

Choosing the proper gas and gas equipment for the laboratory, Part 1: Relationship between gas purity and detection limits in gas chromatography

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Many analytical techniques require the use of specialty gases (e.g., He, H₂, N₂, Ar, O₂, etc.) and/or their mixtures. The purpose of gases for an analytical procedure depends on the technique, and it is a crucial part of the procedure. The quality of the gas used therefore significantly impacts the potential results. The laboratory manager must understand the effects of gas purity on the quality of the results obtained. Most industrial gas companies offer a range of gas purity levels. Frequently, the effect of the gas quality on the obtainable results is not well understood. An order may be placed without reference to the consequences of the purity on the analytical results.

This paper describes the relationship between the gas purity and the obtainable detection limit for the detectors commonly used in gas chromatography. The required gases and the effect of various impurities are first described, followed by a method of estimating the relationship between carrier gas purity and the obtainable detection limit.

Specifications

Gas chromatography is an analytical technique that normally uses a large quantity of pure gases. The nature of these gases is shown in *Table 1* for the main detectors in use today.¹

In gas chromatography, it is well known that water, oxygen, and hydrocarbons are the major critical impurities for chromatographic columns or detector response.¹ *Table 2* shows some disturbances produced by these classic pollutants.

While the consequences of a reduced column lifetime are obvious, the baseline disturbances directly affect the accuracy of the results that are obtainable with the analyzer. In order for analysts to choose the appropriate gas quality in coherence with their analytical needs, a complete product range for analytical chemistry and gas chromatography applications is offered (**Air Liquide Corp.**, Paris, Cedex, France). For each of the gases, a wide range of containers includes cylinders and benchtop generators for on-site production in the case of hydrogen, air, and nitrogen. The simplicity of the range allows the analyst to easily select the appropriate gas purity for the analytical applications (*Table 3*).

The laboratory manager must understand the effects of gas purity on the quality of the results obtained.

A general guideline for selecting the correct carrier, fuel, or make-up gases is to use the correct gas purity that does not interfere with analyses or damage equipment. In other words, if one is working in percent levels, there may be no need for the same gas purity used for ppm or subppm analysis.

Table 1

Gases used with commonly used detectors			
Detector*	Carrier gas	Fuel gas	Make-up gas
FID	He, H ₂ , N ₂	Air + H ₂	N ₂ , He, H ₂
TCD	He, H ₂	None	Same as carrier gas
ECD	N ₂ , He, Ar/5% CH ₄	None	N ₂ , Ar/5% CH ₄
FPD	N ₂ , He	Air + H ₂	Same as carrier gas
HID	He	Air + H ₂	He
NPD	He, H ₂ , N ₂	Air + H ₂	He
PID	He, H ₂ , N ₂	None	N ₂ , He
ELCD	He, H ₂	H ₂	None

* FID: flame ionization detector, TCD: thermal conductivity (or hotwire) detector, ECD: electron capture detector, FPD: flame photometry detector, HID: helium ionization detector, NPD: nitrogen phosphorus detector, PID: photoionization detector, ELCD: electron conductivity detector.

Table 2

Disturbances caused by classic pollutants	
O ₂ or air (in inert gas)	Reduce column life
H ₂ O	
CO ₂	
CO	Baseline disturbances
Hydrocarbons	

Table 3

Gases	Alphagaz 1 and Alphagaz 2 pure gases*	
	Alphagaz 1	Alphagaz 2
Ar, H ₂ , He, and N ₂	H ₂ O < 3 ppm	H ₂ O < 0.5 ppm
	O ₂ < 2 ppm	O ₂ < 0.1 ppm
	C _n H _m < 0.5 ppm	C _n H _m < 0.1 ppm
		CO < 0.1 ppm
Air	H ₂ O < 3 ppm	CO ₂ < 0.1 ppm
	C _n H _m < 0.5 ppm	N ₂ < 0.1 ppm in Ar and He H ₂ < 0.1 ppm in Ar, He, and N ₂

*Air Liquide Corp.

While the above concepts may appear to be self-evident, the question of how to make an appropriate selection without a series of tests is not evident. Thus, a simple calculation method is given that can be used to make the estimation, and charts are provided for the different detectors.

Calculation method

Relationship between gas purity and detector

When a carrier gas containing an impurity arrives at the detector, it produces a signal proportional to the flow rate and to the concentration of this impurity. Also, a GC detector could be represented following its lowest detection limit and its domain of linearity (e.g., FID sensitivity limit: about 10⁻¹² g of C/sec; domain of linearity: about 10⁷) or its field of use (FTIR) (see *Figure 1*).

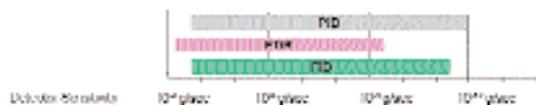


Figure 1 Domain of linearity or field of use for various GC detectors.

Then, considering that Alphagaz 1 is specified to less than 3 ppm of H₂O, 2 ppm of O₂, and 0.5 ppm of C_nH_m as critical impurities, and that the mean carrier gas flow rate into the GC is between about 1 and 60 cm³/min (packed or capillary columns, with or without makeup), the possible range for the quantity of water arriving to the detector per sec can be calculated to be about 10⁻⁹ g/sec. The same reasoning can provide an estimation for hydrocarbons and O₂ impurities challenging the detector.

Alphagaz 1 is therefore the appropriate carrier gas for analyzing samples when more than 10⁻⁹ g of compound/sec reaches the GC detector. The same calculation for Alphagaz 2 shows that this grade is adapted for less than 10⁻¹⁰ g of compound/sec (see Figure 2). Following this method, the addition of other detectors is easily done.

More appropriate scale

While Figure 2 is useful, the units are not immediately evident, since a chemist is more interested in the relationship between the concentration of the analysis and the requisite quality of gas. This problem can be solved by answering the following question: What is the initial sample concentration corresponding to 10^{-x} g/sec arriving on the GC detector?

For liquid sample injection (about 1 µL or 1 µg), consider, for instance, that 10⁻⁹ g/sec will be contained in this 1 µg. Also, it is easy to calculate that the sample concentration is near 1 mg/L.

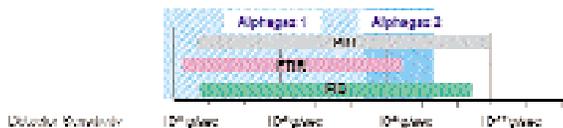


Figure 2 Relationship between gas purity and domain of linearity or field of use for some GC detectors.

In the case of gas analysis, the injected volume is about 100 µL or 4.5 10⁻⁶ mol of gas. Also, assuming a mean molecular weight of 80 g, 10⁻⁹ g/sec or 1.2 10⁻¹¹ mol/sec is present in this volume and the initial concentration will be about 1 ppm.

Using these assumptions, it is easy to transform the initial scale to a working scale. Nevertheless, many hypotheses have been made, and the results must be taken as indications, not as absolute values.

Conclusions

Figure 3 summarizes the calculations for the frequently used detectors in gas chromatography. It is essential to consider the stability of the column against oxygen and/or water. Some columns (containing cyano groups, for example) may be damaged by these impurities, irrespective of the sample concentration. In this case, Alphagaz 2 should be selected as the carrier gas.

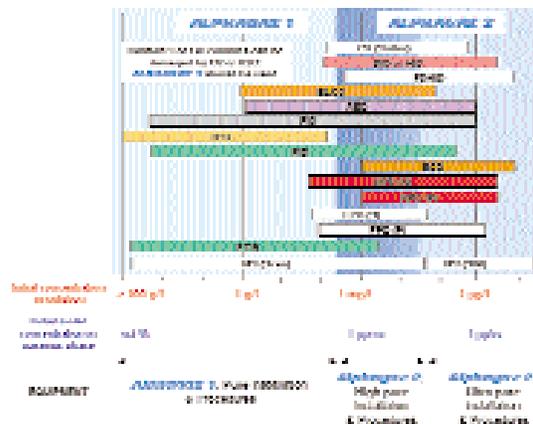


Figure 3 Relationship between gas purity, frequently used GC detectors, and level of analysis. FID: flame ionization detector, TCD: thermal conductivity (or hotwire) detector, ECD: electron capture detector, CD: chemiluminescence detector, DID: discharge ionization detector, PDHID: pulsed discharge helium ionization detector, ELCD: electrochemical detector, AED: atomic emission detector, PID: photoionization detector, HID: helium ionization detector, NPD: nitrogen-phosphorus detector, FPD: flame photometric detector, FTIR: infrared detection detector, MSD: mass spectroscopy detector. Scan: full scan operation, SIM: selective ion monitoring.

In the case of analysis of compounds at concentrations below 100 ppb in gaseous phase or 10 µg/L in solution, Alphagaz 2 is recommended, along with appropriate installations and procedures. For example, a cross-purge assembly will be installed between the cylinder and pressure regulator to prevent contamination of the system during cylinder changes. The valves and pressure regulator parts will be all stainless steel, and their leak integrity will be less than 10⁻⁹ atm.cm³.sec⁻¹. Electropolished tubes will be connected with appropriate fittings or welding. In point of use, gas purifiers will adsorb the last traces of water, oxygen, and hydrocarbons that could interfere with analyses at low concentrations.

Reference

1. Bulletin 898 A. Bellefonte, PA: Supelco, 1997.

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