A STUDY OF GAS SOLID REACTIONS AND AIR POLLUTION DETECTORS (U)
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DAAG29-77-G-0226
A STUDY OF GAS SOLID REACTIONS AND AIR POLLUTION DETECTORS.

Piezoelectric crystal detectors were developed for assay of ammonia, hydrogen chloride, hydrogen sulfide, explosives, organophosphorous compounds, hydrogen sulfide, carbon monoxide, and toluene. Sensitivity was observed in the part-per-billion range, along with fast responses (10-15 seconds) and high selectivity.
A STUDY OF GAS SOLID REACTIONS
AND AIR POLLUTION DETECTORS

FINAL REPORT

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JANUARY 5, 1981

U.S. ARMY RESEARCH OFFICE

DAAG 29-77 - G - 0226

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A. STATEMENT OF PROBLEM

A basic research study was made for specific adsorbents for the detection of various air pollutants. The substance is placed as a coating on a piezoelectric crystal and the device is evaluated as a possible detector for the identification and analysis of these compounds. The detector and each adsorbent was evaluated with respect to sensitivity, linearity of response, accuracy of response, limits of detection, stability, reversibility and selectivity of analysis.

B. RESULTS

Research during the last three years of the ARO Grant was performed in 6 major areas:

(1) Ammonia (2) Detection of gases in aqueous solutions (3) Hydrogen chloride (4) Hydrogen sulfide (5) Explosives (6) Organophosphorus compounds (7) Toluene (8) Carbon monoxide. A total of 12 publications resulted from this ARO-sponsored research, an average of four papers per year. A summary of this work by area is as follows:

(1) Assay of Ammonia

In the first publication we described a method for the selective detection of ammonia in the atmosphere. The method utilizes the adsorption of ammonia on the surface of
A piezoelectric quartz crystal coated with an extract of capiscum annuum pods, ascorbic acid, or ascorbic acid with silver nitrate; the latter is the best substrate (publication 1).

In a later publication two new coatings, L-Glutamic acid-HCl and Pyrodoxine-HCl, were described for the detection of ammonia. Much greater sensitivity and better selectivity were obtained than with previously described substrate coatings. The response time for both coatings is less than 1 min, and complete reversibility of response is observed in 5 min. No significant interferences were found from other gases. The effect of moisture on the coating materials was eliminated by using a gas chromatographic precolumn packed with silica gel (Publication 2).

(2) Adaptation of coated piezoelectric devices for use in the detection of gases in aqueous solution.

A method for the determination of ammonia and hydrogen sulfide in aqueous solution was developed. This method involves the use of gas-permeable membrane which isolates the piezoelectric crystal device from the solution, yet allows the desired gases to pass through. Concentrations up to 0.45 M for NH₃ and 9 x 10⁻⁴ M for H₂S give linear calibration curves of concentration vs frequency change (Publication 3).

(3) Detection of Hydrogen Chloride in Air

A new method for the selective detection of hydrogen chloride in air was developed by coating the piezoelectric device with a mixture of L-Glutamic acid-HCl and Pyrodoxine-HCl. The response time for this coating is less than 1 min, and complete reversibility of response is observed in 5 min. No significant interferences were found from other gases. The effect of moisture on the coating materials was eliminated by using a gas chromatographic precolumn packed with silica gel (Publication 4).
range were developed. Triphenyl amine and trimethyl amine-HCl are the substrate used as coatings. The response times observed using either coating are less than 30 seconds. Ammonia and moisture could cause interference problems using TMA-HCl as the coating material. The application of a gas chromatographic column packed with silica gel eliminates the effect of moisture (Publication 4).

(4) Detection of Hydrogen Sulfide

A method for the selective detection and determination of hydrogen sulfide in the atmosphere was developed. The method utilizes the reversible adsorption of $\text{H}_2\text{S}$ on a piezoelectric crystal coated with an acetone extract of soots resulting from the burning of organochlorine compounds. The extract of a soot prepared from chlorobenzoic acid provided the best substrate. The method is useful in the concentration range 1-60ppm (Publication 5).

(5) Detection of Explosives

A coated piezoelectric quartz crystal, which has potential use as a simple device for assay of explosives, is used for the detection of mononitrotoluenes (MNT). The detector can indicate the presence of trinitrotoluene (TNT), the less volatile parent molecule. Carbowax 1000 was found to be useful as a coating for the sensitive and selective detector. With the coating, MNT vapor in the sub-ppm range can be detected without serious interferences. The response time
observed was only 10 seconds, and a complete reversibility of response was obtained in less than 50 sec. Some parameters that affect the efficiency of the detector (amount of coating, interferences, flow rate, temperature) were also investigated (Publication 6)

(6) Detection of Organophosphorus Pesticides

A piezoelectric quartz crystal coated with 3-PAD, Triton X-100 and NaOH was found to be an excellent detector for the assay of organophosphorus compounds, possessing properties of high sensitivity, excellent, fast and selective response, and long lifetime.

Several coatings were screened for response to organophosphorus compounds: 2- and 3-PAD, 2-PAI, histidine hydrochloride and stearyl choline salts were the most reactive and selective. Of these, 3-PAD was the best coating for compounds of the malathion type (Publications 7 & 3).

In a search for better coatings to detect organophosphorus compounds, a copper (II) chelate of XAD-4 resin linked ethylene diamine was used. Sensitivity in the 0-20ppb range was observed, together with high selectivity for the compound diisopropyl methyl phosphonate (Publication 9).

(7) Detection of Toluene in Ambient Air

Under a joint cooperative effort with the Danish Institute for the Working Environment (helped by a NATO Travel Grant),
a coated piezoelectric quartz crystal for detection and assay of toluene in the workplace has been developed. Carbowax 550 was used as a coating substrate and toluene vapor can be detected in the linear range 30 ppm - 300 ppm with a reproducibility better than 4%. The response time was 30 sec, and a complete reversibility was obtained in less than 40 sec. No interferences were observed at a 5% (v/v) level. The lifetime of the detector is more than two months. Also a portable monitoring device for toluene, which is 20 cm x 14.7 cm x 9 cm in dimensions, and less than 3 lbs in weight, was developed for field use (Publication 10).

(8) Detector for Carbon Monoxide

The search for a specific coating for CO has continued. Of many reactions tried for CO, the best involves the reaction with Cd to produce HgO. The HgO produced is then detected using a gold coated piezoelectric crystal.

The optimum temperature for the reaction:

\[
\text{HgO} + \text{CO} \rightarrow \text{HgO} + \text{CO}_2
\]

was found to be 210°C. HgO decomposes at 500°C; however, at 210°C some HgO decomposes and gives a slightly changing background of the baseline. By using a reference cell, this background is completely eliminated. In the reference cell the CO sample will first pass through Ag2O and is quantitatively oxidized before it reaches HgO. Therefore, only the Hg background is measured in the reference cell.
temperature. Reversibility is achieved by desorption at 130°C. A straight line calibration plot of AF vs concentration was obtained in the ppm range with a 10 ml sample. By varying the sample size, a 10 fold to 100 fold increase in sensitivity in the linear range was achieved (Publication 11).

(9) Review Articles

Three review articles, on the use of piezoelectric crystals for the detection of atmosphere pollutants, were written under this grant (Publications 12, 13 & 14).

C. PUBLICATIONS UNDER SUPPORT OF ARO GRANT


D. PARTICIPATING SCIENTIFIC PERSONNEL

Dr. P. Kuan, Senior Research Associate
Dr. J. Hlavay, Post-Doctoral Research Associate
Dr. Y. Tomita, Post Doctoral Research Associate
Dr. J. Affolter, Post Doctoral Research Associate
Mr. A. Suleiman, Graduate Student (Ph.D. 12/1/81)
Mr. Mat Ho, Graduate Student (Ph.D. 5/1/81)