Technical note TNE-04

Pure gas for gas chromatography

A gas chromatograph (GC) is probably the most versatile gas analyzer on the market today. A number of gases are required to operate the instrument, and the gas quality must be taken into account to ensure a good result.

In a gas chromatograph, the components of a gas or liquid mixture are separated in a column and passed one after the other to a quantitative determination detector. Many types of detectors are available on the market, and are selected based on which components are to be analyzed.

The quality of the carrier gases and detector gases supplied to a gas chromatograph is of the utmost importance for achieving the best results. In particular, capillary columns are subject to problems caused by impure carrier gases. The same is true of detectors with high sensitivity and selectivity. The purity of combustion gases for certain types of detectors is also critical.

The components are transported through a gas chromatograph using a carrier gas. This carrier gas usually comes from a high pressure gas cylinder. Modern gas chromatographs are very sophisticated instruments, but the analysis results will depend on the pure gases used. If gases of the correct degree of purity are selected, the gas chromatograph will also perform to the maximum. If you choose a product with poorer specifications, you risk getting drift in the baseline and thus results with high uncertainty. Or worse, the column or detector can be damaged, leading to interruptions, lost revenue and often equipment replacement.

The detector indicates presence and quantitatively measures the components coming from the column. There is no ideal detector, but Thermal Conductivity Detector (TCD) will almost certainly be called a universal detector.

Always use gases that at least meet the requirements of the instrument manual. Assessments with regard to particularly sensitive applications are necessary in order to be able to approach the detection limit of the instrument. The signal-to-noise ratio can be increased by using high purity and specially adapted gases that promote the lowest detection limits.

Thermal Conductivity Detector (TCD)

The TCD detector is the oldest detector in gas chromatography. It responds to all components that have a different thermal conductivity than the carrier gas. Helium is often used for TCD because it has an exceptionally high thermal conductivity and is chemically inert. For this reason, it gives large differences in thermal conductivity (which gives superior sensitivity) with other compounds, except hydrogen. If hydrogen is used as a carrier gas, the sensitivity will increase by almost 25% compared to helium.

The most common detectors are:

- Thermal Conductivity Detector (TCD)
- Flame Ionisation Detector (FID)
- Electron Capture Detector (ECD)
- Photo Ionisation Detector (PID)
- Flame Photometer Detector (FPD)

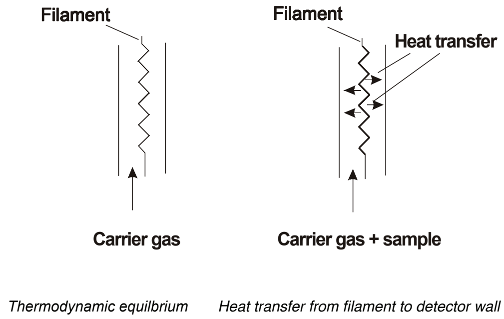

Fig.1 Thermal Conductivity Detector (TCD)

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Critical impurities in the carrier gas for TCD are moisture and oxygen. Since the filaments are hot (the detector is also called a "hot wire detector"), the effect of oxygen and moisture flowing over the hot elements will be that they will oxidize, which eventually reduces the sensitivity and eventually the filaments will break off. Carbon monoxide and carbon dioxide have the same effect on the filaments.

Flame Ionisation Detector (FID)

FID utilizes a flame that is produced by burning hydrogen in air. Few ions are formed until an organic compound enters the flame. Then an increase in the ions will take place. If a collector with a polarizing voltage is applied near the flame, the ions will be attracted to the collector and produce a current, which is proportional to the amount of sample in the flame. The gas stream from the column is mixed with hydrogen and is passed through the flame. The synthetic air is supplied separately. Nitrogen is used as a "makeup" gas for detecting components down in the low ppb areas, see Figure 2.

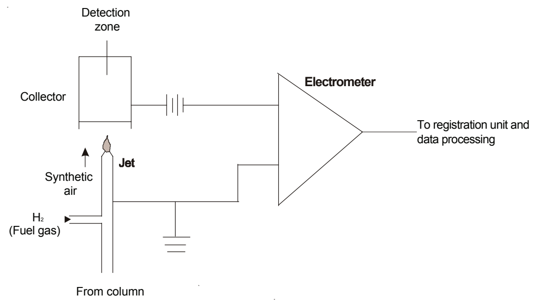

Fig. 2. Flame Ionisation Detector, FID

The modern FID is very sensitive to hydrocarbons, and is used to detect these in the low concentration ranges. Critical contaminants in the working gases (fuel gas, carrier gas, make-up gas and synthetic air) are usually hydrocarbons, as these give a background signal in the detector. This means that the signal-to-noise ratio is significantly reduced.

The background signal can be compared to the length of the grass on a golf course, and the signal from the components with the golf ball. The longer the grass, the harder it is to find the ball. It will be the same with the analysis; it is much more difficult to find the interesting component signal among the noise from the background signal, see Figure 3.

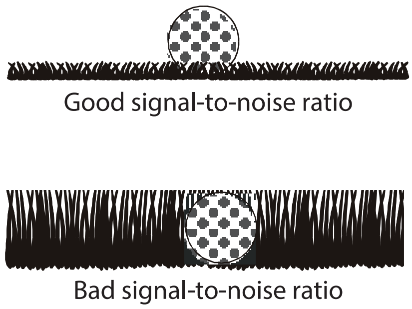

Fig. 3.

Oxidizing compounds such as oxygen, moisture, carbon dioxide and carbon monoxide can cause corrosion of the burner, leading to increased background noise.

Electron Capture Detector (ECD)

The ECD measures the reduction of a signal instead of a positively produced electrical signal. As the carrier gas flows through the detector, a Nickel-63 source will ionize the carrier gas molecules and slow electrons are formed. If a sample containing electron-absorbing molecules is introduced, this current will be reduced. The "loss" of current is a measure of the amount and electron affinity of the compound, see Figure 4.

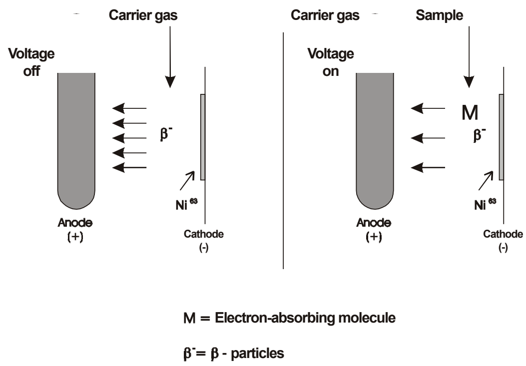

Fig. 4. Electron Capture Detector (ECD)

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Organic polyhalides are very strong electron-trapped compounds. Good examples are chlorofluorocarbons, SF_6 etc. Oxygen compounds, phosphorus or aromatic rings are less sensitive in an ECD. Many compounds, such as paraffins and simple hydrocarbons, are practically transparent to the electrons.

Organic solvents used to clean pipes etc. are very often chlorofluoro-carbons. If not all traces of these solvents are removed from the piping systems before use, the analytical results may be disturbed.

Halogen compounds can produce noise and negative peaks.
Oxygen and moisture can affect the detector response and increase noise.
Hydrocarbons can lower the signal, give negative peaks and "ghost peaks".

Photo Ionisation Detector (PID), Figure 5

The Photo Ionisation Detector consists of a UV lamp and an ionization chamber. The lamp is filled with a gas (usually argon or hydrogen) and produces an emission line that is characteristic of the gas when it is excited. The radiation passes through a window of metal fluoride and into the ionization chamber or cell. Here the sample absorbs the UV radiation and ionizes. Electrodes capture the ions and the measured current is proportional to the sample concentration.

PID responds most strongly to unsaturated and aromatic hydrocarbons and sulfur compounds in the most common environmental and petroleum applications. The optical window is subject to contamination, both from hydrocarbons and background noise from the column, especially if makeup gas is added and the analyzer uses capillary columns. Electron negative compounds (saturated hydrocarbons) reduce the signal. Pure carrier gases and makeup gases will reduce the need for maintenance of the detector.

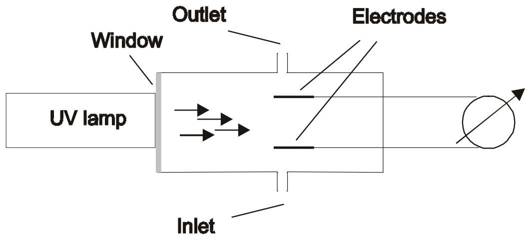

Fig. 5. Photo Ionisation Detector, PID

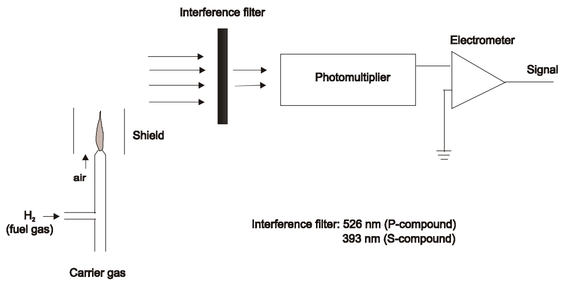

Fig. 6. Flame Photometer Detector, FPD

Flame Photometer Detector (FPD), Figure 6

FPD uses the principle that hydrocarbons that contain sulfur and phosphorus produce chemiluminescent substances if they are burned in an FID-type flame. These substances emit light of characteristic wavelengths in the sample. An optical filter allows light of the desired wavelengths to pass. The light hits a sensor (photomultiplier) and the associated electronics produce a signal.

Contaminants of hydrocarbons and carbon dioxide can reduce the detector's response. Never use compressed air for the flame as it normally contains relatively large amounts of carbon dioxide and smaller amounts of oil and other hydrocarbons.

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The oxygen content of the carrier gas must also be checked as oxygen can have an adverse effect on oxidizable sulfur components such as mercaptans.

Troubleshooting

Detector noise and drift in a GC system also have other causes than the purely electronic ones. Impurities in the gases used for a gas chromatograph are also a source of error. "Ghost peaks", drift in the baseline and noise from the detector that cannot be corrected by other measures can come from contaminants in the carrier gas. Techniques that systematically isolate parts of the gas system are effective when troubleshooting.

The detector is the primary source of information from an analysis system. First, make sure that the detector is working properly by supplying the system with gas from a separate source of known quality from a pre-cleaned distribution system. If that does not help, it is likely that the fault is in the GC. If the problem disappears, the problem is related to either the gas or the gas distribution network.

If the latter is the case, check the entire distribution system, including regulators, valves, pipes, etc. or inside the analyzer itself. Either there is a leak or the gas is in contact with equipment that is not designed for this application, such as equipment that is intended for industrial applications. This equipment is absolutely not suitable for high purity applications such as gas chromatography.

An unsuitable gas handling system can contaminate the internal pneumatic components of the analyzer. If this happens, it can take a long time for the contaminants to come out of the system, if they do at all.

The best approach is to establish a high quality gas distribution system first, as part of the instrument installation.

Column protection

In most quality control laboratories, where routine analyzes with concentrations in the higher areas dominate, experienced laboratory technicians and engineers etc. can say the analysis results by just taking a look at the chromatogram. Stable baselines are not a big deal in these cases. Unstable baselines usually come from impurities in the carrier and detector gases, and if these impurities are allowed to accumulate in the column, the life of the column will be considerably reduced.