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A Programmed Temperature Vaporizing Injector for Large Volume Injections

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Key Words

- PTV Injector
- Large Volume Injection

Introduction

The TRACE™ GC Programmed Temperature Vaporizing (PTV) injector is an extremely versatile injector for Gas Chromatography. Several modes of operation other than traditional pro-grammed temperature vaporization are available, including Cold Trapping of heavier impurities in light gaseous samples, Large Volume Injections with venting of solvent, and Heart-cutting or Pre-cutting of selected compounds with backflush of undesired compounds to vent. With the addition of sub-ambient cooling and a heated solvent vapor exit valve, the PTV becomes one of the most versatile sample introduction devices for Gas Chromatography. The TRACE PTV has several unique modes of operation that allow it to operate as a Large Volume Injector. By employing a packed liner and sub-ambient cooling, the PTV can perform as a trap, collecting the heavier impurities from Ethylene, Propylene, or other gaseous samples. Making a large volume injection with the split valve open can trap higher boiling impurities in a gaseous sample. This allows the majority of the matrix gas to vent. The PTV is then heated to vaporize the collected compounds onto a column for analysis by GC or GC/MS.

Description

Conventional vaporizing injectors are designed with high mass injector bodies and heating blocks to control temperature for large volume inserts. These inlets change temperature slowly, contributing to their temperature stability. They are normally operated at a high temperature so that a sample is completely vaporized in a fraction of a second. Since the entire sample is vaporized, any separation techniques applied to the sample must take place in the chromatographic columns. Techniques such as replaceable guard columns and column switching are used to analyze difficult samples such as those containing high boiling components.

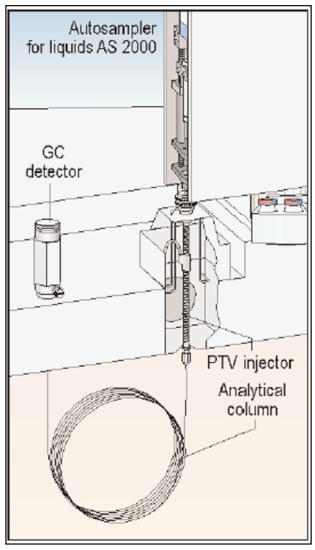


Figure 1: Components of a Programmed Temperature Vaporizing injector instrument

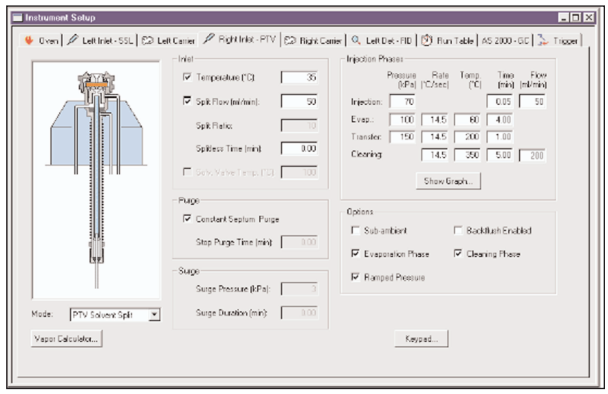


Figure 2: Control parameters for the Programmed Temperature Vaporizing injector

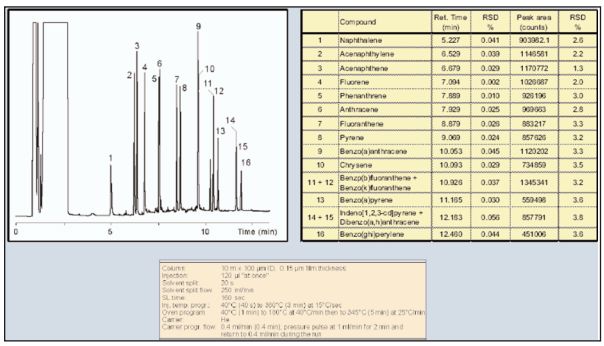
The PTV injector is designed to allow the inlet to perform a pre-separation of target analytes from other components of the sample. The PTV inlet is constructed with a low mass injector body and insert allowing it to be heated with precise control at rates up to 14.5° Centigrade per second. The control precision of the PTV inlet allows techniques such as solvent evaporation from analytes of interest, precutting of light analytes from a heavier matrix, and concentration of heavier impurities from gaseous samples. Without precise control of the injector temperature, retention of target compounds would not be

possible. The PTV can utilize multiple temperature ramps, enabling several techniques to be applied to each sample (Figure 2).

Samples can be injected as a liquid into a PTV at a low temperature. The inlet temperature is then rapidly heated to a temperature high enough to vaporize a solvent or low boiling components with the split vent open, sending these components to vent. With the backflush accessory installed, solvent can be prevented from entering the column during this phase, making this technique ideal for use with GC/Mass Spectrometers. The split vent can then be closed and a second temperature ramp initiated, transferring target analytes to the analytical column. The split vent can then be reopened and backflush flow begun with a third temperature ramp to clean the inlet before cooldown for the next sample cycle. Backflushing heavy components of a sample from the injector minimizes contamination of the column and reduces the requirement to program the column to a high temperature to bake off the heavier compounds.

Similarly, a heavy solvent or the heavier fraction of a sample can be retained in the PTV inlet after the vaporization of lighter compounds into the GC column. An example of this type of analysis is the measurement of fuel dilution in engine oils. In this analysis, the ability of the PTV to retain the bulk of the heavy oil while transferring the lighter components to the analytical column is a key advantage. After the lighter components are transferred, the PTV can be ramped to a high temperature and backflushed to vent, shortening the analysis time. This reduces the method cycle time, and extends the useful life of the column.

With the addition of a heated solvent vapor exit valve, large volumes of solvent can be vented while retaining heavier compounds of interest for injection. The vapor exit valve must be heated to reproducibly vent large volumes of solvent vapors. An unheated solvent vapor exit valve can allow condensation of liquid solvent in the valve, reducing or stopping the flow and resulting in non-repeatable injections. The injection of large sample volumes can be used to decrease method detection limits or to eliminate the need for concentration of extracts.



	Compound	Ret. Time (min)	RSD %	Peak area (counts)	RSD %
1	Naphthalene	5.227	0.041	903962.1	2.6
2	Acenaphthylene	6.529	0.039	1146581	2.2
3	Acenaphthene	6.679	0.029	1170772	1.3
4	Fluorene	7.094	0.002	1026987	2.0
5	Phenanthrene	7.889	0.010	926196	3.0
6	Anthracene	7.929	0.025	969903	2.8
7	Fluoranthene	8.579	0.026	883217	3.3
8	Pyrene	9.069	0.024	857626	3.2
9	Benzo(a)anthracene	10.053	0.045	1120202	3.3
10	Chrysene	10.093	0.029	734859	3.5
11 + 12	Benzo(b)fluoranthene + Benzo(k)fluoranthene	10.926	0.037	1345341	3.2
13	Benzo(e)pyrene	11.165	0.030	559496	3.6
14 + 15	Indeno(1,2,3-cd)pyrene + Dibenz(a,h)anthracene	12.163	0.056	857791	3.8
16	Benzo(ghi)perylene	12.493	0.044	451006	3.8

Figure 3: PAHs Analysis by PTV Solvent Split Large Volume Injection concentration in n-pentane 200 ppb

There are many chromatographic methods for trace contamination where the extraction and concentration of solvent extracts requires more time than the chromatography. In these methods, the ability to inject large solvent volumes of less concentrated extracts can mean a significant increase in laboratory productivity. An example of this type of application is Polynuclear Aromatic Hydrocarbons in ground water (Figure 3).

When a large volume injection technique is used with a GC/Mass Spectrometer, one of the requirements for successful implementation is minimizing the solvent vapor transferred to the Mass Spectrometer. Several microliters of solvent entering the vacuum chamber of the Mass Spectrometer can cause a pressure increase high enough to shut off the vacuum system. Amounts of solvent not large enough to shut off the vacuum will cause background spectra from the solvent for several minutes. The solvent background can interfere with the collection of spectral data.

The PTV with backflush accessory is ideal for sample introduction into a GC/Mass Spectrometer. With the backflush valve enabled in the solvent evaporation phase, all solvent vapors are directed out the split vent. This eliminates the introduction of solvent into the Mass Spectrometer.

Conclusion

The PTV Large Volume Injection technique is applicable to many types of samples. Applications from analysis of impurities in gaseous samples to light impurities in heavy liquids can be successfully implemented.

The use of the PTV Large Volume Injection technique allows higher productivity while maintaining method sensitivity and protecting sensitive detectors or Mass Spectrometers from the introduction of high volumes of solvent. The ability to inject large volumes reproducibly can reduce preparation time for solvent extraction methods. This is an important consideration for an analytical laboratory utilizing methods where sample preparation time is lengthy. Solvent extraction and evaporation is a labor intensive procedure which is not easily automated.

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