

# Measuring Trace Impurities in Air by Infrared Spectroscopy at 20 Meters Path and 10 Atmospheres Pressure

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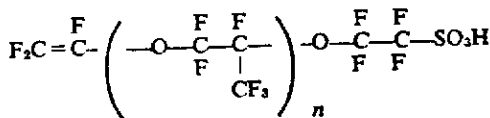
Use of a new type of drying device achieves considerable selectivity in the removal of water from ambient air. The sample may then be compressed to 10 atm, without the separation of liquid water that would otherwise occur. Use of this higher pressure in a 20-meter gas cell permits the infrared spectral detection of many compounds of toxicological interest in the 0.05- to 1-ppm range.

## Introduction

TEN- OR TWENTY-METER-PATH INFRARED CELLS allow one to measure many substances in air in the 1- to 10-ppm range. Compensation of water vapor absorption by a cell in the reference beam permits measurement of bands in all regions except those of most intense water vapor absorption. However, a tenfold increase in sensitivity could be realized if the sample could be examined at 10-atm pressure. Both the Perkin-Elmer 10-meter and the Wilks 20-meter cells are designed to be used at pressures up to 10 atm. But since ambient air samples are always higher than 10% relative humidity, water will condense when the sample is compressed tenfold. Liquid condensate can appear in the lines to the infrared cell or in the infrared cell itself. Water-soluble components of the sample dissolve in the liquid water, salt windows are ruined, and no useful results can be obtained.

When conventional means of removal of water from the gas stream are tried—that is, Drierite or molecular sieve—many compounds other than water are removed. Even small-pore-size 3A molecular sieve, which can be used to dry almost all liquids, is unsatisfactory. It removes a large amount of

many compounds, apparently by nonspecific surface adsorption. One can use, however, a rather special drying device that has considerable selectivity, removing water and certain other specific classes of compounds but allowing many compounds to pass through the dryer with no loss. This dryer (sold by the Perma-Pure Company, of Oceanport, New Jersey) achieves its drying by diffusion of water through a membrane of Du Pont Nafion® perfluorosulfonic acid polymer. Nafion® is a copolymer of tetrafluoroethylene and a fluorosulfonyl monomer having the structure:



In this work two of these dryers were used with an oil-less compressor and a 20-meter cell to obtain 10-atm pressure spectra of trace impurities in ambient air.

## Experimental Procedure

### Apparatus

An air-sampling bag of 60 liters or more capacity is required. Ten-mil Teflon® (Du Pont registered trademark) is the preferred

material, and bags of this material are available from several sources. We used a 30 × 30-inch bag of 70 liters volume, sold by Fluorodynamics Inc., Newark, Delaware, costing about \$100.

The compressor must be noncontaminating—that is, oil-free. A suitable one, having Teflon<sup>®</sup> piston rings, is Bell Gossett's motor compressor unit, Model SYC GH 15-1, costing about \$175.

Two dryers are required, from Perma-Pure Company, Model PD 500-72, at about \$400 each. The dryer consists of a 70-inch length of stainless-steel tubing containing a bundle of small Nafion<sup>®</sup> tubes mounted through headers in a shell-and-tube configuration, so that dry air or nitrogen purge gas can be passed on the outside of the tube bundle. Water diffuses through the wall of the Nafion<sup>®</sup> tubes and is swept away by the purge gas stream.

The long-path cell was made by Wilks Scientific Corp., Norwalk, Connecticut. It is

of variable path, up to 20 meters, and was used at the 20-meter length. Cell volume is 5.4 liters. Cost of the cell is about \$2000. A second cell in the reference beam is sometimes desirable, to compensate remaining trace amounts of water, but not essential for many uses. Any good grating spectrophotometer may be used. We used a Perkin-Elmer Model 457. (A grating instrument is essential for best results, owing to the sharpness of many of the bands in gas spectra.)

### Procedure

The ambient air sample is collected in the 70-liter bag, and the bag is connected to the inlet of one of the dryers, which is connected to the inlet of the compressor. The outlet of the compressor goes to the second dryer, and the outlet of that dryer to the evacuated 20-meter cell, mounted in the spectrophotometer.

Dry nitrogen was used as purge gas on the dryers at a flow rate of 8 liters/min. When

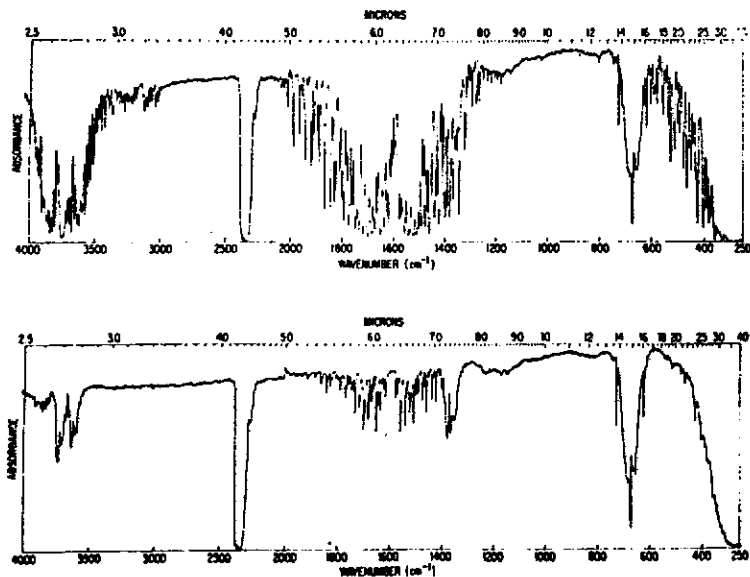


Figure 1. (Top) Twenty-meter spectrum of 50% r.h. air containing 15 ppm  $\text{SO}_2$ . Run at 1-atm pressure. (Bottom) Twenty-meter spectrum of air containing 15 ppm  $\text{SO}_2$ , after passing through the dryer. Run at 1-atm pressure.

the compressor was used, a restricting valve on the outlet of the purge gas of the second dryer was partially closed to raise the nitrogen pressure to 5 atm so that there would be only a 5-atm differential pressure across the walls of the Nafion® tubes.

A new dryer, or one that has been exposed to a large amount of wet air, is slow to condition to an adequately dry state. Therefore, purge gas should be passed in the shell for several hours prior to use. Performance is enhanced if during this period dry gas is also passed through the tubes, as well as around them. Better drying can also be obtained if the exit end of the second dryer is cooled. This is easily accomplished by placing a few ice-bags on top of the tube.

The compressor delivers about 15 liters/min through this system; therefore, it takes about 4 minutes to pump the 20-meter cell to 10-atm pressure.

When a sample was drawn into the evacuated 10-meter cell to be run at 1 atm, it was drawn through a single dryer at 5 to 10 liters/min.

## Results and Discussion

Drying efficiency at 1 atm was determined by drawing room air through one of the dryers into the evacuated cell. Regardless of the original humidity, the dryer lowered it to 2% r.h. The improvement in the spectrum, run without any compensation in the reference beam, was dramatic. The water bands in the 3600- to 3900-cm<sup>-1</sup> and 1900-

to 1300-cm<sup>-1</sup> regions, which on most grating instruments show absorbance values much greater than 1.0 for 50% r.h. ambient air, were reduced to 0.05 to 0.2 unit. This opens up entirely new regions of the spectrum, enabling one, without reference beam compensation, to see ppm amounts of compounds absorbing in the 1900- to 1300-cm<sup>-1</sup> region. For example, Figure 1 (top) is the spectrum of 15 ppm of SO<sub>2</sub> in air, and Figure 1 (bottom) the spectrum after the air has passed through the dryer. The SO<sub>2</sub> band at 1370 cm<sup>-1</sup> can be quantitatively measured in the dried sample; even its qualitative presence is uncertain from the spectrum before drying.

When the compressor was used and the cell filled through the dryers to 10-atm pressure, the resulting spectrum showed water bands no greater than 0.5 absorbance unit, as in Figure 2. When the pressure was reduced to 1 atm, where calibration data were available for the water bands, the sample was found to be about 1.5% r.h. The weak hydrocarbon bands at 3000 to 2900 cm<sup>-1</sup> are from the compressor, believed to be from contaminant introduced when mechanical work was done on the compressor valves.

In ambient air spectra at 20 meters and 10 atm, methane bands appear at 3020 and 1310 cm<sup>-1</sup>; their absorbance is about 0.1 unit. Calculations based on methane standards give good agreement with the natural abundance of methane in the earth's atmosphere, about 2 ppm.

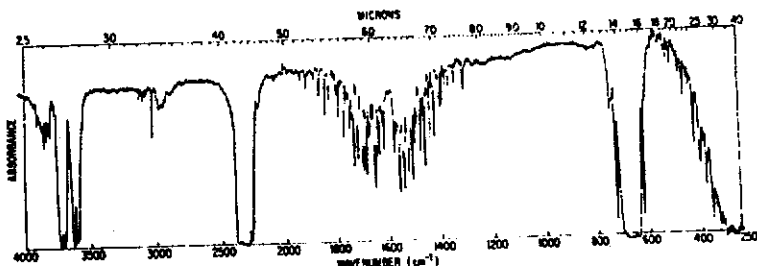


Figure 2. Twenty-meter spectrum of air, after passing through the dryers, compressed to 10 atm.

As a demonstration of the sensitivity of detection of strong infrared adsorbers, the  $1290\text{-cm}^{-1}$  band of  $\text{CF}_4$  has been measured at 10 ppb without difficulty.

In doing calibrations it must be remembered that for certain small molecules it is essential to calibrate at 10-atm if the sample is to be run at that pressure. This is necessitated by pressure-broadening effects, which also dictate that if water vapor compensation is desired, with another 20-meter cell in the reference beam, that cell must also be at 10 atm. The magnitude of this effect is, of course, also related to the resolution of

TABLE II  
Behavior of Classes of Compounds in  
Nafion® Dryer

Class	Not	
	Removed	Removed
Many Inorganic Gases	x	
Hydrocarbons	x	
Cl or F hydrocarbons	x	
Perfluoro acid fluorides	x	
Most esters	x	
Many aldehydes	x	
Water-insoluble ethers	x	
Water-soluble ethers		x
Alcohols		x
Amines		x
Most ketones		x

TABLE I  
Removal of Specific Compounds by the Nafion® Dryer<sup>a</sup>

Class	Amount Removed		
	<10%	10—90%	>90%
Inorganic	CO, CO <sub>2</sub> , SO <sub>2</sub> , CS <sub>2</sub> , H <sub>2</sub> S		
Hydrocarbons	Ethylene		
	Octene-1		
	Benzene		
Cl-hydrocarbons	Decahydronaphthalene		
	CHCl <sub>3</sub>		
F-hydrocarbons	Allyl chloride (3-chloropropene)		
	CF <sub>4</sub> , F-113 (1,1,2-tri- chloro-1,2,2-trifluoro- ethane)		
Acid fluorides	COF <sub>2</sub> , CF <sub>3</sub> COF		
Esters	Amyl acetate		
Aldehydes	Butyraldehyde		Crotonaldehyde
	Acetaldehyde		
Ethers	Diethyl ether		Dioxane
	Furan		
	Methyl vinyl ether		Methylal
	Hexafluoropropylene oxide		
Ketones	Ethyl amyl ketone (20%)		Acetone
	Benzonitrile (50%)		
Nitriles	Acetonitrile (75%)		Methyl isobutyl ketone
Amines	n-Butyl amine		
Alcohols	Methanol		
	t-Butanol		
	n-Hexanol		
Acids	Acetic acid		
Miscellaneous	Nitropropane	Nitrobenzene (30%)	Dimethylform- amide

<sup>a</sup>Sample was drawn through a 70-inch Perma-Pure Nafion® dryer at 8 liters/min. Concentration of compound being studied varied, but the order of magnitude was 100 ppm.

the spectrophotometer. With the Perkin-Elmer Model 457, operated at slit position 7, we found significant difference in intensity at 10-atm compared to 1 atm for the CO (2100  $\text{cm}^{-1}$ ) and CO<sub>2</sub> (2400  $\text{cm}^{-1}$ ) doublets, but little change for methane. (The methane band did show considerable intensity difference between 0.1 atm and 1 atm, however.)

Many inorganic gases and organic vapors are unaffected by the Perma-Pure dryer. Certain others are partially or completely removed, along with the water. Table I lists forty-three compounds that we have studied. Based on the behavior of these specific compounds, generalizations about classes of compounds have been made in Table II.

This behavior is a mixed blessing. For example, we have taken advantage of the removal of methanol to eliminate its interfering bands from the spectrum when another compound was being determined. Removal of methanol by the dryer is quite efficient, as much or more so than removal of water.

### Application

We believe that this technique should find application in the determination of trace impurities in air for industrial hygiene purpose. Long-path infrared spectroscopy is direct, quick, and accurate but has often lacked sufficient sensitivity for measurements of some of the more toxic materials at their threshold limit values. Table III lists seven compounds for which the sensitivity at 1 atm is inadequate, or borderline, but which (with one exception) should be detectable at or near their

TLV's when run at 10 atm. (We have not run 10-atm spectra of all these compounds, but from the generalizations of Table II we would predict that they would not be removed by the dryer.) The ppm detection limits are calculated from standard 1-atm spectra and assume 0.02 absorbance unit as the detection limit. As an example, Figure 3 illustrates the detection of allyl chloride in air at its TLV of 1 ppm, which is near its limit of detection. Allyl chloride is a somewhat weak infrared adsorber, having a band at 930  $\text{cm}^{-1}$  and another at 1270  $\text{cm}^{-1}$ . (The sharp band at 1310  $\text{cm}^{-1}$  is from

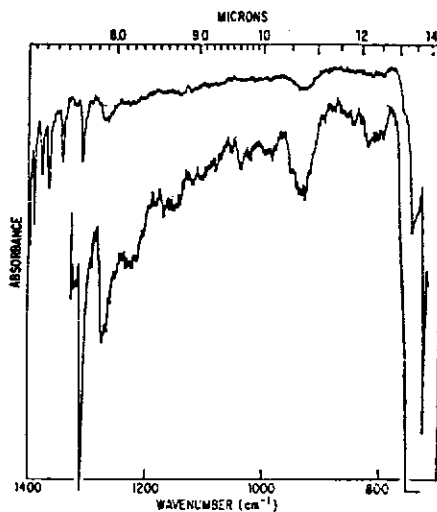


Figure 3. Twenty-meter spectrum of air containing 1 ppm of allyl chloride, after passing through the dryers, compressed to 10-atm. Lower spectrum run at  $5 \times$  scale expansion.

TABLE III  
Estimated Detection Limits for Certain Toxic Compounds  
in Air at 20-Meter Path, 10-Atm Pressure

Compound	Analytical Wavelength	TLV 5 ppm	Detection Limit
Sulfur Dioxide	1374 $\text{cm}^{-1}$	0.2 ppm	0.2 ppm
Benzyl chloride	1269	1	0.8
Phenyl ether	1252	1	0.06
Allyl chloride	935	1	0.5
Chloropicrin	870	0.1	0.1
Phosgene	851	0.1	0.08
Nickel carbonyl	2060	0.001	0.003

methane, and the higher-frequency bands are from water.) When run at  $5\times$  scale expansion the allyl chloride may be more easily measured.

Although equally sensitive gas chromatographic or chemical (colorimetric) methods exist for most of these compounds and others, it is important to extend the sensitivity range of infrared spectrometry because of its inherent advantage as a *qualitative* tool. Infrared identification is usually positive; typical gas spectra are sharp and often so distinctive in shape that the general appearance of the band, as well as its position, can be used for identification. If there are any interferences present, one is almost always immediately aware of them. But, most impor-

tant, one will find the unknown—the unexpected—compound whose presence goes undetected when specific chemical methods are used. Even if gas chromatography detects an extra peak, it remains a formidable task to identify it at less than ppm levels. Thus the long-path infrared scan may present the analyst with more information than originally asked for, but not necessarily more than he needs!

#### Acknowledgment

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