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Analysis of Trace Moisture in HCl by Gas-Phase FTIR

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Synopsis. Calibration of moisture in HCl in the sub-ppm range was performed by gas-phase FTIR spectroscopy, giving a linear correlation between infrared absorbance and the moisture concentration. Minimum detectability was estimated to be 30 ppb with 5-min scan time at 2 cm^{-1} spectral resolution at 1.6 $\mathrm{kg\,cm}^{-2}$ pressure, using an InSb detector and an 8-m-pathlength gas cell.

High purity and extremely dry hydrogen chloride (HCl) gas is required by the semiconductor industry for corrosion prevention in HCl gas-handling systems.[1)] Currently, there is no industrial analytical methodology for the determination of trace moisture in corrosive gases in the sub-ppm range.

A Fourier transform infrared (FTIR) spectroscopy with a long pathlength gas cell can be a good analytical method to measure impurities in corrosive gases. This technique is, indeed, often utilized for the analyses of air pollutants,[2)] automobile exhaust gases,[3)] volatile organic compounds.[4)] Regarding conventional methods for moisture determination in HCl gas, Flaherty et al. measured a dew point in HCl by using a Hamada's chilled mirror to obtain 1—2 ppm of detection limit.[5)] Measurements of moisture in HCl by FTIR had been previously reported by Pivonka[6)] at only one concentration (ca. 25 ppm). He concluded that neither bandwidth broadening nor absorbance attenuation was observed at 3853 cm^{-1} at ca. 25 ppm of moisture in a 62.5% : 37.5% HCl : N_2 matrix, permitting direct application of a H_2O calibration curve in N_2 to quantitation of moisture in HCl. The detection limit was estimated to be ca. 0.1 ppm with 5-min scan time with a 10-m-pathlength Pyrex cell and an MCT detector. In this paper, we have investigated gas-phase FTIR for determination of trace moisture in HCl by varying the moisture concentration in HCl over the range of 0.15—1.5 ppm.

Experimental

Instrumentation. FTIR Spectrometer: Infrared spectra were obtained with a JEOL JIR-100 Fourier transform infrared spectrometer utilizing a liquid-nitrogen-cooled InSb detector, a Ge-on-KBr beamsplitter, and a glober light source.

Gas Cell: A heatable Pyrex cell was used, which had 8-m-pathlength with gold-coated internal optics and quartz windows.

Gas Introduction System: The system consisted of a permeation device as a moisture source, mass flow controllers (MFCs), and a commercial resin type purifier as shown in Fig. 1. Moisture of a fixed concentration in N_2 (@ ~20 ppm H_2O) was further diluted with either dry N_2 or dry HCl.

Chemicals. N_2 gas was dried by passing through a cartridge filled with molecular sieves 3A to the moisture concentration <30 ppb. Hydrogen chloride gas (99.999%) was purified with a commercial resin-type purifier to remove moisture down to less than the detection limit.

Resuts and Discussion

Spectrum Comparison. Infrared spectra of H_2O, CO_2, and HCl were collected in the region between 4000 and 2200 cm^{-1} (Fig. 2). With 2 cm^{-1} spectral resolution, there was neither bandwidth broadening, nor frequency shift in the H_2O spectrum in HCl compared with that in nitrogen. A spectral resolution of 0.5 cm^{-1} showed no significant change in the bandwidth. Other potential impurities could not be observed due to either overlap with HCl peaks or to absorption by quartz win-

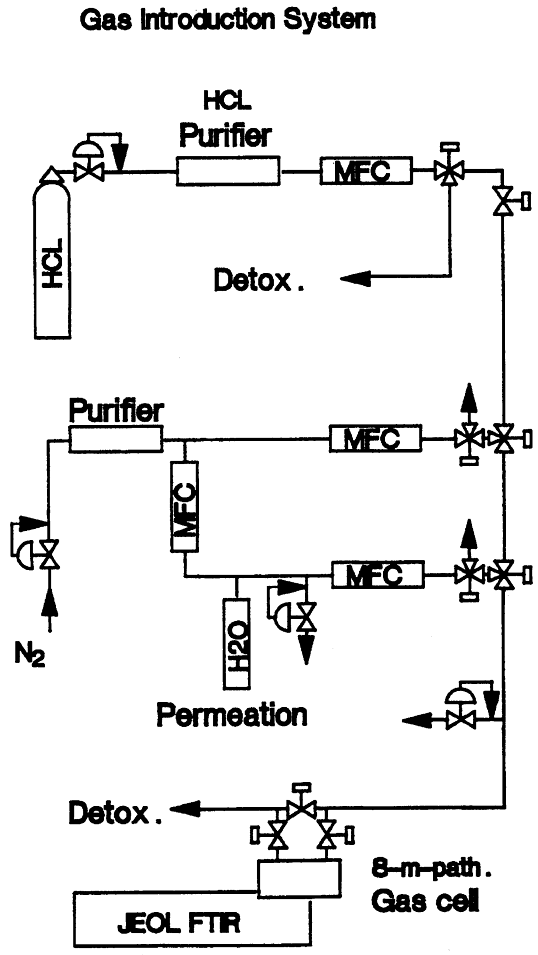

Fig. 1. A flow diagram of a gas introduction system.

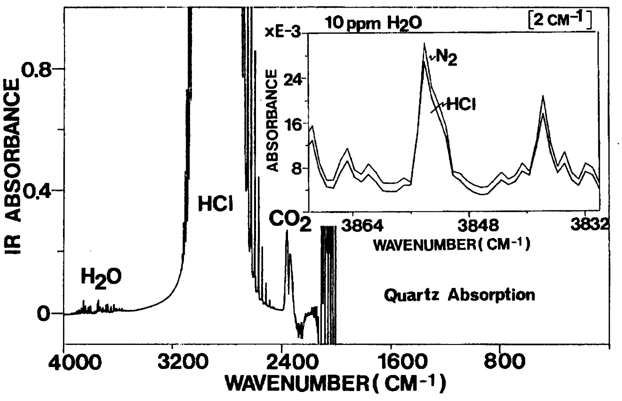

Fig. 2. Gas-phase infrared spectra of H_2O, HCl, and CO_2 (Expanded is overlayed spectra of H_2O in N_2 and HCl matrices).

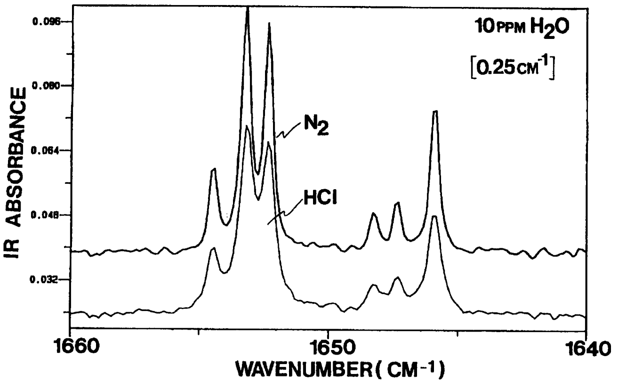

Fig. 3. Bandwidth broadening by 50% HCl matrix in the 1653 cm^{-1} range.

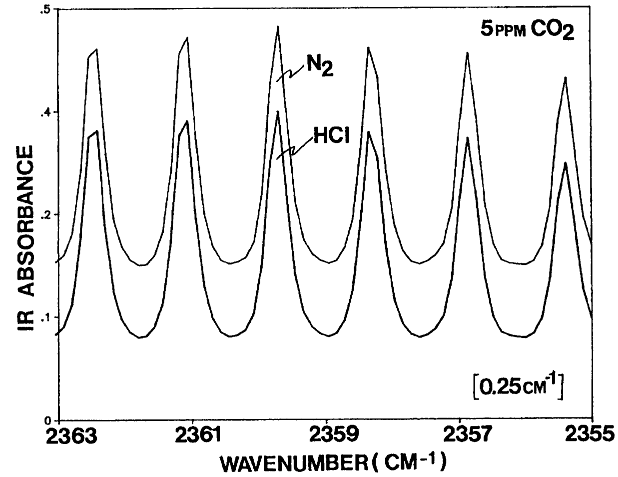

Fig. 4. Spectra of CO_2 in N_2 and HCl matrices.

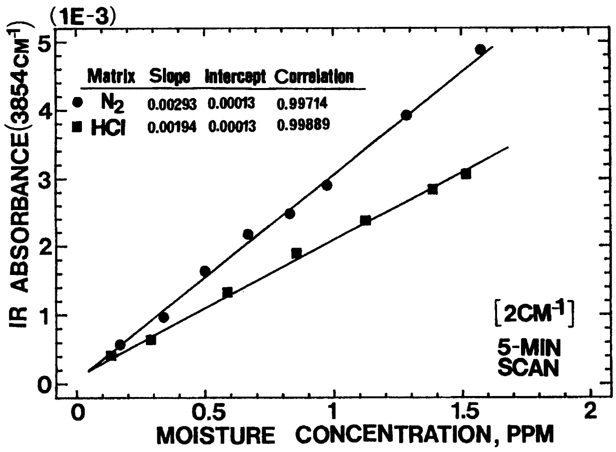

Fig. 5. Calibrations of H_2O in N_2 and in HCl matrices at 1.6 kg cm^{-2} in 0.15—1.5 ppm range.

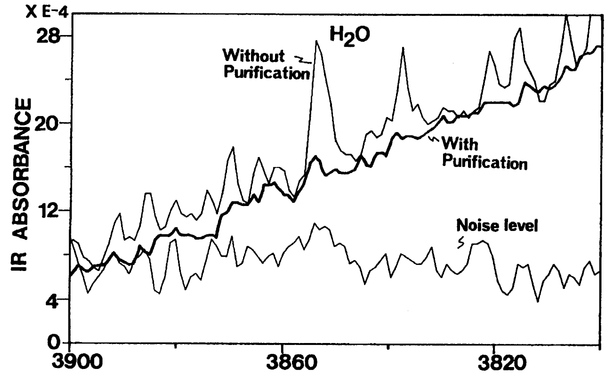

Fig. 6. H_2O spectrum in a 99.999% HCl with and without a purifier.

dows (<2000 cm^{-1}). Peak heights of H_2O in HCl were reduced in different proportions (18—33%) depending on the wavenumber, compared with those in nitrogen. This is in contrast with the previous report by Pivonka who found no change in peak height between N_2 matrix and HCl/N_2 mixed matrix. In order to confirm that the peak reduction was due to the matrix effect and not by other artifacts, the 1800—1600 cm^{-1} region was also observed using an MCT detector and BaF_2 windows. When the spectrum was collected with 0.25 cm^{-1} resolution, a significant bandwidth broadening was observed (Fig. 3). The width at half height of the highest H_2O absorption peak was 0.79 cm^{-1} at 1653 cm^{-1} in HCl while it was 0.45 cm^{-1} in N_2. The spectrum of CO_2 in HCl, on the other hand, agreed with that in N_2, showing no broadening with either 0.25 or 2 cm^{-1} resolution (Fig. 4). Therefore, there seems to be some interactions between HCl and H_2O molecules, causing perturbations in vibration-rotation modes of H_2O molecules.[7]

Preliminary Test. Stability and repeatability tests were carried out at 10 ppm of moisture in nitrogen and in HCl. Before measurements, it was necessary to heat the cell (80 °C) while purging with dry nitrogen. When $H_2O/(N_2+HCl$ 50% each) was introduced into the cell in a dynamic mode, it took 30—60 min with a flow rate of 600 mL min^{-1} to reach the stable H_2O absorption level. When the gas flow was stopped after reaching the stable absorption, it remained stable for a longer period compared with that in N_2.

Calibration Curve. Concentration vs. IR absorbance calibrations were obtained for moisture in N_2 and in 99—93% HCl in the 0.15—1.5 ppm range at 1.6 $\mathrm{kg\,cm^{-2}}$ abs pressure (Fig. 5). Linear correlations were obtained between IR absorbance and concentration in both gases. Difference in sensitivity (i.e. slope) between HCl and N_2 matrix was approximately 30%. Y-intercepts were near zero in both matrices. Detection limit defined as 3s (s=standard deviation) was estimated to be 30 ppb.

Quantitative Analysis of HCl. Moisture in 99.999% HCl cylinder was determined using the calibration curve previously obtained, giving 0.5 ppm H_2O (Fig. 6). As mentioned earlier, the purifier used in this study removed this moisture down to <30 ppb.

In conclusion, gas-phase FTIR technique was found to be useful for the trace moisture determination in HCl gas down to the sub-ppm level. Absorption of H_2O was, however, reduced in HCl compared with that in N_2, indicating some interactions between H_2O and HCl.

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