Combining GC Detectors with Mass Spectrometers

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Mass spectrometry is a powerful measuring technique in analytical chemistry for identifying and quantifying a wide range of chemical compounds. However, it is sometimes inappropriate for certain classes of compounds due to lack of specificity, such as hydrocarbons, or spectral interferences, including nitrous oxide (m/e 44) in presence of usually domineering carbon dioxide (also m/e 44), or attempting to measure low levels of carbon monoxide (m/e 28) in presence of nitrogen (m/e 28). And many mass spectrometers often have limited concentration ranges. A quick screen with a flame ionization detector, with a very wide dynamic range, can make an assessment of concentrations to set automatically the sample loading into the mass spectrometer. The combination of these two detectors on the same instrument setup can facilitate operations with a single set of sample loadings.

Also, "fixed gases", such as hydrogen, helium, oxygen, nitrogen, methane, carbon dioxide and carbon monoxide are better measured with thermal conductivity or pulsed discharge detection. Sometimes this measurement of "fixed gases" can require a different carrier gas than required for the mass spectrometer, such as argon carrier for the measurement of oxygen in ambient air.[1] This analysis cannot be handled by splitting the injection, as argon carrier in not appropriate for capillary chromatography and the mass spectrometer.

To help reduce the analysis times for a wide range of analytes, and to overcome some of the limitations of mass spectrometry, the mass analyzer can be combined with GC detectors, such as flame ionization, thermal conductivity, or electron capture detectors, among others. Several approaches to combining multiple detectors are to either insert a splitter either at the head of the column, or immediately after the column, so a portion of the sample from an injection is directed to one pathway and the balance to a second path. Thus, a single injection can be set up to point the sample to both detectors, operating simultaneously. A major issue with both approaches is that the actual split ratio is not measurable, other than experimentally, with one path ending in a mass spectrometer. Usually the GC detector vents to atmosphere and flow here is easy to measure, while the inlet to the spectrometer is under a hard vacuum and it is hard to get a flowmeter inside there.

PRE-COLUMN SPLITTER

If the split point is installed at the **head** of two columns inserted into a single injector, with attachment of column ends to each detector, flow rates into each column and the split ratio are very dependent on chromatographic conditions, especially resistance to flow through one path versus the other. If one column has different physical dimensions, flow will be enhanced through the one with wider bore and shorter length. And the column attached to the spectrometer will automatically have an increased flow from the vacuum applied to its end. Since the one column inserted into the evacuated chamber of the spectrometer, flow rates cannot be confirmed with a flowmeter. And measurement of the flow with the column removed from the mass spectrometer source is not accurate, as it does not account for the changed flow from the vacuum pull.

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[1] Randall Bramston-Cook, Herb Neumann, "Operating Parameters for the Thermal Conductivity Detector in Varian 3800 and 3900 Gas Chromatographs", Lotus Consulting, 2007.

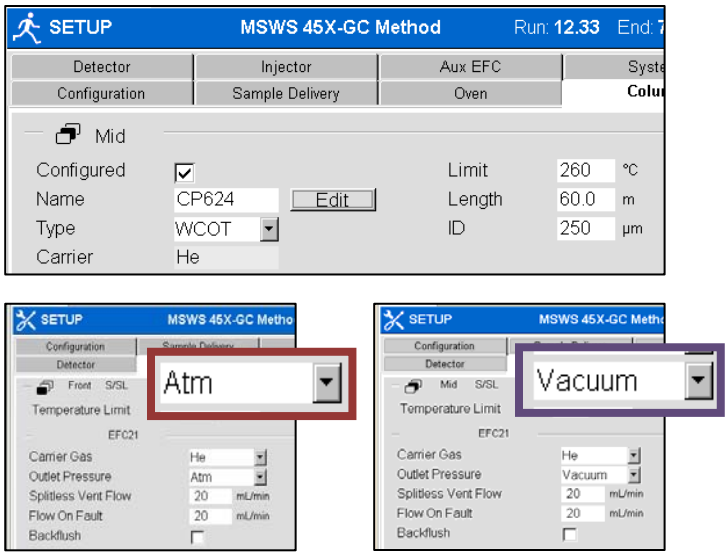
POST-COLUMN SPLITTER

With a simple “tee” splitter installed **post**-column with one leg attached to the GC detector and the other to the mass spectrometer, much of the column effluent will be sucked into the spectrometer’s vacuum, and very little, if any sample is likely to reach the GC detector. And this approach can create backflow of detector gases into the mass spectrometer. Any change in chromatographic conditions, such as column flow or column temperature, can impact this tenuous split ratio. Also, both detectors will suffer reduced sensitivities, especially with most of the sample likely to go to the spectrometer, and substantially less to the other detector. And the two detectors cannot be operated independently, as the sample is always loaded into both detectors.

A mechanism to throttle down the effects of the mass spectrometer’s vacuum can be set up by inserting restrictors after the column, such as narrow-bore capillary tubing. Its length and diameter can only be determined by experiment or by approximations from calculations, but any changes to the chromatographic conditions, such as carrier flow or column temperature, will require a repeat of this process. Various approaches to compute dimensions for these restrictors are available, and many are based on Hagen-Poiseuille’s Law.

$$\text{Flow} = \frac{\pi d^4 \Delta P}{128 L \mu}$$

where d is column diameter, ΔP is column headpressure minus terminus pressure, L is column length, and μ is dynamic gas viscosity. These physical dimensions, appropriate to the installed column, must be entered into the instrument setup to enable this calculation. Head pressure is provided by direct readings from the Electronic Flow Controller.

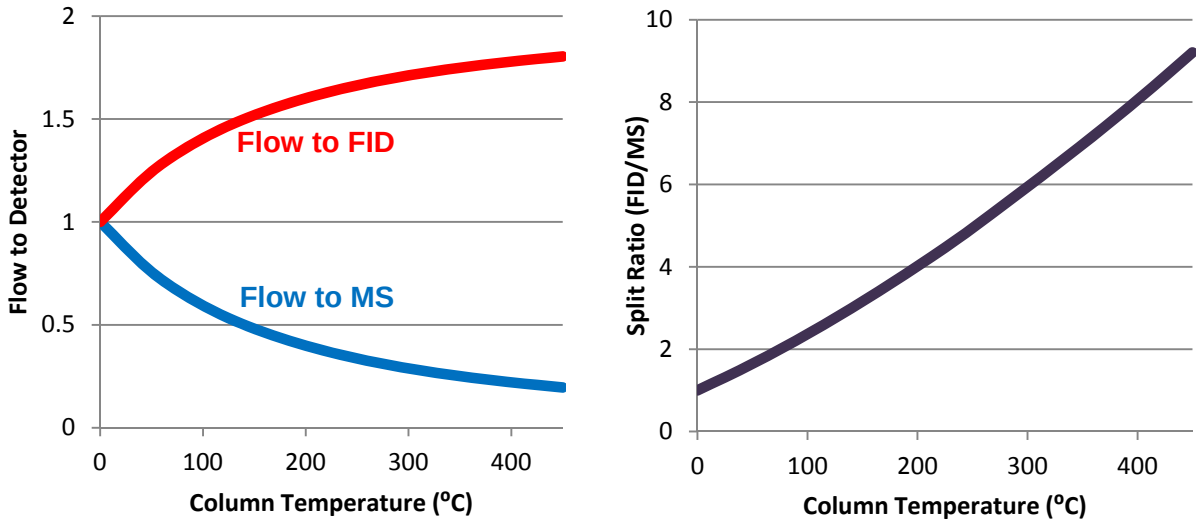


Entry of Column Parameters in Scion 456 Setup. Included is the setting for the column outlet pressure - “Atm” for GC detectors and “Vacuum” for a mass spectrometer - to set the pressure differential factor.

Notable in the equation is that the effect on flow is related to the diameter raised to the fourth power. Even a small dimension error in diameter of ± 4.8% can induce an error in the splitter computation of 22%. Also, since this same relationship is often used to convert pressure settings with split/splitless injectors into a calculated constant flow, the addition of these restrictors at the end of the column introduces significant errors in this calculated flow and associated split ratio.

If restrictors, with differing dimensions than the primary column, are added into the carrier gas pathways after the effluent splitter, this calculation of constant column flow becomes inaccurate.

The dynamic gas viscosity value is a function of temperature. When the splitter is located inside the column oven where its temperature follows the column program, the achieved split will change as the column temperature changes. The effect on a splitter dividing flow between a mass spectrometer and flame ionization detector reduce flow to the mass spectrometer by 66% with a change from 0 ^{o}C to 250 ^{o}C, with an increase to the flame ionization detector by the matching 66%.



Change in effluent split flow through a restrictor, as a function of temperature. Flows are computed with an on-line flow calculator, based on restrictor ID: 100 µ, length: 0.58 m, inlet pressure: 14.7, outlet to vacuum, splitter to MS and FID, and primary column flow: 2 ml/min. No restrictor is attached to FID.

Even adding more to the complication, some post-column splitters add in an auxiliary flow at the split point to ensure that the vacuum from the mass spectrometer does not cause backflow of supply gases from the atmospheric detectors. This action unpredictably changes the effective pressure differential input from the injector pressure reading to the column termination, as required for calculations using Hagen-Poiseuille's Law. And since flow into the mass spectrometer cannot be directly measured with a flowmeter, as it is necessarily under a hard vacuum, the user is unable to verify the actual split ratio.

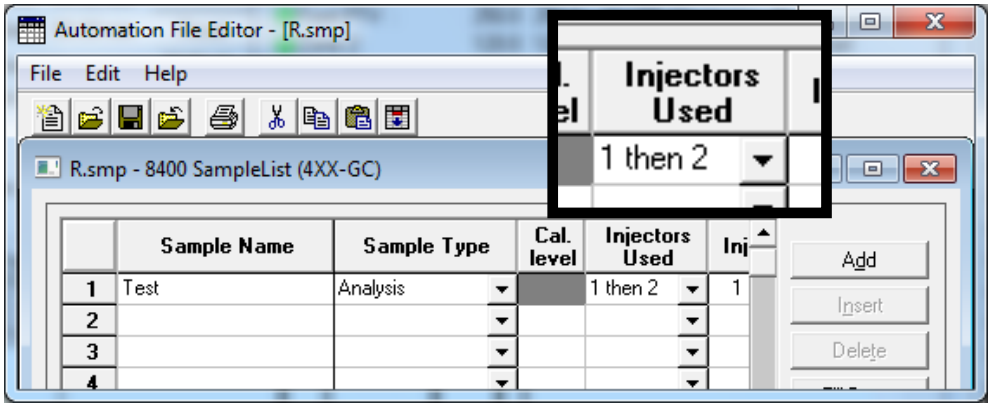
DUAL INJECTIONS INTO SEPARATE PATHWAYS

A better approach is to set up the gas chromatograph with independent sampling and chromatography pathways. Now the “split” ratio between detectors is set by the sample loading for each channel, with a full dose going into each path to the detectors. These independent channels can be operated together or independently simply by activating a method that sets up the correct hardware operations. Any changes in chromatographic conditions will not affect the split ratio. One limitation is that both columns will be operating with the same temperature conditions.

PARALLEL INJECTIONS OF LIQUID SAMPLES

By setting up independent pathways for the double injections, injector splitters can be installed for each channel, for separate and effective adjustment of the sample loading for each column and detector, not possible with a single injection and subsequent splits. And computations of column flow rates, with Hagen-Poiseuille’s Law, are strictly based on each pathway, and a compromise is not required.

Some liquid automated samplers, including the Scion 8400 AutoSampler, have the capacity to load up a single sample to inject into one injector and column, and then reload with the same sample and inject into a second independent injector and second column, all within the same chromatographic run. Although the column temperature conditions must be identical, all other operating parameters can be set independently, as appropriate for the detector involved, especially settings for split/splitless injections.

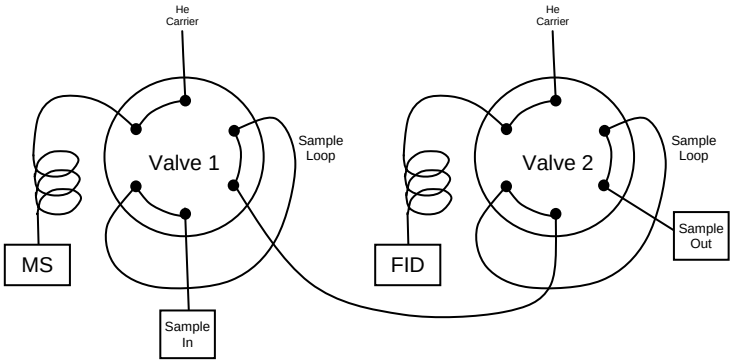


User entry into a sample list specifies
a possible double injection for each line.
Choices are injector 1, injector 2, 1 then 2, or 2 then 1.

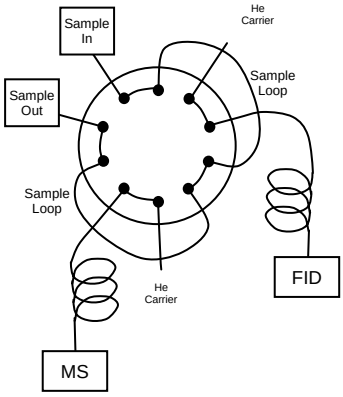
Scion 8400 AutoSampler permits parallel injections of one sample into two independent injectors. And the user can still make manual injections without moving hardware.

SIMULTANEOUS INJECTION OF GAS SAMPLES

Gas sampling valves for setting the sample injection volume can be set up with two valves involving concurrent sample loading, and then programmed to inject either both loops, or a single injection to one column and detector with activation of just one of the valves. Or a single valve can be installed with two loops, and both loops are injected together with rotation of the valve. As before, both columns will mandate identical temperature conditions, but the effective “split” ratio is strictly defined by the ratio of the sample loop volumes. This operation becomes useful for number of sampling techniques, such as headspace sampling. The amount of sample directed to each pathway is under full control and independent of the characteristics of the detector, be it venting to atmosphere or under vacuum.



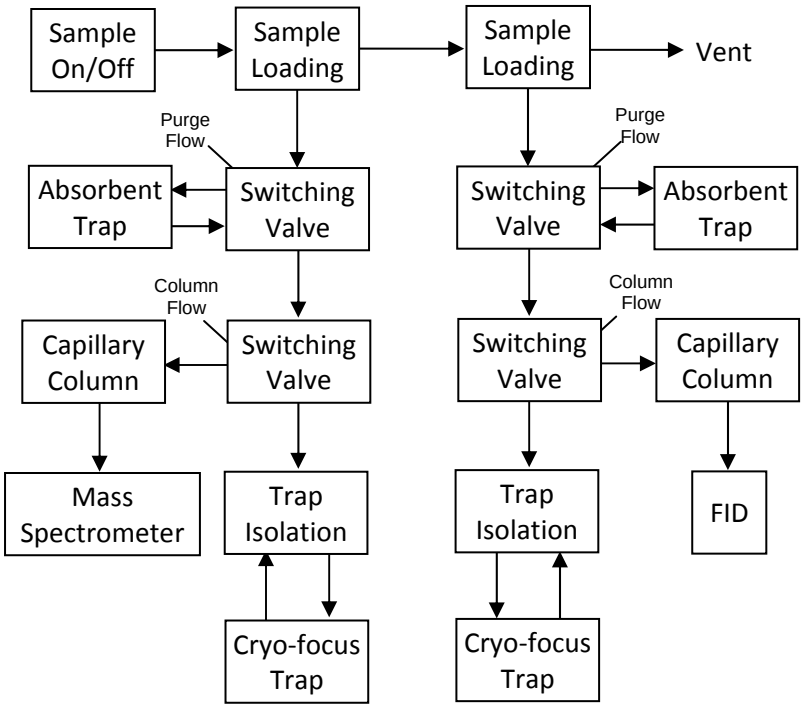
Two independent gas sampling valves with potential concurrent sample loading, or independent injections.



Dual gas sampling valve with two separate sample loops, injected simultaneously.

DUAL CHANNEL TRACE-COMPONENT CONCENTRATOR

A combination of absorbent and cryofocus traps permits low level analytes to be effectively concentrated and then injected into a column. By incorporating two separate, duplicate pathways within a single chromatograph, the “split” ratio of the sample loading to each detector fully controlled by the user. Operations become very predictable and reproducible, with full independence of chromatographic settings, except the column temperatures. Several examples include the concurrent operations of mass spectrometer for toxics and flame ionization detector for hydrocarbons, simultaneous measurements of toxics by mass spectrometry and sulfur gases by pulsed flame photometric detection, and prescreening by flame ionization detector with automatic adjustment of sample loading for toxics by mass spectrometry, based on the flame detector responses.



Dual, independent concentrators with a single sample inlet.

SUMMARY

Proper design of a dual detector chromatographic system allows multiple detectors to be set up for optimized detection of a variety of analytes, with best operating conditions for each measurement. With suitable hardware, operations can be fully automated and without any hardware changes or modifications to switch operating modes. Then the analysis can take advantage of the performance of each injector and detector without impacting the operations of the other pathway. And the complete sample injected into each pathway is directed to its related detector. This operation is critical for measurements with a flame ionization detector, as this detector is a perfect carbon counter for hydrocarbons, and the response for one known hydrocarbon can be applied to all others. This action does not apply if the post-column split changes over the run.

With this approach involving simultaneous injections, especially with valved schemes, a third detector, and even a fourth one, can be added into the mix by extending the operations with added valves. Possible candidates are flame ionization, electron capture, thermionic specific (N-P), thermal conductivity, pulsed flame photometric and pulsed discharge detectors. And each one can have optimized injection and column conditions, appropriate to that detector.

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