# Detection of Ammonia in Ambient Air with Coated Piezoelectric Crystal Detector

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Two new coatings, L-glutamic acid·HCl and pyridoxine·HCl, are described for the detection of ammonia. Much greater sensitivity and better selectivity are 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.

Ammonia is a common air contaminant resulting from the combustion of fuels, decay of vegetation, and decomposition of nitrogen-containing organic substances. Evidence shows that ammonia, present in ambient air at low concentrations (ppb), plays an important role in the formation and stabilization of ambient polluting aerosols, and these aerosol particles can potentially cause unfavorable health effects in humans. Consequently, there is a need for a sensitive method for continuously monitoring gaseous ammonia at ambient levels.

A method for the detection of ammonia with coated piezoelectric crystals has been developed (1, 2), using Ucon 75-H-90 000 and Ucon-LB-300X as coating materials (1). On exposure to nitrogen dioxide, these compounds formed new compounds on the surface of the crystal which were sensitive to both nitrogen dioxide and ammonia in the ppb concentration range. Atmospheric moisture and high concentrations of organic pollutants caused interference problems. Furthermore, nitrogen was needed as a carrier gas in this method.

Extracts of *Capiscum annuum* seed pods and ascorbic acid treated with silver nitrate were used as coatings by Guilbault and Webber (2). Ammonia was detected from 1 ppb to 10 ppm. Sulfur dioxide, nitrogen oxide, and trimethylamine interfered at high concentrations. This paper describes new coatings on the piezoelectric quartz crystals for the specific detection of ammonia, even at less than ppb concentrations.

## EXPERIMENTAL

The experimental setup used, with the piezoelectric crystal detector in a flow system, is the same as reported previously for detection of hydrogen chloride in air (3). Air was supplied by a vibrating air pump. A gas chromatographic column packed with silica gel was placed in the flow system in order to adsorb moisture from the air.

The crystals used in these studies were 9 MHz AT cut quartz crystals plated with gold, silver, or nickel metal electrodes on both sides (International Crystal Mfg. Co., Oklahoma). A low frequency OX transistor oscillator was built from an oscillator kit (International Crystal Mfg. Co., Oklahoma) and powered by a Heathkit Model IB-28 power supply. The voltage applied was a constant 9 V dc. A Systron-Donner frequency meter, Model 8050, with a range of 0–30 MHz and a resolution of 0.1 Hz, was used for a

digital read-out of frequency. This frequency counter was modified by a digital to analog converter, so that the frequency could be recorded (Bristol Model 570 Dynameter).

The change in frequency of the oscillating quartz crystal was calculated according to the Sauerbrey equation (4, 5).

**Reagents.** L-Glutamic acid hydrogen chloride, $C_5H_9NO_4 \cdot HCl$ (Nutritional Biochemicals Corporation, Cleveland, Ohio) and pyridoxine hydrogen chloride, $C_8H_{11}NO_3 \cdot HCl$ (Eastman Kodak Co., Rochester, N.Y.), were used as coating substrates. $NH_3$, $NO_2$, CO, $SO_2$, $H_2S$, $CO_2$, HCl (Matheson Co., Inc.), were used from lecture bottles.

**Coating Method.** Glutamic acid·HCl was dissolved in alcohol and this solution was applied over the surface of the crystal on both sides with either a cotton swab or a tiny brush. The alcohol evaporated quickly leaving the substrate on the surface of the crystal.

Pyridoxine·HCl was dissolved in a water–alcohol mixture and this solution was put over the surface of the electrode as mentioned above. The crystal was placed in the oven at 80 °C for an hour to evaporate the solvent. Care was taken to apply the coating as uniformly as possible.

**Gas Dilution Method.** The test gases were diluted with air by the syringe method earlier described by Karmarker and Guilbault (6) and Karasek and Tiernay (7). A 5-mL test mixture was always injected to observe the change in frequency.

**Infrared Measurements.** In order to determine the type of reaction which occurs between ammonia and the coating materials, infrared spectra were taken. Pyrex glass cells with KBr windows were built (1). A small amount of L-glutamic acid·HCl and pyridoxine·HCl was ground with Nujol and was placed on the KBr windows. The cell was evacuated by rotary pump. Ammonia was injected into the cell, sufficient time was allowed for the reaction to occur, and the cell was again evacuated. Infrared spectra of pure coating compounds and of the coatings after the reaction with ammonia were taken, respectively. A Perkin-Elmer 238 infrared spectrophotometer was used to obtain the spectra.

## RESULTS AND DISCUSSION

Both L-glutamic acid·HCl and pyridoxine·HCl showed a very strong reaction with ammonia and good sensitivity. To plot the change in frequency vs. concentration over a large range, i.e., from 1 ppb to 100 ppm, on one calibration curve, the logarithm of both sides of Sauerbrey's equation was taken and plotted. In a given experiment, the change in the frequency can be expressed as (3):

$$\Delta F = K \cdot \Delta C$$

where $\Delta F$ = the change in frequency due to the coating (Hz); $\Delta C$ = concentration (ppm); $K$ = constant which refers to the basic frequency of the quartz plate, area coated, and a factor to covert the weight of injected gas (g) into concentration (ppm).

At 10 ppm of ammonia, the frequency change observed was about 740 Hz, when L-glutamic acid was used as the coating substrate. At 1 ppb of ammonia, the frequency change was about 420 Hz compared to about 110 Hz using the ascorbic acid–silver nitrate coating (2). Using the L-glutamic acid·HCl as coating, an increase in the slope of the calibration curve was observed, providing a much more sensitive assay. The response curve for ammonia in the 1 ppb to 10 ppm con-
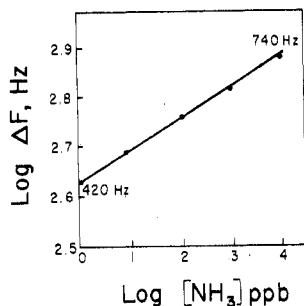
**Figure 1.** Calibration curve for assay of $NH_3$ using a L-glutamic acid·HCl coating
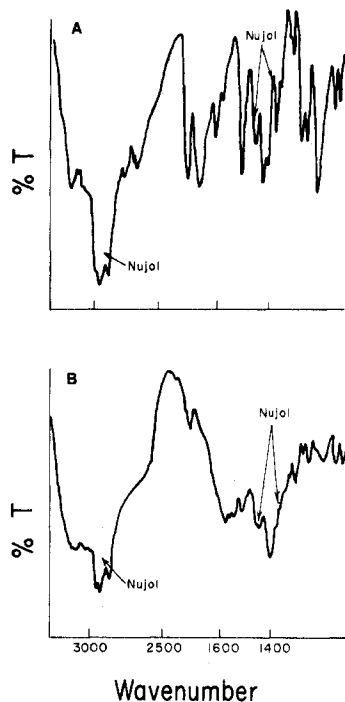


**Figure 2.** Infrared spectra of pure L-glutamic acid·HCl (A) and L-glutamic acid·HCl exposed to ammonia (B)

**Table I. A Study of Interferences in the Assay of Ammonia. L·Glutamic Acid·HCl Coating**

| gas | concn, ppm | $\Delta F$, Hz[a] |
|---|---|---|
| $NH_3$ | 10 | 740 |
| CO | 1000 | 0 |
| $NO_2$ | 100 | 25 |
| HCl | 100 | 20 |
| $SO_2$ | 1000 | 55 |
| $H_2S$ | 1000 | 59 |
| $CO_2$ | 1000 | 36 |
| dry air | | 0 |

[a] Response of the piezoelectric crystal to the gaseous pollutants at the concentration stated.

**Table II. A Study of Interferences in the Assay of Ammonia. Pyridoxine·HCl Coating**

| gas | concn, ppm | $\Delta F$, Hz[a] |
|---|---|---|
| $NH_3$ | 1.0 | 1190 |
| CO | 1000 | 33 |
| HCl | 100 | 43 |
| $NO_2$ | 100 | 30 |
| $H_2S$ | 1000 | 25 |
| $SO_2$ | 100 | 38 |
| $CO_2$ | 1000 | 40 |
| TMA | 100 | 20 |
| dry air | | 0 |

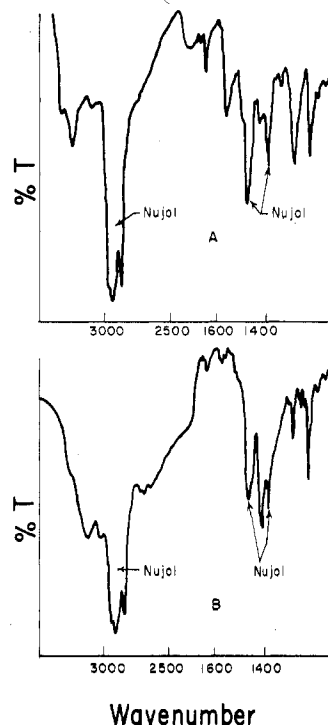[a] Response of the piezoelectric crystal to the gaseous pollutants at the concentration stated.



**Figure 3.** Infrared spectra of pure pyridoxine·HCl (A) and pyridoxine·HCl exposed to ammonia (B)

centration range is shown in Figure 1; $\log \Delta F = \log K + \log \Delta C$ is plotted.

The precision of the method was demonstrated by a series of measurements at 1.0 ppm ammonia, the average frequency change for 7 measurements was 510 Hz, with an average deviation of 4.42%. Dilutions at ppb concentration levels become difficult to reproduce, and measurement errors could result.

The reaction between the L-glutamic acid·HCl and ammonia was investigated by infrared methods. Infrared spectra of pure L-glutamic acid·HCl (A) and L-glutamic acid·HCl exposed to $NH_3$ (B) are shown in Figure 2; 2900, 2840, 1450 and 1370 cm$^{-1}$ are the absorption bands of Nujol. The absorption band at 3140 cm$^{-1}$ in spectrum A indicates the $\nu_{O-H}$ stretching vibration and the strong bands at 1715 and 1670 cm$^{-1}$ are from the $\nu_{C=O}$ stretching vibration. In spectrum B, the absorption bands of the C=O group decreased in intensity and a broad absorption band between 3200 and 3000 cm$^{-1}$ ($\nu_{N-H}$ stretching vibration in $NH_4^+$ group) can be seen. The new, broad absorption band at 1400 cm$^{-1}$ indicates the $\delta_{N-H}$ bending vibration of $NH_4^+$ group and the $\nu_{O^-+NH_4}$ for the ammonium salt formed. According to the infrared spectra, a reaction between the carboxyl group and ammonia could have occurred, yielding the ammonium salt of the carboxylic acid.

Interferences from other gases in the assay of $NH_3$ are listed in Table I. No significant effect was observed from any other gases. The effect of moisture from air was eliminated using

a gas chromatographic precolumn packed with silica gel.

The response time using the L-glutamic acid·HCl coating was less than 1 min and complete reversibility of response was observed in about 5 min. The total reversibility of the reaction between the coating substrate and ammonia makes it possible to detect ammonia gas in the ppb concentration range.

Using pyridoxine·HCl as the coating material, a very high sensitivity of detection of ammonia was found even in the parts per trillion (ppt) concentration range. At 1 ppm of $NH_3$, a frequency change of 1190 Hz was observed. At 0.01 ppb of

$NH_3$, the frequency change obtained was about 386 Hz. A plot of the logarithm of change in frequency (log $\Delta F$) vs. the logarithm of concentration ($\Delta C$) is linear over the range of concentrations 0.01 ppb to 1 ppm.

Table II illustrates the results of an interference study. Since the concentrations of all the interfering substances are much higher than the concentration of ammonia injected, and the responses are much less than the responses of ammonia observed, no interference is expected. The response time observed was less than 30 s using the pyridoxine·HCl coating and a complete reversibility of response was observed in 4 min.

In order to determine the type of reaction which exists between pyridoxine·HCl and ammonia, infrared spectra were taken. Infrared spectra of pure pyridoxine·HCl (A) and pyridoxine·HCl exposed to ammonia (B) are shown in Figure 3. In spectrum A, the absorption band at 3250 cm$^{-1}$ is from $\nu_{O-H}$ stretching vibration. In spectrum B, this band disappeared and a new, broad band between 3150 and 3100 cm$^{-1}$ can be seen, which indicates the presence of the $NH_4^+$ group ($\nu_{N-H}$ stretching vibration in $NH_4^+$ salts). The absorption band at 1400 cm$^{-1}$ is from $\delta_{N-H}$ bending vibration and provides an evidence that the reaction between the hydroxyl group and ammonia has occurred, yielding the ammonium salt of pyridoxine·HCl.
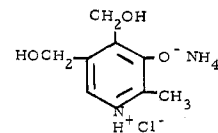
As the pyridoxine·HCl coating is very sensitive for ammonia, the detection of trace quantities of ammonia is possible. Consequently, if the coating substrate is exposed to a higher concentration of ammonia, the pyridoxine·HCl could be saturated and less reproducibility is obtained. Care must be taken to use this sensor only for ppt and ppb concentrations of ammonia.

### LITERATURE CITED

(1) K. H. Karmarkar and G. G. Guilbault, *Anal. Chim. Acta*, **75**, 111 (1975).
(2) L. M. Webber and G. G. Guilbault, *Anal. Chem.*, **48**, 2244 (1976).
(3) J. Hlavay and G. G. Guilbault, *Anal. Chem.*, **50**, 965 (1978).
(4) G. Z. Sauerbrey, *Z. Phys.*, **155**, 206 (1959).
(5) G. Z. Sauerbrey, *Z. Phys.*, **178**, 457 (1964).
(6) K. H. Karmarkar and G. G. Guilbault, *Anal. Chim. Acta*, **71**, 419 (1974).
(7) F. W. Karasek and J. M. Tiernay, *J. Chromatogr.*, **89**, 31 (1974).

# Continuous Determination of Hydrogen Extractable Nitrogen from Silicon–Iron by an Ammonia Gas Sensing Electrode

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**A technique has been developed to continuously monitor the nitrogen egress from bulk samples of 3% Si-Fe annealed in hydrogen. The apparatus and technique are applicable to variable heating rates, isothermal conditioning, and other metal systems. By comparison with published data on nitride solubilities and by selecting materials of different chemistry, peak assignments have been made for "Soluble" nitrogen, $\alpha$-Si$_3$N$_4$, AlN, and BN. These species help define the nature and role of nitrogen bearing species in the secondary recrystallization of silicon–iron. Examples are shown in application of this technique to generically different silicon–iron compositions.**

In silicon–iron processing, many agents, which are reported to promote selective grain growth, have been studied. These include aluminum nitride, vanadium nitride, manganese sulfide, silicon nitride, solute sulfur, and solute boron. In addition to the above agents, nitrogen is a controlled element and is present in most commercial melts at significant levels (30 to 100 ppm). This nitrogen has been shown to play an active role in the secondary recrystallization phenomenon (*1*).

Most studies of nitrogen in silicon–iron involve chemical dissolution of the matrix and separation of an insoluble residue. The fraction of the species dissolved is termed the soluble portion and the undissolved fraction is considered the insoluble portion. Soluble and insoluble in this context refer to chemical, not metallurgical solubility. Metallurgically soluble or "hydrogen extractable" nitrogen is believed to be more significant in understanding secondary recrystallization.

A method has been reported (*2*, *3*) for the determination of "hydrogen extractable nitrogen" in low alloy steels by isothermal annealing at 500 °C. The ammonia formed by the extraction of nitrogen from the steel by hydrogen is absorbed in dilute acid and the ammonium measured spectrophotometrically. Headridge and Long (*4*) improved on the method by substituting an ammonium ion sensitive electrode to continuously measure the ammonia captured in an aqueous solution.

While Headridge and Long succeeded in continuously monitoring a solution for ammonium ion, they measured a cumulative or integrated ammonium concentration and not a real time concentration in the hydrogen carrier gas. The technique reported herein utilizes an ammonia gas-sensing electrode to measure the dynamic evolution of nitrogen (as a function of temperature) from a bulk sample directly in the gas phase.

## EXPERIMENTAL

A system is provided which heats a sample at a known and controllable rate while simultaneously allowing that sample to interact with the surrounding atmosphere.

The heating chamber consists of a tube furnace capable of continuous operation at temperatures up to 1250 °C with a thermal controller able to maintain a top soak temperature of ±2 °C. A 30-inch long quartz (2.5-cm i.d.) tube serves as the sample retort. Stainless steel caps fit over the ends of the quartz tube and are bolted against rubber O-rings providing for a tight gas seal (Figure 1). The incoming hydrogen gas passes through an anhydrone drying tower, a regulating valve, a calibrated flow