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PASSIVE PIEZOELECTRIC HYDROGEN CHLORIDE MONITOR

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The purpose of this project was to develop a prototype piezoelectric crystal monitor for hydrogen chloride. The initial evaluation was to concentrate on developing selective coatings for HCl and the preliminary design of the monitor.

A preliminary prototype PZ instrument was developed and the performance of some very promising coatings has been evaluated with respect to sensitivity, selectivity, stability, reversibility and other important analytical parameters. The proposed coatings (THEED, amine 220 and mercury) can be successfully used for the detection of low concentrations of HCl, either continuously or as a dosimeter.

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SUMMARY

A research study was conducted to develop a prototype piezoelectric crystal detector for hydrogen chloride. This study showed that a piezoelectric crystal coated with tetrakis(hydroxyethyl)ethylenediamine (THEED), amine 220 and mercury can be successfully used for the detection and determination of HCl at very low concentration ranges. The sensors exhibited good sensitivities and reproducibilities and potential to be used either continuously or as dosimeters.

A portable prototype instrument was developed that meets the criteria outlined in the Phase I proposal. The self-contained instrument features a reference and a sampling crystal, rechargeable battery, air pump and digital displays. It is 20 x 14.7 x 9 cm in dimension and weighs less than three pounds.

The proposed technology will lead to the development of piezoelectric crystal dosimeters and continuous monitoring devices for HCl and for other toxic compounds if the proper coatings are developed. The developed devices could have many applications in industrial hygiene monitoring in both military and civilian sectors.

PREFACE: Passive Piezoelectric Hydrogen Chloride Monitor
U.S. Air Force Project F08635-89-C-0346
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SECTION I

INTRODUCTION

A. STATEMENT OF PROBLEM

Hydrogen Chloride is a very corrosive gas, widely used in industry for the production of several organic compounds and is a noxious by-product of certain rocket exhaust gases. The high degree of corrosiveness and toxicity justify the importance of developing a cumulative (dosimeter) sensor, as well as personal and field monitors for the detection of low levels of HCl.

Although, several techniques have been devised for the detection and determination of hydrogen chloride gas, it was pointed out that some of these techniques have serious disadvantages. In addition, selectivity was mentioned as a primary shortcoming in all of these methods (Reference 1).

In 1959, it was suggested that the piezoelectric crystal could be used as a sensing device for the measurement of the thickness of thin films, and Sauerbrey described the relationship between the mass of a film deposited on an oscillating quartz crystal and the corresponding change in the resonant frequency of the crystal (Reference 2) by the following equation:

$$\delta F = 2.3 \times 10^{6}\ F^{2}\ \delta M/A$$

Where δF = the change in frequency due to a coating (Hz), F is the resonant frequency of the piezoelectric crystal, A is the area coated (cm^2) and δM is the mass of the deposited coating. Thorough reviews of the theory and applications of piezoelectric crystal detectors in the gas phase have been presented (References 3 and 4). The potential applications of these detectors seems only to be limited by the ingenuity to develop selective coating materials. Basically, the frequency of the oscillating crystal is decreased by the adsorption of the analyte gas onto the coating; the magnitude of that decrease is proportional to the concentration of the gas.

B. OBJECTIVES

The objectives of Phase I were: 1) the development of optimum coatings useful for the detection and determination of HCl, 2) the evaluation of these coatings, and 3) the development of a preliminary prototype.

SECTION II

EXPERIMENTAL

A. APPARATUS

A schematic of the instrumental set up is shown in Figure A-1. The instrumentation consisted of a low frequency mode OX transistor oscillator (International Crystal Co.) powered by a regulated power supply model IP-28 (Heath Zenith Electronics), modified by a digital-to-analog converter so that changes in the frequency of the crystal could be recorded. The piezoelectric crystals used were gold coated, 10 MHz, AT-Cut, quartz crystals

(Bliley, Erie, PA). Calibrated and bubbler flowmeters were purchased from Suppelco and Alltech Associates, respectively. Temperature monitoring was made with a digital multimeter (Radio Shack), and the relative humidity was monitored with a digital hygrometer (model HI8064, Cole Parmer Ind. Co., Chicago, IL). The various concentrations of hydrogen chloride were prepared by the permeation method. A certified hydrogen chloride permeation tube (VICI Metronics, Santa Clara, CA) and a calibration system (model 570, Kin-Tek Laboratories, Texas City, TX) were used.

B. MATERIALS

Amine 220, tetrakis(hydroxyethyl)ethylenediamine (THEED) and other gas chromatography stationary phases were obtained from Alltech Associates (Deerfield, IL). Other chemicals were analytical grade reagents and used as received from commercial suppliers.

C. METHODS

1. Coating Procedure:

The same general coating procedure was used for all crystals. The coating material was dissolved in an appropriate solvent, then the crystals were coated by addition of known volumes of respective solutions, onto both electrodes of the piezoelectric crystal, using a microsyringe, and spreading the solution with a glass rod. The coated crystal was usually placed in an oven, at a specific temperature, depending on the coating material and the solvent, to allow the solvent to evaporate, leaving a film of coating on the surface. The amount of coating applied to the crystal was determined by monitoring the frequency change of the crystal due to the coating.

2. Measurements:

All frequency measurements were made in a flowing stream of gas at a predetermined flow rate. Base frequency measurements of the uncoated crystal were made after a stable background was established. After drying, the base frequencies of the coated crystals were remeasured to obtain a new base frequency shift as a result of the coating. In either of these two cases, only pure background gas was allowed to come in contact with the crystal.

for actual sample measurements, the coated crystals were allowed to come to a stable baseline in the pure background carrier has. To make a measurement, a four-port valve was used to redirect the sample vapors to the crystal chamber. Changes in frequency were recorded every 30 seconds as the sample continuously flowed past the crystal, for two minutes, before switching back to the pure background carrier gas. To repeat a measurement, a five minute recovery period was needed for the crystal to return to the pre-sample introduction frequency and also to purge the system of any sample that might be in the crystal chamber.

At the beginning of each day, the system was purged with the vapors saturated with the sample, to minimize the absorption of sample by the different components of the generation system. Initially, a single crystal chamber made from glass was used. Then a new chamber made from polycarbonate (Lexan) was designed to hold two crystals and to provide the same degree of exposure to the substrate. In the final stages, the exposure chamber was replaced with a two liter glass round bottle fitted with two side inlet and outlet Swagelok fittings for sampling gas introduction and evacuation.

The neck of the bottle was fitted tightly with a teflon block which encapsulated two thin stainless steel rods. Two sockets were soldered to the ends of both rods to provide an easy way to connect or remove the piezoelectric crystal.

For passive measurements, the bottle was first evacuated, then a stream of the sampling gas with a known HCl concentration was allowed to flow through for two hours at a flow rate of 100 mL/min. The flow rate was then decreased to 5 mL/min to eliminate the effect of flow rate on the response, compensating at the same time for possible adsorption of the HCl onto the glass. The coated crystal was then mounted on the teflon block and its frequency was monitored versus time.

SECTION III

RESULTS AND DISCUSSION

A. DEVELOPMENT OF THE COATING

An extensive study was conducted to evaluate possible coating materials. Inorganic salts of mercury, copper and silver, as well as several organic and organometallic compounds and gas chromatographic stationary phases were tested. Table B-1 shows a partial list of these coatings and their responses. The highest response was obtained using the coatings amine 220, THEED and Carbowax 1000 monostearate. Subsequent studies were conducted, largely using THEED and, to a lesser extent, amine 220.

A set of experiments was performed to determine the amount of THEED coating to be applied to the crystal. It is evident from Table B-2 that the response increases as the amount of coating increases, because of an increased probability of interaction between the coated material and the HCl molecules. However, higher amounts of coatings overloaded the crystal and impaired the vibration. Generally, if high amounts of coatings are used, it is difficult to obtain a uniform dry film which results in poor precision and longer recovery times. It was determined that, for both good response and reproducibility, an amount of coating which causes a decrease of about 16,000-25,000 Hz in the crystal frequency is sufficient.

B. EFFECT OF TEMPERATURE

Figure A-2 shows the effect of temperature on the response of the detector. In this study, the carrier gas was passed through a coil which was placed in a thermostated bath and the exposure chamber was wrapped with a heating tape to obtain a constant temperature. The adsorption of HCl by the coating and the sensitivity decreased as the temperature increased. However, the magnitude of the response at about 40°C is still large enough to perform useful analysis pending recalibration.

C. EFFECTS OF INTERFERENTS

Several inorganic and organic potential interferents, which would be expected to exist in combat areas and around launch sites, were tested. The effects of water, benzene, toluene and sulfur fumes were tested by a continuous process method. Other gases, including NH_3, CO, H_2S, $COCl_2$, SO_2 and auto exhaust were tested by the syringe dilution method. Water and very high concentrations of benzene, toluene and sulfur dioxide caused high frequency changes in comparison to these obtained for HCl. To improve the detector selectivity, a major effort was directed to eliminate the effect of moisture which was the most troubling factor. Several approaches were evaluated, using several desiccants, molecular sieves and hydrophobic membranes. It was concluded that magnesium perchlorate can be used to eliminate the effect of moisture and other interferents without seriously affecting the sample integrity and the response. Although, the use of the scrubber increases the response time (Figure A-3), it is possible to increase the flow rate to decrease the response time if desired, as in the case of continuous monitoring.

D. ANALYTICAL CHARACTERISTICS

Typical calibration plots of frequency change versus concentration are shown in Figure A-4 and A-5 using THEED and amine 220 coatings, respectively. Both plots were linear in the concentration range of 1.5 - 9.5 ppm (V/V) of HCl, and exhibited good linearities ($r^2 = 0.992$ for THEED; $r^2 = 0.950$ for amine

220). The concentration range studied was limited by the permeation tube and the generation device used, and it should be possible to measure higher or lower concentrations by varying the sampling time. The feasibility of using the coated crystals as a cumulative (dosimeter) sensor was next investigated. The responses of the two coated crystals versus time at two different HCl concentrations are shown in Figures A-6, A-7, A-8 and A-9. Although, this study was not completed due to time limitations, there seems to be a definite relation between the concentration of HCl in the sample and the exposure time. All parameters affecting the performance of the cumulative sensor will be optimized in Phase II. The useful lifetime of a single coating was more than five weeks (approximately 500 assays) without significant loss in sensitivity. The useful shelf lifetime of a single coating was checked periodically over a period of five months. It was concluded that a coated crystal could be stored for even longer periods and still be used with remarkable reproducibility.

E. AMALGAM APPROACH

The use of elemental mercury as a coating offers a very promising alternative especially since the effects of moisture and other interferents can be significantly minimized, if not eliminated. Several gold coated crystals were exposed to mercury vapors and amalgam films were formed. A representative plot of response versus time is shown in Figure A-10. The initial study shows that this approach is quite promising and useful in developing both continuous and cumulative type detectors for HCl. It is noteworthy to mention that one crystal exhibited only a 2 Hz natural drift over two hour period, while the same crystal was used for three consecutive determinations without regeneration at sampling times of seven minutes with good reproducibility. This approach should by further investigated in Phase II.

F. CONCLUSIONS

A piezoelectric crystal coated with THEED or amine 220 possesses good sensitivity, reversibility, reproducibility and selectivity for the continuous active and passive monitoring of HCl. Additionally, a mercury coated crystal seems even to hold more promise and will probably exhibit better analytical characteristics as a dosimeter sensor. All of these exciting possibilities will be followed up in Phase II and optimized systems developed.

In Phase II, the current technology will be redesigned in order to reduce the size of the prototype developed in Phase I to that of a portable continuous monitor and a badge type detector. Both instruments will have memory capabilities in order to give concentration versus time profiles (continuous) as well as total dosage (dosimeter). The final design of the monitor dosimeter will be similar in shape to a radiation badge housing a piezoelectric crystal to be worn by concerned personnel or a small assembly, to be mounted at selected locations. The frequency of the crystal can be monitored at any time by plugging the badge into a readout unit. Also, the final unit will be miniaturized and microprocessor memory capabilities will be incorporated. Calibration curves of frequency change (δF) versus gas concentration will be established by actual exposure experiments and will be programmed into the monitor microprocessor to obtain total concentration readout.

The program outlined will lead to the development of devices which could by useful to many government agencies and could have several commercial applications.

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1) Gregory, G.L., Measurement Techniques Investigated For The Detection Of Hydrogen Chloride In Ambient Air, NASA. TND-8352, 1976.

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3) Guilbault, G.G. and Jordan, J.M., "Analytical Uses Of Piezoelectric Crystals", Critical Reviews In Analytical Chemistry, 19, (1), 1-28, 1988.

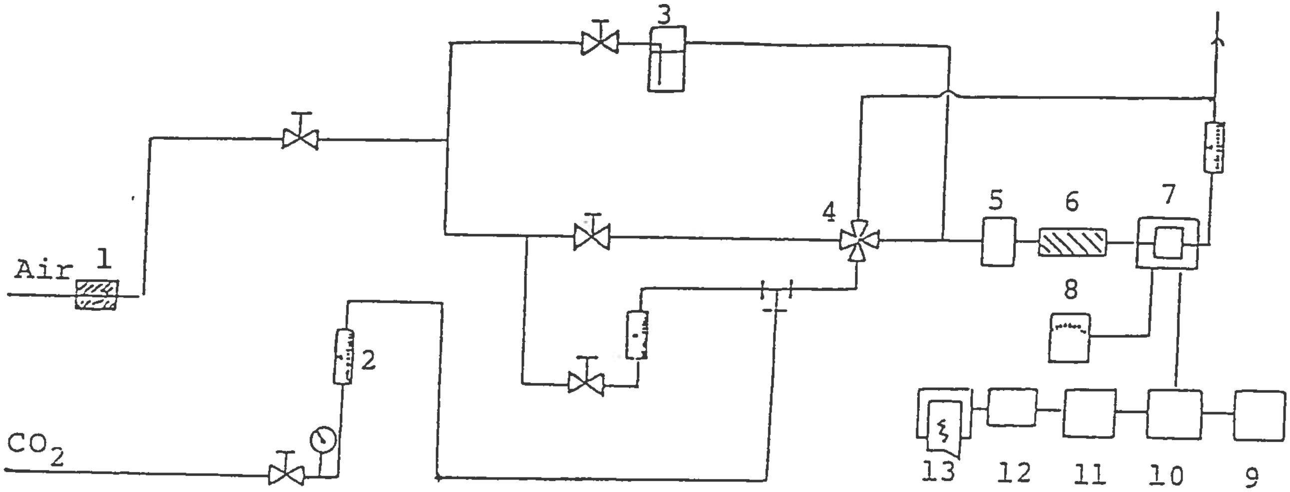
4) Alder, J.F. and McCallum, J.J., "Piezoelectric Crystals For Mass And Chemical Measurements", Analyst, 108, 1169-89, 1983.

APPENDIX A

FIGURES

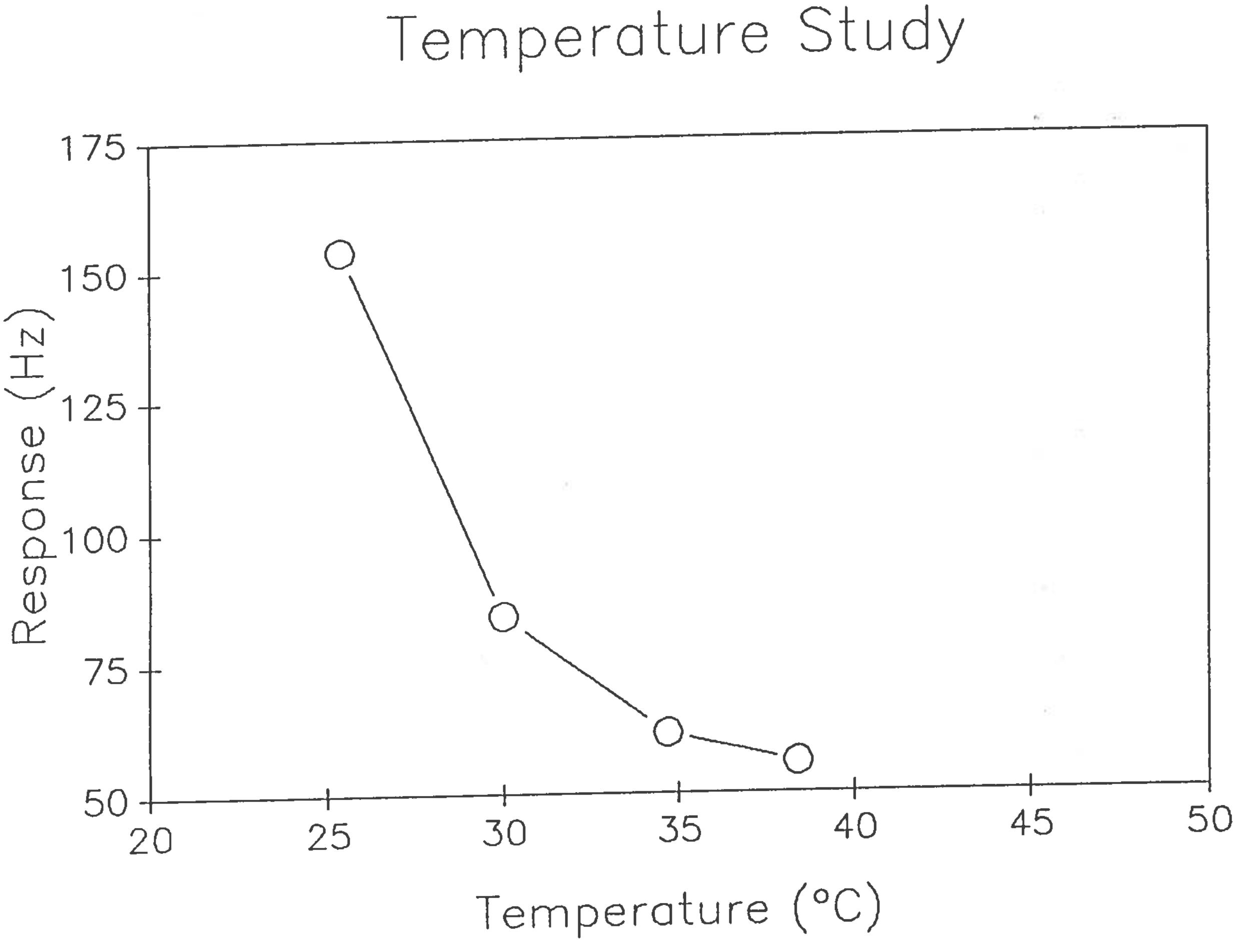
FIGURE 1

SCHEMATIC REPRESENTATION OF THE EXPERIMENTAL SETUP



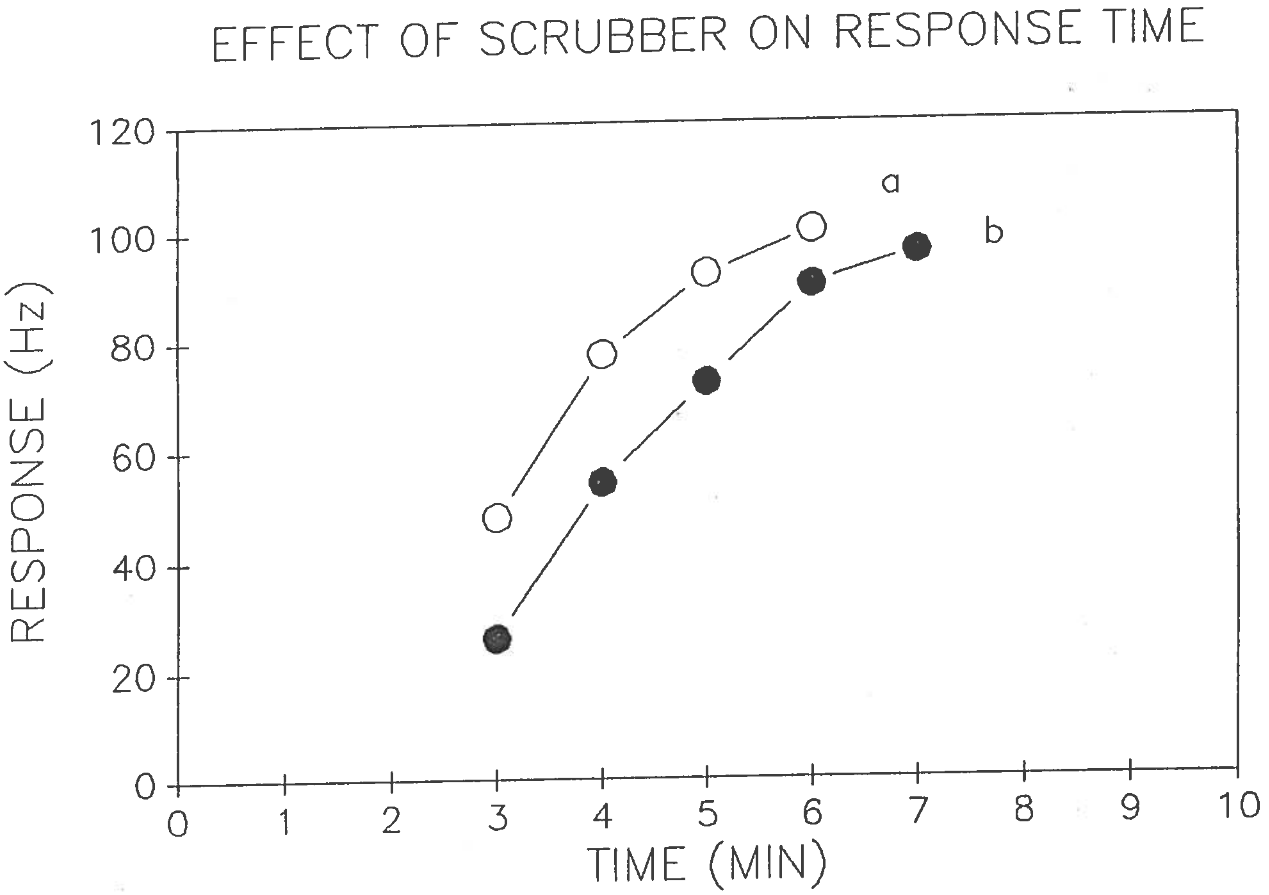
1) Silica gel column; 2) flow meter; 3) humidity source; 4) four-way valve; 5) hygrometer; 6) column; 7) test cell; 8) temperature control; 9) power supply; 10) oscillator; 11) frequency counter; 12) digital-to-analog converter; 13) recorder.

FIGURE 2



C_{HCl} = 9.4 ppm; Flow Rate = 100 mL/min; Coating = THEED

FIGURE 3



C_{HCl} = 8 ppm; (a) Flow Rate = 40 mL/min; (b) Flow Rate = 20 mL/min

FIGURE 4

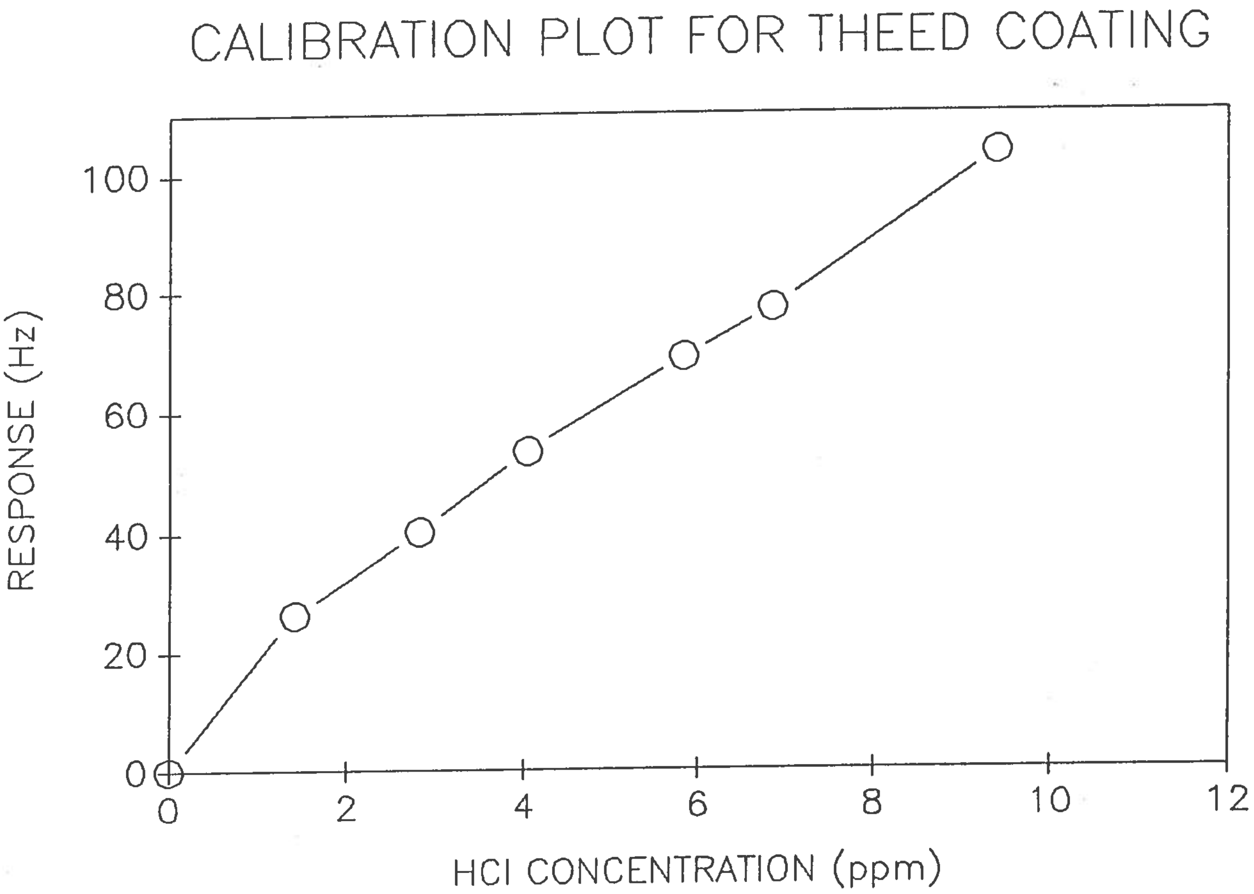

CALIBRATION PLOT FOR THEED COATING
RESPONSE (Hz)
0
20
40
60
80
100
0
2
4
6
8
10
12
HCl CONCENTRATION (ppm)

FIGURE 5

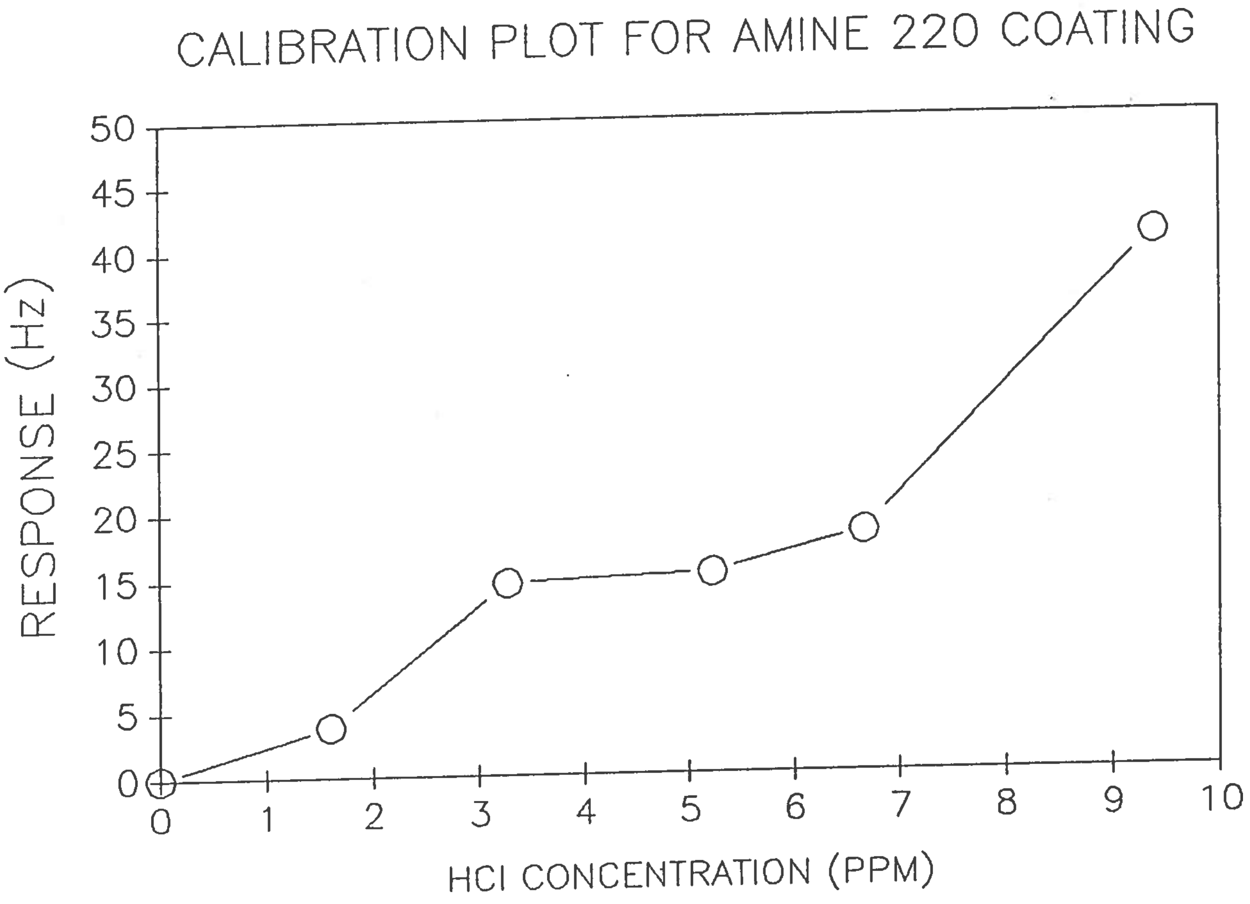
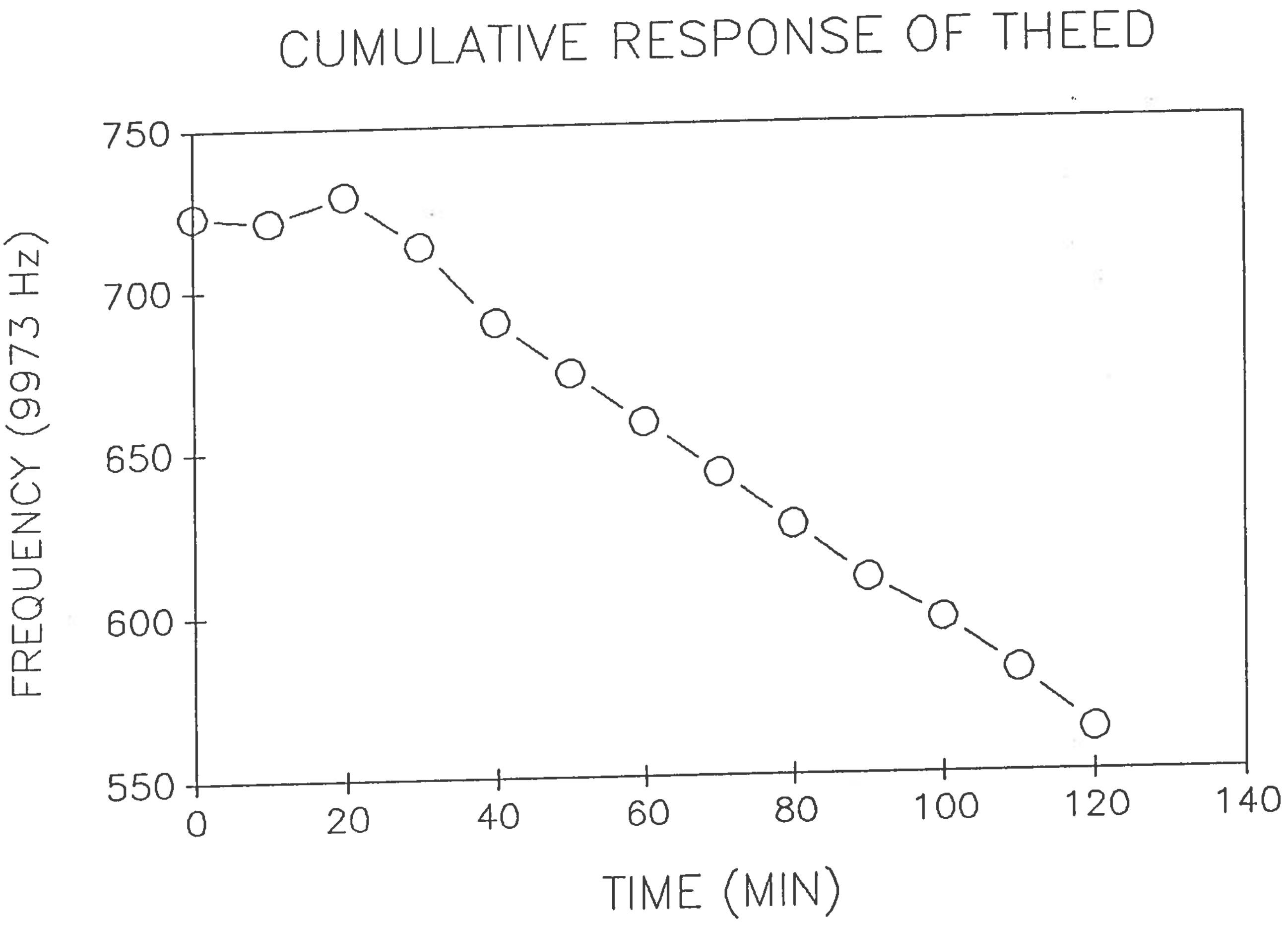
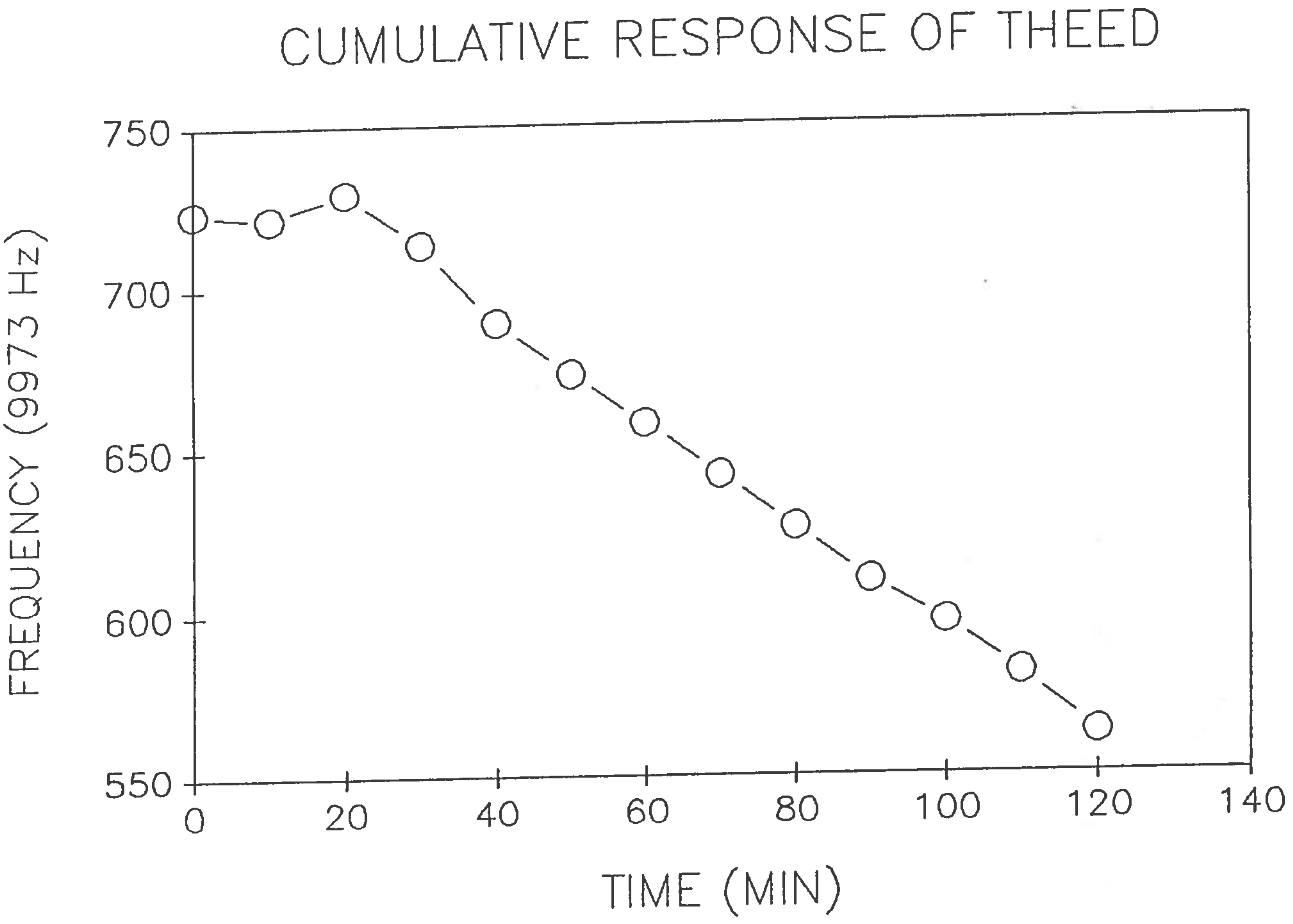

CALIBRATION PLOT FOR AMINE 220 COATING
RESPONSE (Hz)
50
45
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
10
HCl CONCENTRATION (PPM)

FIGURE 6



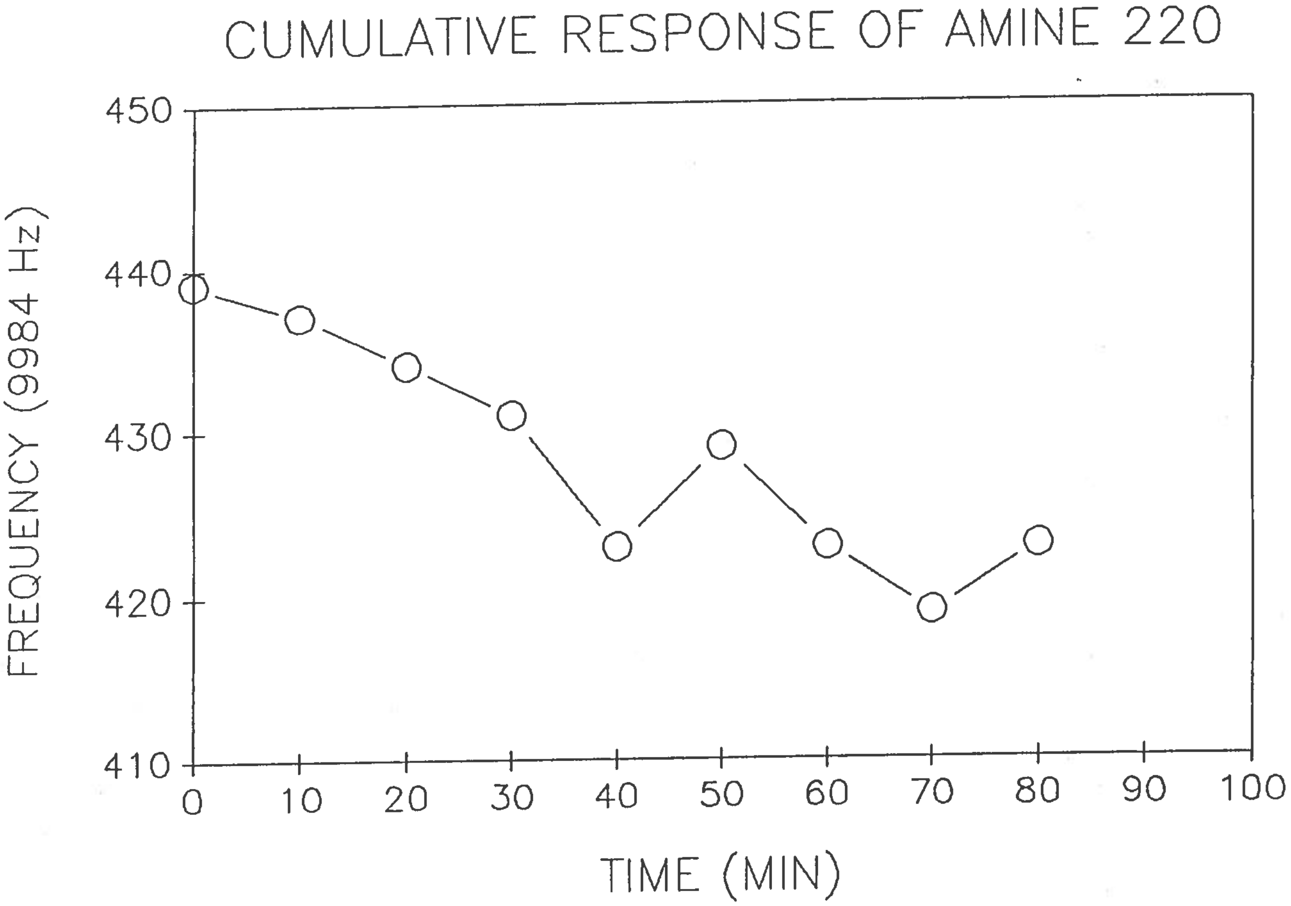
C_{HCl} = 9.4 ppm

FIGURE 7



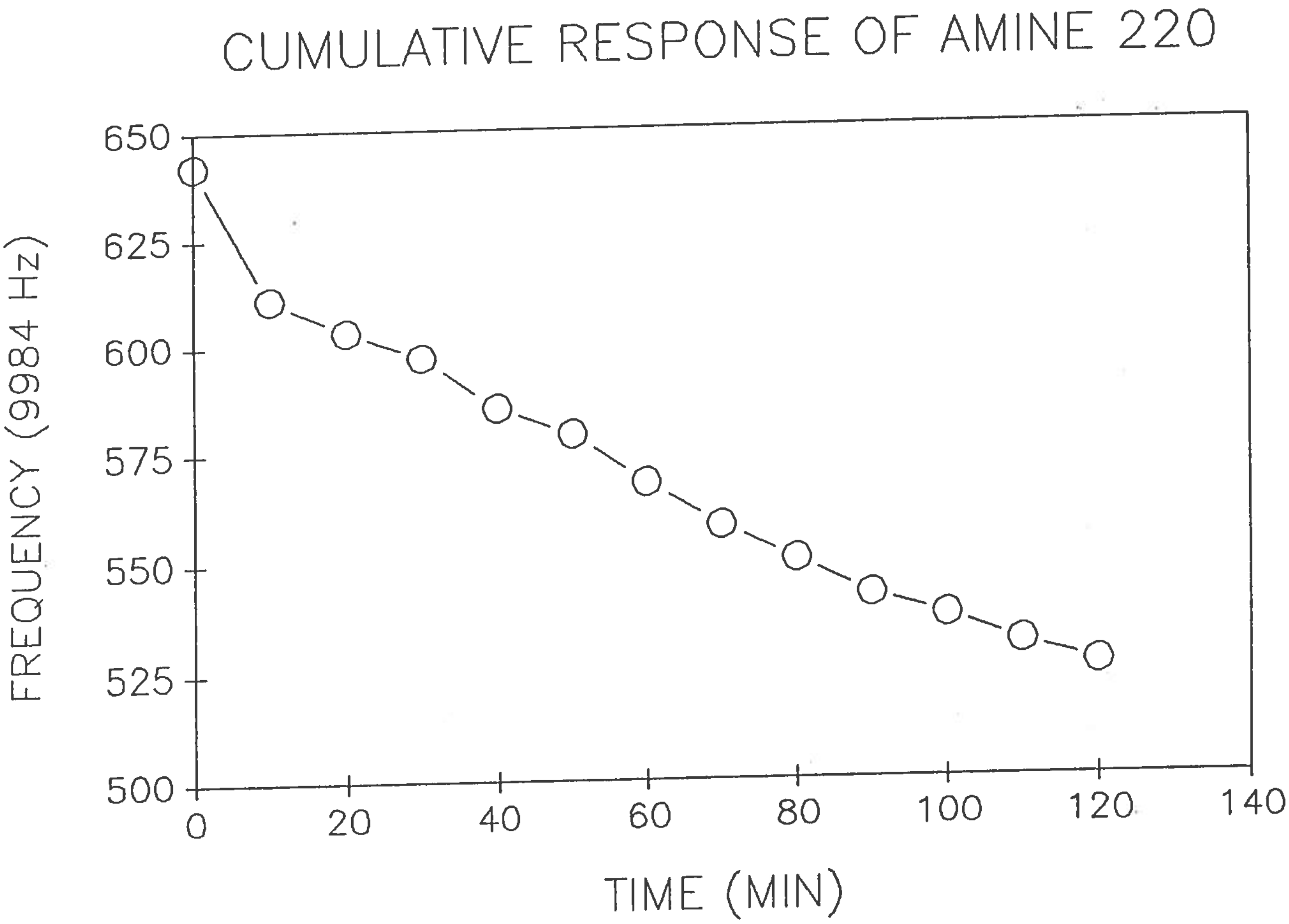
C_{HCl} = 4.5 ppm

FIGURE 8



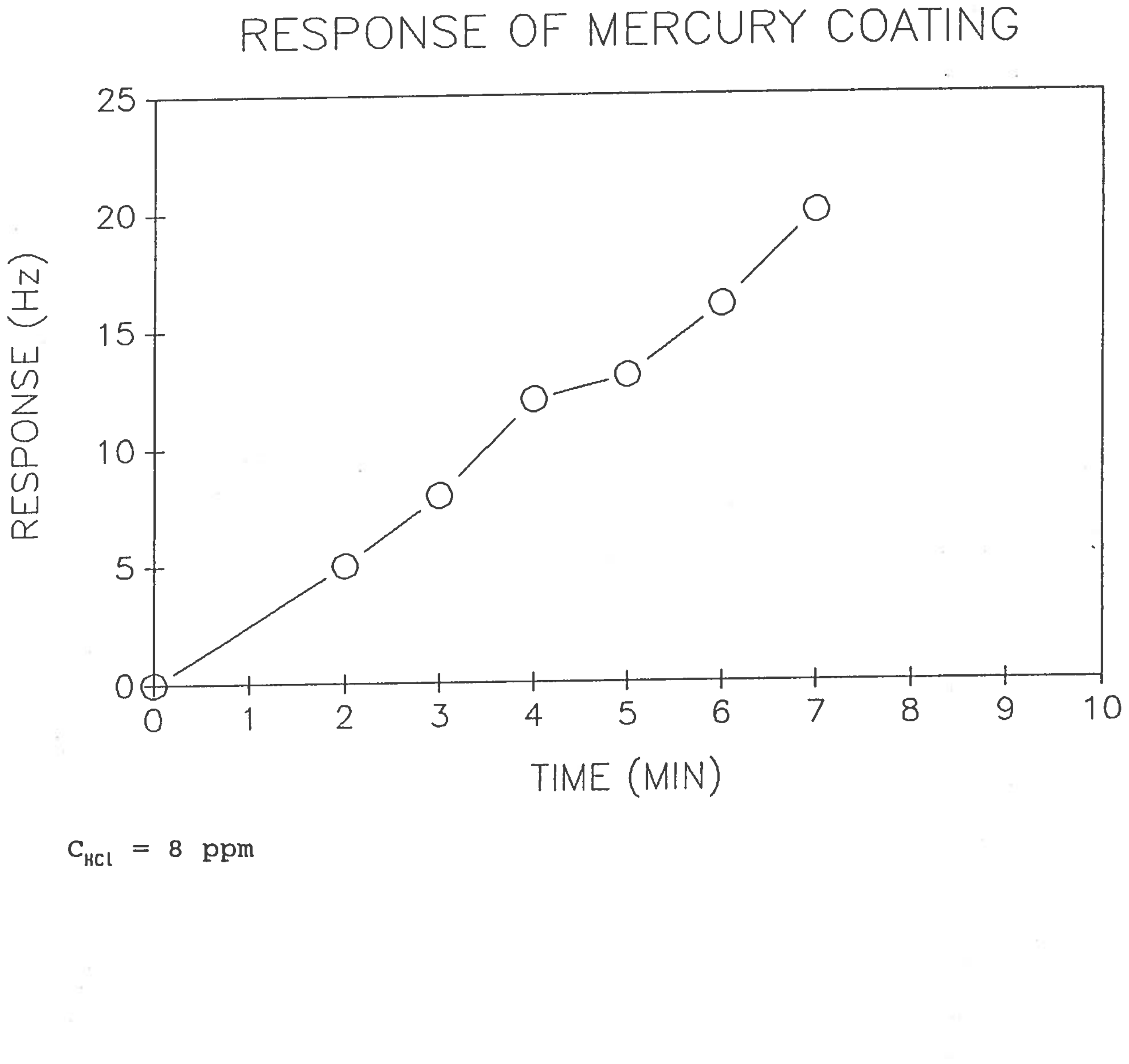
C_{HCl} = 4.5 ppm

FIGURE 9



C_{HCl} = 9.4 ppm

FIGURE 10



C_{HCl} = 8 ppm

APPENDIX B

TABLES

TABLE 1

COATING MATERIALS	RESPONSE TO HCl (Hz)
Carbowax 1000 Monostearate	42.00
Cyanethyl Sucrose	15.80
N,N - Bis (2-cyanoethyl) Foramide	30.00
B,B Thiodipropic Nitrile	21.30
Triethanolamine	28.00
Versamide 90	10.20
Tergitol NPX	32.00
Ucon LBL - 300X	19.25
1,6 Hexane Diol Dimethylacrylate	0.00
AT 220	39.00
Apiezon J	20.25
Ethylene Glycol Adipate	34.40
GPIII Ucon	25.80
Tween 80	23.40
THEED	67.00
Trimethylamine HCl	12.60
Armeen 25	6.00
2,3 - Diaminonaphthalene	Unsuitable
N,N' Bis (2-hydroxyethyl) ethylene diamine	19.40
AT 1200	0.00
Phenyl diethanolamine succinate (PDEAS)	12.00

C_{HCl} = 8.0 ppm; Flow Rate = 100 mL/min

TABLE 2

THE EFFECT OF AMOUNT OF COATING

AMOUNT OF COATING (Hz)	RESPONSE (Hz)
14331	61
16778	116
19258	92
19823	101
20851	82
23013	132
24142	123

C_{HCl} = 8 ppm; Flow Rate = 100 mL/min; Coating = THEED