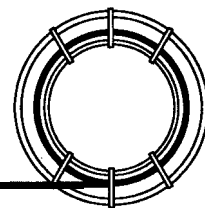


Hints for the Capillary Chromatographer



Using Flame Ionization Detectors

The flame ionization detector (FID) is the most widely used GC detector. The FID is a destructive, mass flow dependent detector that utilizes a flame source to ionize compounds. Compounds responding to FIDs include all organic compounds that ionize in a hydrogen and air flame. Many of these compounds are found in petrochemical, industrial, environmental, clinical, and flavor and fragrance analyses.

The FID is considered a universal detector since it responds to a wide variety of organic compounds. However, carbon dioxide, carbon monoxide, nitrogen, oxygen, carbon disulfide, and inert gases produce little or no response by FID. Formaldehyde, formic acid and heavily halogenated compounds produce a low or non-linear response, because of the few carbon/hydrogen bonds present.

Detector Operation

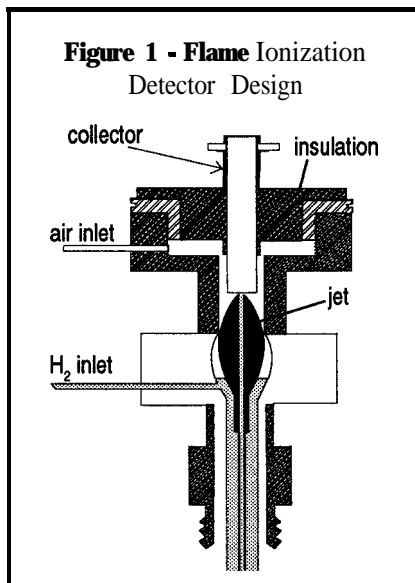
A signal for an FID is produced when a sample combusts in a hydrogen/air flame and ionizes (Figure 1). Because the FID is a mass sensitive detector, it will respond to the amount of material passing through the flame at a given time. The response of a component is directly proportional to the amount injected.

FIDs can detect concentrations of saturated compounds as low as 20pg. However, FIDs are not practical for quantitating compounds below 0.1ng because baseline noise from air movement around the collector, electrical noise, gas contaminants, and column bleed reduces FID sensitivity (signal/noise ratio). In addition, the presence of compounds with minimal carbon/hydrogen bonds (i.e., carbonyl, alcohols, halogens, amines, etc.) also make detectability below 0.1ng difficult. When an increase in concentration no longer produces an increase in response, the detector has reached its maximum linear range. The FID has the largest linear range of all the common GC detectors, 10^7 times the minimum detectable level of a hydrocarbon.

FID jet orifices range from 0.011" to 0.030". In general, the smaller the jet orifice, the more sensitive an RD. Internal diameters of 0.011" are used for narrow bore capillary columns (<0.25mm ID) when high sensitivity is desired. However, smaller orifices are prone to plugging and are impractical for packed columns or thick film capillary columns. Some packed columns with high phase loadings require a 0.030" jet. In most cases, jet orifices of 0.018" are used.

Detector Gases

FID gas flow rates are generally optimized at 30cc/min. hydrogen, 30cc/min. carrier plus make-up gas, and 300cc/min. air.



Hydrogen gas is heated as it flows around the side of the jet and is mixed with the make-up gas and sample effluent exiting from the column. The combined gases travel through the jet tail and combust as they exit the jet orifice. Because there is an applied voltage across the jet, a current is produced by the ionized particles as they reach the collector and is measured by an electrometer.

Sensitivity can be increased by decreasing the hydrogen flow rate relative to the carrier and make-up gas. Usually, a 1: 1.25 ratio of hydrogen to carrier gas (25cc/min H₂, 30cc/min carrier + make-up) increases sensitivity. However, at lower hydrogen flow rates, the flame is prone to extinguishing as large volumes (>2μl) of water elute. A higher than optimum hydrogen flow rate is usually necessary when using water as a solvent to ensure the flame remains lit at all times. Increasing the air flow rate above 300cc/min. has little effect on FID sensitivity. However, increasing the air flow rate to 400-450 ml/min. will extend the linearity of the FID when high concentrations of analytes are injected. Since there are variations in detector design, consult your instrument manual for optimum gas settings.

Carrier, hydrogen, and air should be of high purity or the FID background noise will increase. Excessive moisture in the hydrogen or air is particularly a problem. Make-up gas is frequently recommended with capillary columns to optimize detector performance, reduce dead volume, and minimize band broadening. Without make-up gas to augment the typical 5cc/min. carrier gas flow rate of a capillary column, the flame burns rich which results in increased noise and non-linearity.

Detector Maintenance

FIDs can become contaminated from stationary phase bleed and sample residue. Most stationary phase bleed consists of low molecular weight silicone polymer fragments that form a white silica powder when burned in the flame. This contamination can deposit on the jet tip and collector increasing background

noise. In cases of severe contamination, noise spikes occur as the silica particles are carried into the flame. Other stationary phases such as Carbowax™ and high molecular weight sample contaminants form a residue that coats the detector surfaces. As the coating builds, noise increases and sensitivity diminishes.

Figure 2 shows a chromatogram obtained before and after a new jet was installed. In the first chromatogram, active compounds such as benzoic acid and 2,4-dinitrophenol (peaks 3 & 5) are tailing and produce a reduced response. By installing a new jet, peak shape and response could be restored. The problem was identified as stationary phase contamination from a Carbowax® column that was previously installed in the GC. Because the Carbowax™ column has a lower maximum temperature than an XTI®-5 column (250°C vs. 360°C), the stationary phase decomposed when the detector temperature was increased to elute higher molecular weight compounds.

In addition to stationary phase bleed and sample residue, glass fragments or short pieces of fused silica tubing can break off and become lodged in the small jet orifice causing peak tailing or adsorption. This can occur during installation as the column is inserted into the jet and pushed as close to the orifice as possible. Often, excessive tailing solvent or sinusoidal baseline signals indicate a fused silica fragment lodged in the jet.

Inexpensive FID cleaning kits are available from most chromatography suppliers and contain jet reamers, tube brushes, and emery cloth to make cleaning easy. Avoid using kits with brass brushes which leave metal fragments inside the FID. To clean an FID, cool the detector, disassemble the collector assembly, and remove the jet. It is important to inspect the FID base for particles by shining a flashlight into the oven and through the fitting until the light exits the top of the FID where the jet is attached. Rotate the light to look for particles or contamination

that might be on the FID base wall. Clean the detector base with a 1/4" brush. Next clean the jet orifice with a jet reamer and a stainless steel toothbrush. Shine a flashlight through the jet bore and look for dull spots or particles lodged in the bore. Clean the jet in an ultrasonic bath with solvents such as methylene chloride to remove the contamination. Discard the jet if it can not be cleaned. Finally, clean the electrometer metal contacts and spring clips with emery cloth to ensure a noise free signal. Wipe off the metal dust by using a Kimwipes® or cloth moistened with solvent. Reassemble and allow the detector temperature to reach 150°C before installing a column or lighting the flame.

FID Operating Hints

The FID temperature should always be operated above the final oven temperature to prevent stationary phase or sample components from condensing in the detector. Since the column is installed in the detector's heated zone, never heat the FID above the stationary phases maximum operating temperature or decomposition and excessive bleed will occur. Never set an FID temperature below 100°C or water vapor from the flame will condense in the detector. Always install the capillary column as close to the jet orifice as possible to prevent sample adsorption or decomposition on the metal surfaces of the jet. Inert Silcosteel® FID jets should be used with active samples to prevent adsorption or decomposition. In addition, ceramic jets for high temperature applications are used by some instrument companies for MXT® or fused silica lined metal capillary columns to prevent grounding of the electrical signal.

Due to its ease of use and nearly universal response to most organic compounds, the FID has become the most commonly used GC detector. Proper care and routine maintenance is required to keep an FID working at maximum sensitivity with minimum background noise.

Figure 2 - Peak tailing and adsorption occur when sample residue or stationary phase bleed deposits in the FID jet tail and interacts with the sample stream.

