

CHROM. 19 130

EVALUATION OF THE EFFECTIVENESS OF VARIOUS CARRIER GAS PURIFIERS

REGINALD J. BARTRAM*, WILLIAM J. PINNICK and ROBERT E. SHIREY

Supelco, Inc. (Subsidiary of Rohm and Haas Company), Supelco Park, Bellefonte, PA 16823-0048 (U.S.A.)

(Received September 4th, 1986)

SUMMARY

The capabilities of carrier gas purifiers for removing oxygen and moisture were evaluated with gas containing known concentrations of these contaminants. Purifiers with O-ring seals and permeable plastic bodies allow large amounts of oxygen and water to enter the system and contaminate previously pure gas. Oxygen-removing purifiers generally perform well, but those with poorly designed seals admit moisture.

Color indicators were evaluated for sensitivity to oxygen or moisture. Indicators containing Hercules Nanochem® resin were sensitive to 1 ppm of oxygen or water in carrier gas, but cobalt chloride-based indicators were insensitive to water levels below 110 ppm.

INTRODUCTION

Much has been written on the effects of oxygen and moisture on gas chromatography (GC) columns, samples, and detectors^{1,2}. Some phases are destroyed by oxygen and phase polarity is altered by moisture. Polarity of absorbent packings is altered or the phase is deactivated by moisture³. Both oxygen and moisture can affect the lower level of detection, and in some cases can even ruin a detector⁴.

Oxygen has detrimental effects on the phases and adsorbents used in chromatography. Porous polymers, for example, react with oxygen and form carbonyls⁵. Furthermore, the higher the oven temperature at which a column is exposed to oxygen, the shorter the column life⁶. Although the effects of oxygen on packed columns are well known, these effects are more pronounced on the thin film of phase used in capillary columns^{7,8}. All capillary column manufacturers warn against using non-purified gases and recommend the use of oxygen traps.

The effects of moisture on the chromatographic process have been looked upon as both an advantage and a handicap. In many cases, variations in moisture level will cause peaks to shift, making it difficult to identify the affected peaks^{9,10}. Some investigators have found the shifts in phase polarity to be beneficial to their separations. But it is difficult to maintain a consistent level of moisture for such systems¹¹. Some polymeric phases such as the polyglycols (*e.g.*, Carbowaxes®), polyesters (*e.g.*, diethylene glycol succinate, ethylene glycol succinate), polyamides, and cyanosilicones

may depolymerize in the presence of moisture¹²⁻¹⁴. Absorbents such as activated aluminas, silica gels, and molecular sieves will be deactivated or their activity will be changed^{15,16}.

The effects of moisture and oxygen on detectors vary according to the type of detector. If the detector is sensitive to oxygen or moisture, the presence of these contaminants makes the detector less responsive to trace components in samples. Because these gases vary in concentration, baselines tend to be unstable¹⁷. Oxygen will shorten filament life in thermal conductivity detectors¹⁸ and cause high noise levels with electron-capture detectors¹⁹. Many other detectors will exhibit similar problems if exposed to oxygen or moisture²⁰⁻²².

These problems make it essential to remove both oxygen and moisture from carrier and make-up gases. Chromatographers are well aware that oxygen and moisture can enter the GC system in contaminated carrier gases (even in supposedly high grade materials), or through valve or fitting leaks, inappropriate or faulty regulator diaphragms, or leaks in septa²³. In attempts to eliminate these contaminants, many analysts use the highest quality gases available and incorporate purifying devices in gas lines. Many column and instrument manufacturers recommend using a regulator with a stainless-steel diaphragm^{24,25} because oxygen can diffuse through a butyl rubber diaphragm.

Yet columns and detectors are still damaged by oxygen and moisture. Very little is known about the ability of gas purifying devices to remove moisture and oxygen from carrier gas streams. This work was done to determine the effectiveness of these devices.

EXPERIMENTAL

Testing procedures

General tests. Carrier gas purifiers can be classified in three groups, based on construction: those with plastic bodies and metal end caps with O-ring seals, those with metal bodies and Swagelok® fittings, and those with glass bodies and Swagelok fittings with Teflon® ferrules. In all, 20 purifiers representing all three forms of construction, and designed to remove moisture, oxygen, or both, were tested by using a two-part procedure. All purifiers were tested as received, except that obvious leaks were sealed by tightening the fittings. In the first part of the procedure, pure carrier gas was introduced into a purifier. The effluent was monitored to determine whether oxygen or moisture entered the device from the atmosphere. In the second stage, carrier gas containing 300 ppm of moisture or 5 ppm of oxygen was supplied to the purifier. The effluent was monitored to determine if the purifier removed the contaminant it was designed to remove. Conditions used for these tests were: carrier gas flow-rate, 100 ml/min; pressure, 70 p.s.i.g.; purifier tube temperature, ambient (unless otherwise noted); relative humidity of atmosphere, 55% (unless otherwise noted).

Contaminant source isolation tests. Because the tests with contaminant-free carrier gas indicated considerable amounts of oxygen and water entered purifiers constructed of plastic, additional tests were performed to determine the source of the problem. A typical polycarbonate purifier tube was emptied, reassembled, and installed in the system. The seals were tested with leak detection fluid and with a GOW-MAC (thermal conductivity) leak detector, and no leaks were found. The empty tube

was purged with contaminant-free carrier gas and oxygen and moisture levels in the effluent were compared with values obtained for the adsorbent-filled tube. To distinguish between leaks at end fittings and permeation of contaminants through the body of the tube, the end fittings on the empty purifier then were sealed with a moisture-barring glue. Oxygen and moisture levels in the effluent from the sealed tube were compared to those for the empty, unsealed tube and the adsorbent-filled tube.

Two additional tests were performed on empty polycarbonate tubes. A tube was placed in a GC oven and connected to the system. The temperature was varied (20, 25 and 45°C) to determine if contamination in the effluent gas increased with increasing temperature, as permeation theory predicts. Finally, contaminant levels for empty 15 and 35-cm tubes were compared to determine the relationship between permeation and surface area.

Equipment

A system was established to introduce known concentrations of moisture into a purifier and recover the effluent for analysis (Fig. 1). The major components of the system are: moisture monitor, DuPont Instruments Model 26-303 (range, 1–1000 ppm water, built-in flow controller); high-capacity carrier gas purifier, Supelco; pressure regulator, Veriflow; four- and six-port valves, Valco; moisture source, 30 cm × 3.7 cm polycarbonate tube with metal caps glue sealed to the plastic body; nitrogen source, liquid nitrogen with vaporizer.

To prove the system was inherently dry and leak free, a length of stainless-steel tubing was connected to the six-port valve, in place of the purifiers to be tested. After the system was purged, the valves were switched as they would be during the experiment. Moisture readings of less than 1 ppm were obtained in all positions. Likewise, a reading of 300 ppm was maintained when the moisture source was incorporated in the flow pathway.

A second system was used to introduce known concentrations of oxygen into a purifier and recover the effluent for analysis (Fig. 2). The major components of the system are: oxygen analyzer, Lockwood & McLorie Model GP (range, 1–200 ppm oxygen); high-capacity carrier gas purifier, Supelco; pressure regulator, Veriflow; flow

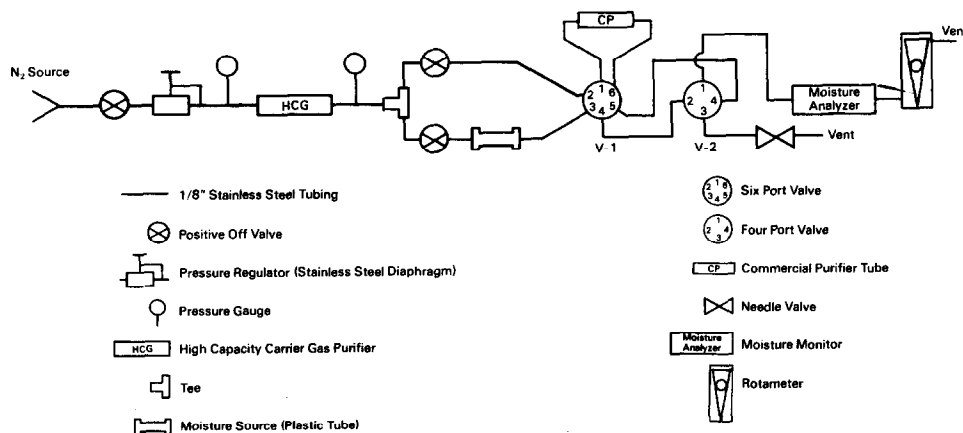


Fig. 1. Moisture analyzer system.

TABLE I
 PURITY OF CARRIER GAS PASSED THROUGH DEVICES DESIGNED TO REMOVE MOISTURE

Purifier source	Composition and type of fittings	Adsorbent	Oxygen in outlet gas (ppm)			Water in outlet gas (ppm)			Color change in indicator
			0 ppm introduced	5 ppm introduced	Color change in indicator	0 ppm introduced	300 ppm introduced	Color change in indicator	
Supelco OMI-1™ tube	Glass/Teflon® seals	Nanochem® resin	0.0	0.0	Yes	0.0	0.0	Yes	
R & D Separations moisture trap GHT	Glass/Teflon seals	Indicating mol. sieve/mol. sieve	3.0	NT*	No	0.6	0.6	Yes	
Supelco high temperature purifier	Metal/Swagelok® metal seals	Oxygen getter	0.0	0.0	NA**	0.0	0.0	NA	
Supelco drying tube	Metal/Swagelok fittings	Mol. sieve	0.5	NT	NA	0.5	NT	NA	
Analabs dryer tube	Acrylic/O-rings	Mol. sieve/silica gel	0.0	5.0	NA	11.0	NT	NA	
Lab-Clear refill gas filter	Polycarbonate/O-rings	Mol. sieve/Drierite	0.5	NT	No	13.8	14.4	Yes	
Alltech gas purifier	Polycarbonate/O-rings	Indicating Drierite/mol. sieve	1.25	NT	No	1.8	1.8	Yes	
Alltech economy gas purifier	Polycarbonate/O-rings	Indicating Drierite/mol. sieve	2.0	NT	No	6.0	6.4	Yes	
Alltech hydro purge	Polycarbonate/O-rings	Indicating mol. sieve/mol. sieve	3.5	NT	No	0.8	0.8	Yes	
Chrompack moisture filter	Polycarbonate/O-ring	Indicating mol. sieve/mol. sieve	5.0	5.0	No	95.0	NT	Yes	
R & D Separations	Polycarbonate/O-rings	Mol. sieve	6.5	9.2	NA	18.0	NT	NA	
Pierce gas dry filter	Polycarbonate/O-rings	Mol. sieve/Drierite	7.0	10.5	No	19.0	NT	Yes	
Alltech disposa purge	Polycarbonate/O-rings	Indicating mol. sieve/mol. sieve	8.0	NT	No	6.0	5.6	Yes	
Alltech hydro purge II	Polycarbonate/O-rings	Indicating mol. sieve/mol. sieve	13.3	NT	No	2.5	2.6	Yes	
			14.5	NT	No	5.0	5.0	Yes	

* NT = Not tested.

** NA = Not applicable.

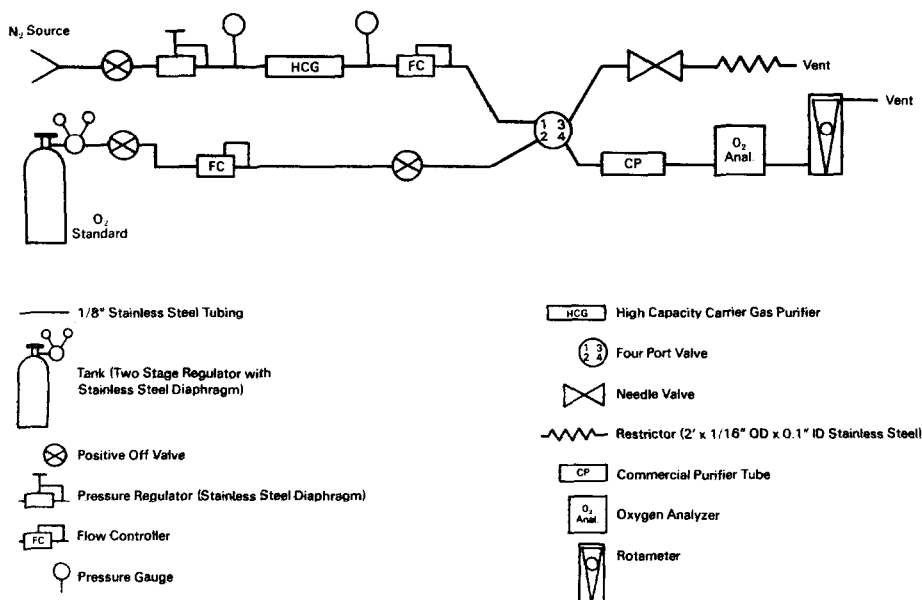


Fig. 2. Oxygen analyzer system.

controller, Veriflow; four-port valve, Valco; 5 ppm oxygen in nitrogen standard, Scott Gas; nitrogen source, liquid nitrogen with vaporizer.

The system was checked for leaks with a leak detector solution, then with a thermal conductivity detector. To obtain the greatest sensitivity from the thermal conductivity detector, helium was used to purge the system. Oxygen-free nitrogen and nitrogen containing 5 ppm oxygen were passed sequentially through the system. Readings obtained from the oxygen meter confirmed the oxygen concentrations. During these testing procedures, a length of stainless-steel tubing was connected to the four-port valve, in place of the commercial purifiers.

Other major equipment used in this work included: relative humidity gauge, Airguide Instrument; gas chromatograph, Varian Model 3700; thermal conductivity leak detector, GOW-MAC (GOW-MAC Instrument).

RESULTS AND DISCUSSION

Table I summarizes the results obtained for moisture traps and Table II summarizes results for oxygen traps. Purifiers for which both capabilities are claimed are included in both tables. The tables reveal several important points. First, many of the purifiers contaminate carrier gas streams, often with a contaminant the device was not designed to remove (*i.e.*, purifiers designed to remove moisture allowed oxygen into the gas; purifiers designed to remove oxygen allowed moisture into the gas). Second, purifiers having plastic bodies and O-ring seals gave the worst performance. Third, moisture-trapping purifiers introduced more contamination than oxygen-trapping devices.

TABLE II
 PURITY OF CARRIER GAS PASSED THROUGH DEVICES DESIGNED TO REMOVE OXYGEN

Purifier source	Composition and type of fittings	Adsorbent	Oxygen in outlet gas (ppm)		Water in outlet gas (ppm)		Color change in indicator	300 ppm introduced	Color change in indicator
			0 ppm introduced	5 ppm introduced	0 ppm introduced	0 ppm introduced			
Supelco OMI-1™ tube	Glass/Teflon® seals	Nanochem® resin	0.0	0.0	0.0	0.0	Yes	0.0	Yes
R & D Separations	Glass/Teflon shield	MnO ₂	0.0	0.0	2.8	2.6	Yes	2.6	No
O ₂ remover	Teflon seals								
Supelco high temperature purifier	Metal/Swagelok metal seals	Oxygen getter	0.0	0.0	0.0	0.0	NA*	0.0	No
Oxiclear disposable gas purifier	Metal/Swagelok metal seals	MgO/CuO/mol. sieve	0.0	0.0	0.5	NT	NA	NT	No
Supelco	Metal/Swagelok metal seals	Al ₂ O ₃ /CuO	0.0	0.0	0.5	0.5	NA	0.5	No
Supelpure™ O ₂	Metal/Swagelok fittings								
Messer Griesheim GMBH	Metal/O-rings	MgO/CuO/mol. sieve	0.0	0.0	9.5	NT**	NA	NT**	No
Oxisorb®	Polycarbonate/glass/O-rings	MnO ₂ /MgO/CuO	0.5	0.5	5.0	NT	Yes	NT	No
Chrompack O ₂ remover									

* NA = Not applicable.

** NT = Not tested.

Because results obtained with plastic, O-ring sealed purifiers were especially poor, tests were performed to determine the source of oxygen and water in gas leaving these devices. A polycarbonate device was emptied, carefully sealed, and purged with moisture-free gas. After water levels in the effluent were monitored, each end was sealed at the ferrule and at the connection between the plastic body and the metal cap by using a moisture-barring glue.

Results of these tests are presented in Table III. The "Emptied/resealed" value indicates that 60 ppm moisture entered the intact purifier from sources other than the carrier gas. The adsorbent in the purifier reduced this concentration to 18 ppm ("Intact tube" value). About 30 ppm moisture entered the empty tube after the ends were sealed. Therefore, small leaks at the end fittings and permeation through the plastic body apparently contribute equally to moisture entering the intact tube. In routine use, much of the drying capacity of this purifier would be used to remove moisture not present in the incoming carrier gas.

These results are consistent with subjective observations and previous investigations. The O-rings do not appear to provide an effective seal for plastic bodied carrier gas purifiers. In the process of installing these devices for testing, the end fittings often had to be tightened several times. Furthermore, small changes in temperature cause leaks.

Permeation of moisture through plastic is a well documented and understood phenomenon. According to Brown²⁶, permeation depends on several factors. The solubility of moisture in a polymer is defined as that volume which dissolves in a unit volume of the polymer under an applied unit pressure of moisture. It can be expressed by Henry's law

$$C = SP \quad (1)$$

where: C = volume of moisture (STP), S = solubility coefficient, and P = applied pressure. Fick's first and second laws can be used to describe steady state diffusion

TABLE III

CONTRIBUTIONS OF LEAKS AND MOISTURE PERMEATION INTO CARRIER GAS PURIFIERS TO GAS CONTAMINATION

Polycarbonate tube used at 20°C, 55% relative humidity, unless noted otherwise.

	<i>Water in outgoing carrier gas (ppm)</i>
<i>Relative contributions of leaks and permeation</i>	
Intact tube (filled with molecular sieve)	18
Emptied/resealed	60
Ends sealed	30
<i>Temperature effects (empty tube)</i>	
20°C	60
25°C	150
45°C	410
<i>Surface area effect (empty tubes)</i>	
147 cm ² surface	60
340 cm ² surface	140

of a gas or vapor through a polymer, and non-steady state diffusion when the concentration gradient is a function of time. From these relationships, an equation can be generated to describe the steady state permeation of moisture through a polymer

$$Q = DS \quad (2)$$

where: Q = permeability coefficient, D = diffusion constant, and S = solubility coefficient. The diffusion constant, D , is related to the permeated area. Thus, purifier tube dimensions can affect the amount of moisture entering the carrier gas, as we will show later.

The dependence of the permeability coefficient on temperature can be expressed by the Arrhenius relationship:

$$Q = Q_0 \exp(-E_p/RT) \quad (3)$$

where: Q_0 = permeation constant per type of material, E_p = activation energy for the permeation process, R = gas constant, and T = absolute temperature. Other factors affecting permeation are the thickness of the plastic, the amount of surface area exposed to the atmosphere, and the moisture content of the room air.

With so much known about permeation of moisture through plastics, one must question why these materials are used in devices intended to remove moisture from gas streams. Our work, summarized here, proves that the amount of moisture permeating into the system can be high enough to affect column performance.

Purifiers are exposed to varying temperatures when used in conjunction with a gas chromatograph. For example, the oven may blow hot air on the purifier during the cool down stage. Consequently, the empty tube from the permeation and leak experiments was used at two additional temperatures, 25 and 45°C, to evaluate temperature effects. The results are presented in Table III. It was assumed that the moisture content of the air would not change with the increased temperature because there is a rapid exchange of air in the GC oven.

The results indicate that moisture permeation increases drastically as the temperature rises. Oxygen permeation increases in the same way. For polycarbonates, the permeation constants for moisture and oxygen are 9900 and 300 ml/mil/100 in²/24 h/atm²⁷, respectively. Because the oxygen permeation constant is only 1/33 that for moisture, we would expect oxygen permeation values of 1 ppm or less for our tests at room temperature. Our oxygen meter was not sufficiently sensitive to detect differences at this level.

Eqn. 2 indicates that permeation will increase in direct proportion with surface area. A comparison was made between two empty 3.7 cm O.D., 2.6 cm I.D. tubes, one 35.0 cm long and the other 15.1 cm long (the length we used for most of our work), with inside surface areas of 340 cm² and 147 cm², respectively. The ratio between the two surface areas is 2.32:1. If moisture permeation varies directly with surface area, moisture should enter the two tubes in the same ratio. The values obtained were 140 and 60 ppm, respectively (Table III), a ratio of 2.33:1. This value is in agreement with the ratio for surface areas. Therefore, as the surface area of a purifier is increased, proportionally more moisture permeates the device. Analysts who use larger purifiers expect to replace the device less often, yet these data indicate that much of the additional drying capability may be wasted.

Plastic and glass bodied purifier tubes are used to provide visual information on tube performance. Two types of color indicating oxygen traps are used in purifiers and were evaluated in this study. Most of the devices use manganese dioxide, which changes from green to brownish black when exposed to oxygen. The other material, Hercules Nanochem resin, changes from black to brown. Both materials respond to very low concentrations of oxygen (1 ppm or less), and change color in seconds.

Moisture indicators used were cobalt chloride (blue to pink) and the same Hercules Nanochem resin used to indicate oxygen (black to brown). The cobalt chloride color change involves an equilibrium reaction with moisture and is dependent on the partial pressure of moisture present in the system. The color change transition occurs at concentrations of about 110 ppm moisture at 70 p.s.i.g. manifold pressure²⁸. Thus, this material is insensitive to moisture levels encountered in GC. The Nanochem resin, on the other hand, is sensitive to moisture, as well as to oxygen, at a level of 1 ppm, and therefore is ideal for GC use.

CONCLUSIONS

An analyst must be very careful in choosing a purifier to remove moisture and oxygen from carrier gas. Many of the available devices actually reduce the quality of the gas they are intended to purify. All plastic bodied purifiers are permeable to moisture. Devices with O-ring seals appear to be highly susceptible to leaks, and also should be avoided. Only all metal or glass devices with Swagelok fittings appear to be leak and permeation free. Manganese dioxide and Hercules Nanochem resin are effective color indicators for oxygen. The only color indicator available that works effectively for moisture is Nanochem resin.

REFERENCES

- 1 D. David, *Gas Chromatographic Detectors*, Wiley, New York, NY, 1974.
- 2 J. Ševčík, *Detectors in Gas Chromatography, Journal of Chromatography Library*, Vol. 4, Elsevier, Amsterdam, 1976.
- 3 R. Villalobos, *Testing for Water in the Carrier Gas*, Beckman Representatives Memorandum, Beckman, Fullerton, CA, Jan. 23, 1967.
- 4 D. M. Ottenstein, *CHEMTECH.*, (1974) 705.
- 5 M. G. Neumann and S. Mocalles T., *J. Chromatogr.*, 74 (1972) 332.
- 6 *Technical Bulletin 739*, Supelco, Bellefonte, PA, 1984.
- 7 R. R. Freeman, *High Resolution Gas Chromatography*, Hewlett-Packard, Avondale, PA, 1979, p. 41.
- 8 W. Jennings, *Gas Chromatography with Glass Capillary Columns*, Academic Press, New York, 1980, pp. 164-165.
- 9 R. Villalobos, *Effect of Water in the Carrier Gas on Gas Chromatographic Analysis*, Beckman Representatives Memorandum, Beckman, Fullerton, CA, Jan. 16, 1967.
- 10 R. Villalobos, *Instrum. Technol.*, Oct. (1967) 59-62.
- 11 A. Nonaka, *Anal. Chem.*, 44 (1972) 271.
- 12 R. T. Morrison and R. N. Boyd, *Hydrolysis*, Allyn and Bacon, Boston, MA, 1973, pp. 589, 638, 671-672, 686.
- 13 J. R. Conder, N. A. Pruittawla and M. K. Shinagar, *J. Chromatogr.*, 269 (1983) 171.
- 14 J. E. Purcell, *Chromatographia*, 15 (1982) 546.
- 15 B. Thompson, *Fundamentals of Gas Analysis by GC*, Varian, Palo Alto, CA, 1974, pp. 3-13.
- 16 W. Supina, *The Packed Column in Gas Chromatography*, Supelco, Bellefonte, PA, 1974, pp. 39-42.
- 17 A. T. Blades, *J. Chromatogr. Sci.*, 14 (1976) 45.
- 18 L. S. Ettre, *Chromatographia*, 13 (1980) 203.

- 19 W. A. Aue and S. Kaplia, *J. Chromatogr. Sci.*, 11 (1973) 255.
- 20 B. A. Schaefer, *J. Chromatogr. Sci.*, 16 (1978) 211.
- 21 S. S. Brody and J. E. Chaney, *J. Chromatogr. Sci.*, 4 (1966) 42.
- 22 D. J. Von Lehmden, *Suppression Effect of CO₂ on FPD Total Sulfur Air Analyzers and Recommended Corrective Action, Proceedings of the 4th Joint Conference on Sensing of Environmental Pollutants, 1978.*
- 23 P. K. Wittman and J. W. Mitchell, *Appl. Spectrosc.*, 40 (1986) 156-162.
- 24 R. B. Denyszyn, *Gas Chromatography: Detectors, Gases, Delivery Systems —What are the Variables?* (Parts 1 and 2) Scott Tech Newsletter No. 4 and 5, Scott Instrument, Plumsteadville, PA, Feb., 1982 and Nov., 1983.
- 25 *Supelco Catalog 24*, Supelco, Bellefonte, PA, 1985, p. 91.
- 26 R. P. Brown, *Handbook of Plastic Tests Methods*, George Godwin, Pitman Press, Bath, 1981, pp. 378-381.
- 27 *Lexan Technical Report —Polycarbonate Film and Sheet Properties*, Technical Report No. CDC-396 (Revision F), General Electric, Pittsfield, MA, p. 3.
- 28 *Drierite Equipment Catalog*, W. A. Hammond Drierite, Xenia, OH, 1980, p. 20.