangerous levels workers are unable to notice its presence, and levels can increase suddenly. King[12] first suggested the use of lead acetate, metallic silver, metallic copper, and anthraquinone disulfonic acid as piezoelectric crystal coatings for the selective detection of hydrogen sulfide.

Webber et al.[70] investigated the use of the acetone extracts of various soots. The soots were made by repeatedly dipping a spatula into a particular compound and placing the spatula near a bunsen flame to ignite it. The black residue was then collected and placed in acetone so that it could be easily applied to the crystal. As the acetone evaporates, a film of the residue is left as a coating. The extract of a soot prepared from chlorobenzoic acid provided the best substrate material. The coating was sensitive to hydrogen sulfide in the concentration range of 1 to 60 ppm. The Occupational Safety and Health Administration (OSHA) has established the safe limit of exposure to hydrogen sulfide at 20 ppm, hence this detector would be suitable as an alarm device.

K. Mercury

Mercury is a health hazard because of the strong bonds formed by it with sulfur in the body. This formation of the Hg-S bond interferes with the function and synthesis of both enzymes and proteins. Mercury is also concentrated in the brain, liver, and the other organs and is a cumulative poison.

Bristow[71] was the first to use a gold-plated piezoelectric crystal as a detector for mercury in soil samples. At surface densities in excess of 0.15 $\mu g/cm^3$, a decrease in sensor affinity for mercury is reported, which represents a total absorbed mass on the order of 60 ng for the crystal used. The detection limits are 5 ng/ℓ for mercury vapor in a continuous flow system and 0.7 ng for a total mass of vapor in a drawn soil gas sample. The reaction is reversible by heating the crystal to 400°C.

The use of gold crystals for the detection of mercury vapor has been studied extensively by Scheide and co-workers.[72-75] As part of an air monitoring system, the gold-plated crystals were placed into a variable oscillator circuit, where measurements of the range in frequency due to the adsorption of mercury were accurately carried out to lower than parts per billion concentrations. Reversibility is achieved by heating the detector in an oven at 150°C and flow switching a stream of clean dry air over the crystal. The effects of flow rate, temperature, and interferences were all investigated. The portable detection system was reported in 1978.[75] The instrument was designed to be used as a site monitor, or as a personal dosimeter with an 8-hr operation period. Accumulated dosage could be read by pressing the ON display button. Average exposure is determined by a simple calculation.

Ho and co-workers[76] have described a technique for determining mercury concentrations in water using a gold crystal coupled with a direct reduction technique. Mercury species in an aqueous sample can be reduced to elemental mercury by tin (II) chloride. The mercury vapor that is produced is volatilized from solution and can be detected in the gas phase with a gold crystal. Reversibility is achieved by heating the crystal to 170°C, as hot dry air or nitrogen is used to flush the mercury out of the system. The sensitivity of the detector was reported to be 1.78 Hz/ng with a relative standard deivation of 7%. The effects of flow rate, sample size, and detector cell configuration were all discussed. It is suggested that this technique would also be suitable for mercury determinations in biological samples.

L. Mono-, di-, trimethylamine

Guilbault and co-workers[77] investigated the use of various metal salts as coatings on a crystal for detection of mono-, di-, and trimethyl amines. A large part of this study was directed toward the type of chemisorption reactions that were occurring between the sorbate and sorbent. $FeCl_3$, $ZnCl_2$, $HgBr_2$, $CoCl_2$, and ZnI_2 were each tested for sensitivity toward these amines. The iron (III) chloride coating was found to be the most sensitive toward the amines with greatest sensitivity toward trimethyl amine. Isotherms covering 20 to 100 mmHg pressure were constructed for this amine.

M. Mononitrotoluene (Explosive Vapors)

Mononitrotoluene (MNT) has been used as a simulant for trinitrotoluene (TNT) in the development of explosive materials. Tomita and co-workers[78] examined a number of commercially available materials for the detection of MNT, among which Carbowax 1000 was the most sensitive. The optimum conditions for the detection of MNT were reported to be a flow rate of 30 mℓ/min, a cell temperature of 50°C, and a 30 μg coating of Carbowax 1000. The response was linear over the range of concentrations of 3 ppb to 7.5 ppm, with reported frequency changes of -17 and -193 Hz, respectively. A detection limit of 1 ppb was suggested. No interferences from any inorganic gases at a concentration of 100 ppm were observed. High concentrations of organic solvents and some selected perfumes did cause some interference; however, it is claimed that these concentrations are much higher than what would be expected in normal atmospheres. It was also suggested that fluctuations in the percentage of relative humidity could act as an interferant. The useful lifetime of the carbowax coating for the detection of explosives has been estimated to be about 1 month.

N. Nitrogen Dioxide

Nitrogen dioxide is a very dangerous atmospheric pollutant generated from a variety of industrial and consumer sources. Karmarkar and Guilbault[79] have described a coated piezoelectric crystal for the selective detection of NO_2. Two Ucon compounds were tested as coatings by first being dissolved in chloroform and then applied to the electrode surface of the crystal. Ucon fluids and lubricants are polyalkylene glycols of lesser-known structures. These coatings, Ucon-75-H-90,000 and Ucon-LB-300X, required further treatment with nitrogen dioxide and nitrogen (1:3 mixture) to form a different compound that is sensitive to nitrogen dioxide in the parts per billion and parts per million range. The fact that new compounds are formed is evident in the appearance of new bands and some band shifts in the infrared spectra. The response of these coatings to NO_2 was linear between 1 ppb and 1 ppm with both coatings. At 1 ppm the curves bend, but become linear and remain so over quite a large concentration range. The response is fast and reversible at low concentrations, but at concentrations above 1 ppm a long recovery time is reported (about 20 to 30 min). It is recommended that some type of desiccant be used to remove water vapor, since the coatings are highly hygroscopic.

O. Organophosphorus Compounds

Synthetic organic pesticide use began in the early 1940s when DDT, an organochlorine compound, was introduced as an effective contact insecticide. A wide spectrum of pesticides have since been produced that are based on organophosphorus compounds. These are more popular because of their low persistence and biodegradability. Organophosphorus pesticides are potent cholinestease inhibitors similar to chemical warfare agents, hence their toxicity to humans is greater than other types of pesticides. The organophosphorus pesticides are all structurally related and undergo similar reactions. They contain either phosphoryl or thiophosphoryl groups. The thiophosphoryl pesticides readily undergo oxidation reactions to produce phosphoryl compounds. Diisopropylmethyl phosphonate (DIMP) is a phosphoryl-containing compound that has a relatively low human toxicity, but a similar reactivity as a G-type chemical warfare agent. As a result, it is used most often in studies of piezoelectric detectors for organophosphorus chemicals.

Guilbault and Scheide[80,81] were able to detect DIMP in the parts per billion range by using various inorganic salts ($FeCl_3$, $CuCl_2$, $NiCl_2$, $CdCl_2$) as a coating for the piezoelectric crystal. Mercury (II) bromide[80] was studied in detail as a coating for 9 and 14 MHz AT-cut crystals. The coating was applied by dipping the entire crystal in to 0.01 *M* solutions of the salt. The results were obtained from a vacuum system used to introduce and evacuate DIMP from the detector. The responses were linear with a vapor pressure detection limit of 10^{-4} mmHg of DIMP. The response of the coating to DIMP was attributed to a strong chemisorption, thus complete reversibility was not possible.

Scheide and Guilbault[81] studied $FeCl_3$ complexes with DIMP and Paraoxon (*O,O*-diethyl-*O-p*-nitrophenyl phosphate). The $FeCl_3$-DIMP complex was used to detect DIMP at very low concentrations with a high specificity to DIMP. Likewise, the $FeCl_3$-paraxon coating gave a -44 Hz response to paraoxon at a 100 ppm concentration, with a detection limit of 10 ppb. Little interference from DIMP was reported with this coating.

Shackelford and Guilbault[82] also found 2-pyridylaldoxime methiodide (2-PAM) and isonitrosobenzoylacetone (IBA) to be sensitive coatings for organophosphorus compounds. Both (2-PAM) and IBA had been used as reagents toward these compounds in solution. 2-PAM was reported to be too volatile for use in a flowing gas stream analyzer, but IBA, when used as the sodium salt, proved to be very stable, selective, and sensitive. Unfortunately, the reaction between IBA and the organophosphorus compound was irreversible, and sensitivity decreased with each assay. Both DIMP and DDVP (dimethyldichloro-vinyl phosphonate) were studied. A cobalt complex of IBA was found to remedy this situation. The complex was dissolved in methylene chloride and applied to both sides of the crystal. The resultant detector was stable, selective, sensitive and, more important, completely reversible. The substrate could be modified further by adding the organophosphorus compound of interest to the methylene chloride solution of the cobalt complex. It was found from this study that the most sensitive and selective coating was for paraoxon, using the cobalt-IBA-paraoxon complex as the coating. A parathion detector was also constructed in this manner. Interferences were only significant at levels greater than, or equal to, 100 ppm. Water vapor interference was compensated for by using a reference crystal coupled to a mixer circuit in the instrument. The detection limit was estimated to be less than 10 ppb for organophosphorus pesticides.

Guilbault and Tomita[83] investigated a ternary mixture of 3-PAD, Triton X-100, and NaOH for use as an organophosphorus detector coating. 3-PAD (1-*n*-dodecyl-3-(hydrox iminomethyl) pyridinium iodide had been used previously in solution as an effective nucleophilic reagent with organophosphates.[84] The optimum mixture was found to be 31% PAD, 56% Triton X-100, and 13% NaOH. The sensitivity of the detector was tested with DIMP. A linear response over the range of concentrations from 1 ppb to 15 ppm, with a −63 Hz response to 1 ppb DIMP and −612 Hz response to 15 ppm was reported. No interferences from organic or inorganic sources were reported. The lifetime of the coating is estimated to be approximately 1 month.

Also mentioned in this paper is an excellent coating for the detection of malathion.[83] Using L-histidine hydrochloride as the coating, malathion can be measured in the range 1 ppb to 10 ppm. At 1 ppm malathion a −1414 Hz response was reported with no interferences from possible atmospheric contaminants.

Copper complexes were also evaluated as coatings for the detection of organophosphorus compounds.[85,86] Several papers have been published on catalysts for the hydrolysis of phosphorus esters citing the use of copper complexes. The overall reaction occurs in two steps: first, the copper complex binds the phosphorus ester reversibly; second, the adduct-product is irreversibly broken down by hydrolysis. The reversible property of the first reaction is useful for gas phase detection systems. The copper complexes can adsorb and desorb phosphorus esters in air. The hydrolysis reaction is unlikely to occur on a complex used as a crystal coating because of the low water content in air. Bidentate copper complexes were found to possess the highest activity for DIMP, and this was enhanced by binding the complex to the polymer XAD-4. The calibration curve for the XAD-4-Cu^{++} diamine coating was linear up to 20 ppb DIMP, which was the principal range of interest. No interferences were noted to common atmospheric constituents, as well as samples of automobile exhaust gas. Compared to previous coatings for DIMP (i.e., 3-PAD), the XAD-4-Cu^{++} diamine provides a 50% increase in sensitivity.

Guilbault and co-workers[87,88] investigated the use of hydrophobic and hydrophilic polymers with copper (II) chelates. Substrates of Tetramethyl-ethylene damine copper (II) chloride (TMEDA) connected to poly(vinylpyrolidone) (PVP) and poly(vinylbenzyl chloride) PVBC were evaluated. PVP is a hydrophilic polymer, whereas PVBC is a hydrophobic polymer. The PVP-TMEDA complex had a linear response to DIMP between 0 and 30 ppb. The PVBC-TMEDA complex had a linear response between 0 and 20 ppb. At higher concentrations the coatings become saturated and the responses are nonreproducible. These coatings offer much higher sensitivity and better reproducibility at these concentrations than any of the other coatings developed earlier for organophosphorus compounds. The response and recovery times are on the order of minutes for the PVP-TMEDA coating and on the order of seconds for the PVBC-TMEDA coating. Essentially no interferences were reported. The lifetimes of the coatings were measured under a continuous carrier gas flow. After 25 days of use, the loss in sensitivity for the PVP-TMEDA complex was 20% and only 8% for the PVBC-TMEDA complex.

Kristoff and Guilbault[89] investigated the response of uncoated crystals with different metal electrodes for the detection of DIMP. Linear calibration curves in the μg/ℓ range were obtained with the gold, silver, and nickel electrodes. The nickel-plated crystal showed the highest sensitivity, −113 Hz at 30 μg/ℓ, but the reproducibility is poor and response and recovery were slow. Better results were obtained for the silver-plated crystal, −85 Hz at 30 μg/ℓ, good reproducibility but long recovery times. The gold-plated crystal was rated the best for DIMP detection, where a very reproducible response of −45 Hz at a concentration of 30 μg/ℓ was reported. No interferences were found with the gold electrode. Water vapor was not expected to be a problem. For 50 μg/ℓ DIMP, the gold crystal gave a −50 Hz response to DIMP and a −55 Hz response to DIMP + water vapor.

Van Sant[90] was the first to report the use of enzymes as coatings for piezoelectric crystals to detect organophosphorus compounds. In recent years, bioassay techniques have been developed as alternatives to chemical assay procedures. Cholinesterase has been used in the analysis of organophosphorus insecticides in samples of surface water with acetylcholine or indoxyl acetate as the substrate. Van Sant used acetylcholinesterase on the electrode of a piezoelectric crystal for the gas phase detection of DIMP and malathion. A direct, selective determination of organophosphorus pesticide with sensitivity at the parts per billion level is reported. With this coating, detection limits of 0.4 ppm (180 ng) DIMP and 5 ppb (4 ng) malathion were observed. Since this was only a preliminary study, much work was left to be done such as the optimizing of experimental parameters (optimum glutaraldehyde/enzyme ratio, effectiveness of other binding agents, determination of the response to other cholinesterase enzymes, and response to other organophosphorus compounds).

In subsequent studies,[91,92] various cholinesterases were tested as coatings on a piezoelectric crystal immobilized with different binding agents: glutaraldehyde, bovine serum albumin, diazo coupling, and carbodiimide. Eel cholinesterase, immobilized with glutaraldehyde, exhibited the highest sensitivity for DIMP. Using 20 μg of coating, a −450 Hz response to 4 ppm DIMP was reported, with a response time of 4 to 6 min. A coefficient of variation of 5.6% was also reported. The effect of moisture on a cholinesterase coating was also studied. It was found that with increasing humidity the response of the coating to DIMP also increases linearly. This is probably due to the hydration of the enzyme. No interferences from common atmospheric constituents were found.

Novel use of an antibody as a coating on the piezoelectric crystal was reported by Guilbault and co-workers.[93] The use of antibodies and antigen/antibody interaction for the direct assay of complimentary gas-phase antigens in this study is the first ever reported. A parathion antibody was used as the coating on a crystal for the selective detection of parathion vapor. This paper reports results demonstrating the usefulness of the approach for selective gas phase detection. A − 108 Hz response to 36 ppb of parathion was reported. A linear response over the range of concentrations from 2 to 35 ppb parathion with a standard deviation of 6% was reported. A number of organophosphorus compounds tested as interferences elicited a response from the coating only at concentrations much higher than the detection range for parathion. Usually, 3 to 20 times more interferent was required to produce a comparable change in frequency. The effect of temperature and moisture was also studied. The lifetime of the antibody coating is approximately 7 days.

P. Ozone

Ozone is a bi-free-radical of triatomic oxygen and is generated from biatomic oxygen on exposure to radiation between 185 and 210 nm. As a pollutant in the lower atmosphere, ozone is generated around sources of ultraviolet-radiation, X-rays, welding equipment (electrical arcs), mercury vapor lamps, and in the vicinity of electrical sources accompanying electrical discharges. Ozone is also used as an oxidizing agent in the chemical industry for the purification and sterilization of public water and for the bleaching of oils, paper, textiles, waxes, starch, and sugar. Fog and Rietz[94] have developed a piezoelectric crystal monitor for the detection of ozone in the ambient air of working environments. The detection principle is based on a nonreversible reaction between an unsaturated hydrocarbon polymer (1,4-polybutadiene) as a coating and ozone, with the formation of ozonides as a possible reaction product. A linear response to ozone was observed from 70 to 425 ppb with a detection limit below 10 ppb reported. Interferences from nitrogen oxides, formaldehyde, carbon monoxide, and phenol were reported to be insignificant. The sensor has a very short lifetime, but it is not considered to be an essential drawback. A comparison of results with known methods is also presented.

Q. Phosgene

Phosgene is a colorless, highly toxic gas that is an insidious poison, as it is not irritating to a human immediately, even when fatal concentrations are inhaled. Phosgene is used in the preparation of a variety of chemicals and it is also used as a chemical warfare agent. Suleiman and Guilbault[95] have developed a piezoelectric crystal coating for the sensitive detection of phosgene in the low parts per million range. Methyltriocytylphosphonium dimethyl phosphate was dissolved in chloroform and applied to the crystal by placing a drop of the solution on each side using a syringe. The crystal was then placed in a desiccator for 2 hr for evaporation of the solvent, leaving a thin film on the electrodes. The crystal is later heated in an oven at 70°C for 2 hr to ensure the complete removal of the solvent. The optimum coating amount was reported to be 15 to 20 μg at an optimum flow rate of 10 mℓ/min. For the rapid removal of the substrate after each measurement, the flow rate was increased to 70 mℓ/min, resulting in a completely reversible reaction. The response to phosgene was linear over the concentation range of 8 to 200 ppm, with a standard deviation of 2.5% for 150 ppm and 12% for 8 ppm. Interferences from various atmospheric constituents were tested and high concentration of hydrogen chloride, ammonia, and hydrogen sulfide, as well as water vapor, were found to interfere with phosgene measurements. The lifetime of the detector is estimated to be approximately 1 month.

R. Propylene Glycol Dinitrate

Propylene glycol dinitrate (PGDN) is a commonly used propellant for torpedoes. It is handled in all servicing shops and production facilities, thus presenting a health hazard. Low concentrations (0.1 ppm) can induce headaches and nausea, and exposure to high concentrations can produce methemoglobin. The present TLV for PGDN in the U.S. is 0.05 ppm. Turnham and co-workers[96] have developed a complete piezoelectric detection system for very low concentrations of PGDN in a working environment. OV-275, a dicyanoallysilicone used as a gas chromatographic stationary phase, was found to have the highest sensitivity for PGDN. At 1 ppm PGDN a response in excess of 100 Hz ppm was reported. The response at low concentrations is complete in less than 30 sec, with full recovery within 1 min. The response is linear only over the concentration range below 10 ppm. To eliminate certain interferences, two identically coated crystals were incorporated, one preceded by a trap that specifically adsorbs PGDN. In this design, interferences such as water or 2-propanol would be adsorbed by both crystals and the difference in their oscillating frequencies will not change. When PGDN is introduced, the trap preceding one of the crystals will specifically adsorb PGDN and the difference in frequencies between these two crystals is proportional to the concentration of PGDN present. The trap is constructed of cellulose acetate isobutyrate (CAIB) and reported to be functional for "a number of years" without needing replacement. The detection limit is estimated to be 50 to 100 ppb with the addition of an autozero to the instrument. Every 30 to 40 min the inlet tube for both crystals is switched through a PGDN trap and the instrument is zeroed. The drift of the two crystals is corrected automatically in this way every half-hour. A description of the final instrument is also given.

S. Sulfur Dioxide

A major source of sulfur dioxide is the effluents of industrial stacks of oil refineries and pulp mills discharged into the surrounding atmosphere. The burning of high-sulfur fuels in automobiles is another cause of pollution at the ground level.

Several reports have been published describing the use of coated piezoelectric crystals as highly sensitive detectors for sulfur dioxide. The first report was by Guilbault and Lopez-Roman,[97] who utilized the West-Gaeke reaction for the determination of SO$_2$ in air samples by coating the piezoelectric crystal with sodium tetrachloromercuriate and also using some gas chromatographic liquid phases. Among the gas chromatographic phases tested, apiezion N, silicone SE-30, silicone QF-1, carbowax 20 *M*, and versamid 900, none were as sensitive to SO$_2$ as sodium tetrachloromercuriate. This coating was able to adsorb from 0.18 to 4.01 μg SO$_2$, in a 15 min period.

In a more extensive study of the gas chromatographic substrates for SO$_2$[98], carbowax 20

M coated on a 9-MHz crystal was found to be the best sensor for use as a general purpose gas chromatograph detector for the assay of sulfur dioxide. The response was linear over the range 1 to 100 ppm SO_2 with a response time of 5 sec and a recovery time of about 1 min. Essentially no interferences from other inorganic gases were reported.

Frechette and co-workers[99,100] studied the response of 14 coatings to SO_2. The only interference was found to be nitrogen dioxide, which gave half the response of SO_2. Tridodecylamine and tripropylamine were found to have a high sensitivity for SO_2, but thay were too volatile for a stable piezoelectric crystal coating. In addition, they were also slightly irreversible. The best coating was with an SDM polymer (styrene-dimethyl-aminopropyl maleimide 1:1 co-polymer). Small sample cell volumes were found to offer the highest sensitivity.

Karmarkar and Guilbault[101] developed a new, more efficient detector cell constructed of glass to be used with a piezoelectric crystal for the detection of sulfur dioxide. The important feature of the new design is the splitting of the gas chromatograph column effluent into two equal streams that directly and simultaneously impinge on the opposite faces of a quartz crystal. This design improves the sensitivity, response time, and recovery time. Various amines were examined as coatings for SO_2 detection with the new cell. Amine 220, Armeen 25, triethanolamine, and quadrol (*N,N,N′,N′*-tetrakis [2-hydroxyphopyl] ethylenediamine) were all tested. Of these, triethanolamine and quadrol were found to be the most sensitive coatings. Both had fairly linear responses from 10 ppb to 30 ppm concentrations of SO_2. A linear response for 10 ppb to 30,000 ppb SO_2 was reported with the triethanolamine coating. Responses were on the order of a few seconds, and, especially with quadrol, a complete recovery is possible in 5 min. Nitrogen dioxide and moisture were major interferences. A hydrophobic membrane filter was later added to eliminate the moisture interfence when using the quadrol coating.[102] The response due to moisture in laboratory air was reduced from -300 Hz to -70 Hz using a 0.45-μm-pore size Acropor filter membrane. Further development of this system led to a portable detector for SO_2 using the quadrol coating.[103] The portable instrument, operating on an automobile battery, was used to monitor sulfur dioxide concentrations in automobile exhausts and refinery stack gas emissions. The concentrations of sulfur dioxide in the auto exhaust were found to be between 20 to 50 ppm and up to 300 ppm in refinery stack gases. Four hydrophobic membrane layers were used to reduce the moisture reaching the detector.

Chency and co-workers[104,105] studied the use of triethanolamine as a sensitive SO_2 coating also. They reported on a study of response times at 90, 95, and 99% complete response to 25 and 761 ppm SO_2 using a triethanolamine coating. At 25 ppm the responses were between 90 and 99% complete from 9.25 to 11 min and at 761 ppm, between 1 and 5.25 min. A wide range of sensitivities as a function of temperature was also reported. A study of the responses below 25 ppm was not possible due to the amount of time required for the reaction to be even 90% complete. The triethanolamine coating was also modified with triisopropanolamine (TIP) on Teflon® in an attempt to reduce the volatility but sensitivity was sacrificed as a result.

Cheney·et al.[106] also used cotton swabs to coat a crystal with ethylene-dinitrotetraethanol for the detection of SO_2. The coating technique was checked for reproducibility of both coating amount and sensitivity. The best sensitivity to SO_2 was obtained by coating a 9-MHz crystal only on the electrode rather than coating the entire crystal. This coating also offered better SO_2 sensitivity at higher temperatures and flow rate.

Suleiman and Guilbault[107,108] reported a sensitive assay technique for the determination of the sulfur content in organic liquids. This technique utilizes an oxidative combustion process coupled with a piezoelectric crystal. The SO_2 evolved upon combustion of the organic liquid is bubbled through a mercurous nitrate solution. The mercury vapor produced is detected by a gold-plated piezoelectric crystal due to the formation of a mercury amalgam.

The response of the detector to sulfur was found to be dependent on the volume of the sample used. For 5 ℓ, a linear response curve from 1 to 400 ppm was possible, whereas with 10 ℓ, a linear response curve from 1 to 150 ppm was possible. The only major interferent was from sulfide gases at concentrations exceeding the TLV set by OSHA. The effects of temperature and flow rate were also examined.

T. Toluene Diisocyanate

Toluene diisocyanate (TDI) is used in the manufacture of various polyurethane resins and foams. The present TLV value for TDI as set by OSHA is 10 ppb. Alder and Isaac[109,110] reported the development of a portable instrument for personal monitoring in shipboard use utilizing coated piezoelectric crystals. In the report the desired requirements of a detector for this use were outlined and a number of coatings were examined. Polyethylene glycol 400 was used as model compound for the development studies. This coating was found to be unsuitable for TDI detection due to its high water vapor sensitivity and irreversible adsorption of TDI. An extrapolated limit of detection, using statistical analysis of the data, was found to be on the order of 6 ppb in dry air. Due to the irreversibility of the reaction, it was suggested that the detector could be used to give an indication of the time weighted average (TWA) exposure of the operator to TDI.

Morrison and Guilbault[111] described new coatings for the detection of TDI in the low parts per billion concentration range. Silicone Fluid FS-1265, DC high vacuum silicon grease, and Silastic LS-420 were tested as the coating material. At 100 ppb TDI, using 12.5 μg of coating of the FS-1265, a −98 Hz response in approximately 3 min was reported, with a recovery time of approximately 4 min. The FS-1265 coating had a linear response to TDI over the range of concentration between 10 ppb to 10 ppm. No interferences from inorganic gases were reported. Of the organic interferants tested, only ketones and alkylbenzenes interfered. The lifetime of the silicone-coated crystals was on the order of 5 to 6 weeks.

U. Vinyl Chloride

Vinyl chloride (chloroethene) constitutes the monomer for a series of thermoplastic resin polymers and copolymers that are widely used for container wrapping film, electrical insulation, pipe, conduit, and a variety of other industrial and consumer products. It has been identified as a human carcinogen and as such is strictly regulated by the OSHA, which has set an emergency temporary standard limit of 50 ppm. Through the use of the chemical oxidation of vinyl chloride to produce HCl, a sensitive piezoelectric crystal detector was developed by Van Sant.[90] Vinyl chloride is oxidized with chromate to produce HCl, which is then adsorbed by an Amine 220-coated crystal, resulting in an irreversible change in frequency. A detection limit of 100 ppb, with a linear response up to 80 ppm, was reported. No interferences from common atmospheric constituents were reported. Water vapor is removed in a prereaction chamber. It is suggested that this detector would be quite suitable for field applications.

XII. SOLUTION MEASUREMENTS

A. Ammonia

Webber and Guilbault[112] have used nickel dimethylglyoxime as a coating for the detection of ammonia in solution. The effects of moisture were minimzed using hydrophobic membranes between the sample solution and the crystal. Alternatively, the crystal was allowed to reach equilibrium above a sample of distilled water and then transferred to a sampling chamber. An aqueous concentration of ammonia of 0.15 *M* gave a response of −135 Hz. The calibration graph was linear over the range of concentrations up to 0.45 *M* ammonia. Using quadrol as the coating, sulfur dioxide was measured under the same conditions in the parts per billion range.

B. Cyanide

Nomura and co-workers[113-115] have utilized piezoelectric crystals for the detection of cyanide in solution. Silver-plated gold electrodes of 9 MH AT-cut crystals were used. In an initial study,[113] a constant volume of the sample or standard solution was adjusted to pH 9.6 with either a dihydrogen phosphate-borate or borate-hydroxide buffer. The solution was kept at a constant temperature of 25°C in a water bath. For the measurement, the solution is stirred at 430 rpm and the crystal, whose frequency had been previously determined, is then immersed in the solution for 15 min. The crystal is then removed and washed, first with water and then acetone, and placed in a constant stream of air kept at 30°C. After 1 min the new frequency is measured. A linear range for the determination of cyanide was reported to be from 10^{-7} to 10^{-5} *M*. Interferences from cations, forming complexes with cyanide, were eliminated by the addition of EDTA. In a follow-up study,[114] the cyanide solution was allowed to pass over only one side of a crystal and the frequency was monitored. The change in frequency was found to be dependent on the density (d, g/cm^3) and the specific conductivity (K, $^{-1}$ cm^{-1}). The following equation was derived for the change in frequency:

$$\Delta F = \Delta F_k - \Delta F_d = 2.87 \times 10^3\, K^{0.611} - 8.69 \times 10^3 (d - 1)^{1.02}$$

Using this technique, cyanide solutions over the range 10^{-6} to 5×10^{-5} *M* were determined.

This was followed by another, simplified technique[115] in which only one drop (5 μℓ) of the sample solution, adjusted to pH 10.4, is placed on the electrode of a horizontal crystal in a constant temperature air bath. The frequency was measured after the drop was applied and again 4 min later. A linear range of 10^{-4} to 4×10^{-3} *M* cyanide was reported using this technique. The only interferences reported were silver (I) and mercury (II) in the presence of the complexing agent, ethylenediaminetetraacetic acid (EDTA).

C. Bacteria and Fungal Growth

Downs[116] reported a preliminary study into the use of quartz crystals to measure the rate of growth of bacteria or fungi on its surface. The study was unsuccessful in measuring any mass changes caused by the growth of these living systems. It is believed that the growth rate for the cells was very slow and it was also hypothesized that the cell membranes were being ruptured by the high oscillation frequency.

D. Measurement of Density and Viscosity of Solutions

Nomura and co-workers[117,118] have used a piezoelectric crystal completely immersed in organic solutions to measure their properties of density and viscosity. The frequency of the quartz crystal is directly dependent on the viscosity, density, and specific conductivity of the solution. As the concentration of an electrolyte or density and viscosity of the organic solution increases, the frequency of the oscillating quartz crystal decreases. In liquids of high density and viscosity, such as carbon tetrachloride, the crystal ceases to oscillate. Nomura and Okuhara[118] have derived an equation to describe the relationship between the observed change in frequence (ΔF) and the density (d) and viscosity of the solution:

$$\Delta F = a d^{1/2} + b\, \eta^{1/2} - c$$

where a, b, and c are constants that depend on the properties of the crystal.

E. Silver

It was found by Nomura and Maruyama[119] that metal ions spontaneously electrodeposit on one of the electrodes of the crystal due to the formation of a potential of about 1.5 V between the two electrodes in solution. The only ions to do this were copper (II), mercury

(II), and silver. A method for the specific determination of silver in solution has been developed by Nomura and Tsuge[120] using a transistorized oscillator. This type of oscillator was found to have a much smaller frequency drift than a previously described integrated circuit oscillator.[121] Silver is determined in solution by a three-electrode deposition system consisting of the platinum-plated gold electrode of a crystal as the cathode, a coiled platinum wire anode, and a silver-silver chloride reference electrode. 1×10^{-3} *M* EDTA is added to the test solution to form a stable complex with the interfering ions in solution. Mercury (II), even in the presence of EDTA, deposited on the electrode, but a method is described for the determination of both mercury and silver in solution together. The response to silver was linear over the range 10^{-6} to 3×10^{-5} *M* after 10 min of electrodeposition and 2×10^{-7} to 1×10^{-6} *M* after 1 hr.

F. Iodide

Nomura and co-workers[122] developed a sensitive technique for the determination of iodide in solution using a silver-plated piezoelectric crystal. In the determination, a reagent blank solution is first passed through the cell at 11.2 mℓ/min until the frequency of the crystal has stabilized (F_1). The sample or standard solution is then passed through the cell for exactly 5 min and then replaced with the reagent blank solution until the crystal comes to equilibrium again (F_2). The frequency change, $\Delta F = F_1 - F_2$, is proportional to the concentration of iodide. The iodide can then be removed from the electrode by passing a 0.01 *M* ammoniacal buffer solution (pH 9.4) containing 2 m*M* sodium thiosulfate through the cell for 30 sec per 50 hz (ΔF) due to the deposited iodide. At least 30 determinations can be done before replating of the electrode is required. Iodide can be determined by this technique over the range of concentrations from 0.5 to 7 *M*. Thiosulfate, cyanide, sulfide, Fe (III), Hg (II), and silver interfere, but procedures for eliminating their interference are given. Also studied in this report was the dependence of the crystal frequency on the temperature of the solution in which it is immersed, the ambient temperature of the oscillator, and the specific gravity, specific conductivity, and viscosity of the solution using both transistorized and integrated circuits.

G. Immunoassay in Solution

The advent of bioassays, and the ability of specific antibodies to recognize and combine with nanogram levels of complimentary antigens in a mixture of similar molecules with little or no separation, makes this an attractive analytical approach. In the past, enzyme immunoassays and radioimmunoassays have been very popular with clinical chemists and toxicologists. Since a study at the National Institutes of Health has shown that solid-phase assays are more sensitive than solution assays and capable of detecting picomolar amounts of complimentary antigen,[123] interest has centered on the use of piezoelectric crystal for both the separation and microassay (weighing) steps. The frequency of the crystals coated with the specific antibody are measured, then they are immersed into a solution of the antigen to be assayed. The antigen-antibody layer is formed on the crystal, the crystal is then removed from solution, washed to take off excess unbound antigens and interferences, dried, and the frequency measured. The frequency difference is then equated to the amount of antigen present, using the Sauerbry equation.[124-127] In all of these studies the reactions are carried out in the liquid state, in contrast to the immunoassays in solution described by Guilbault et al.[93]

XIII. COMMERCIALLY AVAILABLE INSTRUMENTATION

A coated piezoelectric crystal analyzer sensitive to water vapor as low as 0.1 ppm was developed by King.[13] This sorption hygrometer has been commercially available since 1964

(Du Pont Instruments, Wilmington, Del., Model 560®). The instrument has a very high sensitivity, fast response, and long lifetime, with an accuracy of about 5%.

A gas chromatography apparatus using a piezoelectric crystal detector was designed and developed for the determination of effluents in the boiling range up to 200°C. The qualitative and quantitative performance of this chromatographic detector was investigated by Karasek et al.[21-23] Janghorbani et al.[24] pointed out that piezoelectric detectors in chromatography can be interfaced to a large, general purpose, time-sharing computer for on-line data acquisition and processing with simple and inexpensive equipment. A prototype piezoelectric crystal mass detector for GPC was compared with the refractometer detector.[26] The experience gained on the new type of sensor indicated that more measurements are needed to develop a generally useful detector.

Two commercially available aerosol mass concentration analyzers were described by Daley and Lundgren[44] for the determination of aerosols and particulates. The instruments are both portable, relatively rugged, and operate on ordinary commercial power. Sem and Tsurubayashi,[128] using an electrostatic precipitator, have developed a portable system that is commercially available for mass concentration measurements in the 100 g/m^2 range of airborne dust particles smaller than 10 m. Chuan[39] also reported using a typical commercial instrument based on the piezoelectric quartz crystal microbalance for the rapid assessment of particulate mass concentrations in the atmosphere. The adhesive coating used in the device is nonhydroscopic and nonreactive to the usual concentrations of pollutant gases in the atmosphere, such as CO, SO_2, NO_x, and hydrocarbons.

Detection of various gases in ambient air (sulfur dioxide, ammonia, hydrogen sulfide, hydrogen chloride, phosgene, etc.), organophosphorus compounds (such as pesticides and aromatic hydrocarbons), has already been demonstrated with piezoelectric crystals. Portable instruments for monitoring gaseous components in air are commercially available in a unit that has rechargeable batteries, a variable-speed pump, digital display of f, and alarm signals that can be preset for certain levels (Universial Sensors, Inc., PZ Model 101®, P. O. Box 736, New Orleans, La., 70148).

A hand-calculator-sized instrument with a digital readout for measuring mercury vapor concentrations in air and/or personal exposure to mercury vapor was developed and evaluated by Scheide.[129] Measurements of concentrations below 15 ppb have a precision of 10%, with uncertainties of 5% above this level.

Fog and Rietz[94] developed a portable instrument for use as dosimeter or personal monitor for ozone detection in the parts per billion concentrations. The accuracy of the instrument is comparable to the results obtained with the portable AID ozone analyzer and Drager detector tubes.

Turnham and co-workers[96] designed and developed a working monitor for propylene glycol dinitrate. The dual crystal design containing a trap for PGDN on the reference crystal eliminates frequency stability and selectivity problems utilizing an auto-zero function. A detection limit of better than 0.05 ppm is possible with this device. It is highly selective for PGDN over all other normal atmospheric contaminants and is insensitive to fluctuations in humidity.

XIV. CONCLUSION

The future of piezoelectric crystal detectors in analytical chemistry is quite bright. Instrumentation is commercially available and coatings for the assay of most common pollutants have been described. Our new research in the area of protein coatings will open up the entire fields of enzymology and immunochemistry, formerly limited to only solution work, to direct assays in the gas phase.

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