Instant Connect Gas Sampling Valve Module Introducing a New Flexibility in Gas Sampling for GC and GCMS

Stefano Pelagatti, Paolo Magni, Fausto Pigozzo

Thermo Fisher Scientific, Rodano (Milan), Italy

Overview

Purpose: We present a newly developed gas sampling valve module for the Thermo Scientific™ TRACE™ 1300 Series Gas Chromatograph (GC).

Gas injection through a gas sampling valve is one of the most reliable and wide-spread technique to inject a vapor sample into a gas chromatographic system. Nowadays development of this technology relies on the attempt of different Valve suppliers to improve material reaching higher temperature and/or longer life time of mobile parts, reduce internal volumes for improving chromatographic performance and reduce overall valve size.

Introduction

This paper describes a new modular concept that instrument manufacturer has undertaken to integrate latest valve technology, into a handling, plug-in module, full incorporating heating control of the valve, miniaturized pneumatic circuits for carrier gas supply and split as well as valve backflush to the vent. This modular design allows a new level of instrument flexibility, where inlets and/or detectors selection is based on the application in use, and can be changed in a matter of few minutes by the operator when a new analytical need or application requires different injector and/or detectors.
On top of improved technical performance in terms of injection repeatability and stability, this work shows the simplicity and flexibility in configuration setting provided by this Instant Connect modular design.
Without further hardware complexity the gas sampling valve module can be set to back flush to vent undesired part of sample, therefore offering an easy and integrated set-up for more complex analysis. Data showing performance of this solution are illustrated and discussed.

Methods

All experiments described below use a TRACE 1300 ™ series GC equipped with a gas sampling valve (GSV) module (Figure 1) as injection port and a thermal conductivity detector (TCD) module in series with a flame ionization detector (FID) module. In Figure 2 the GC setup is showed. Moreover, for the determination of nitrous oxide in air, an electron capture detector (ECD) module has been used.

FIGURE 1. GSV module.

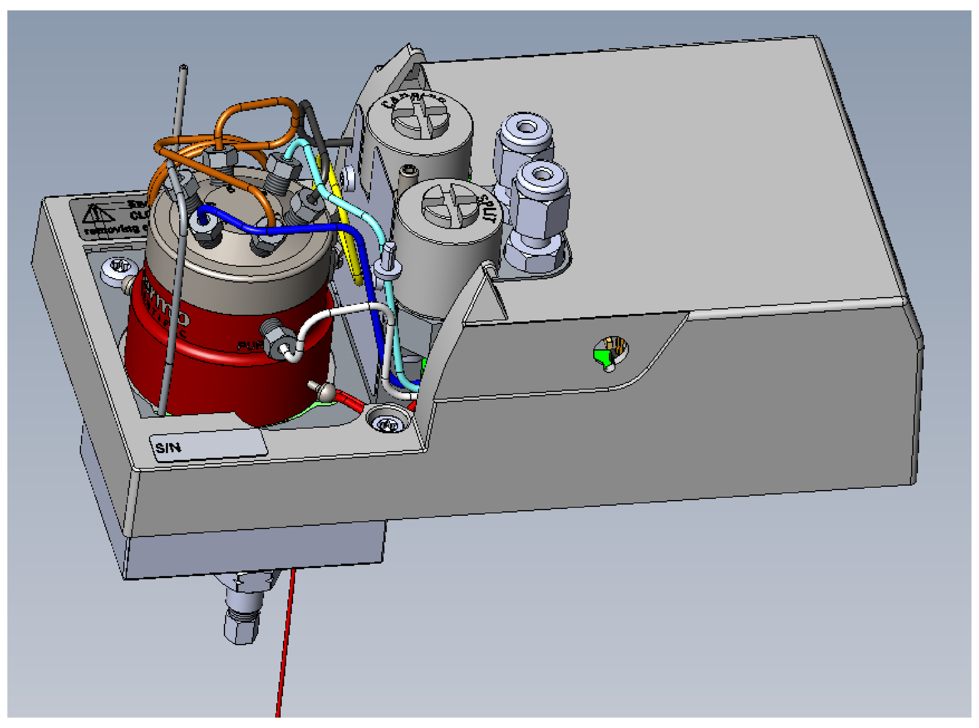


FIGURE 2. TRACE 1300 equipped with GSV module and FID-TCD in series

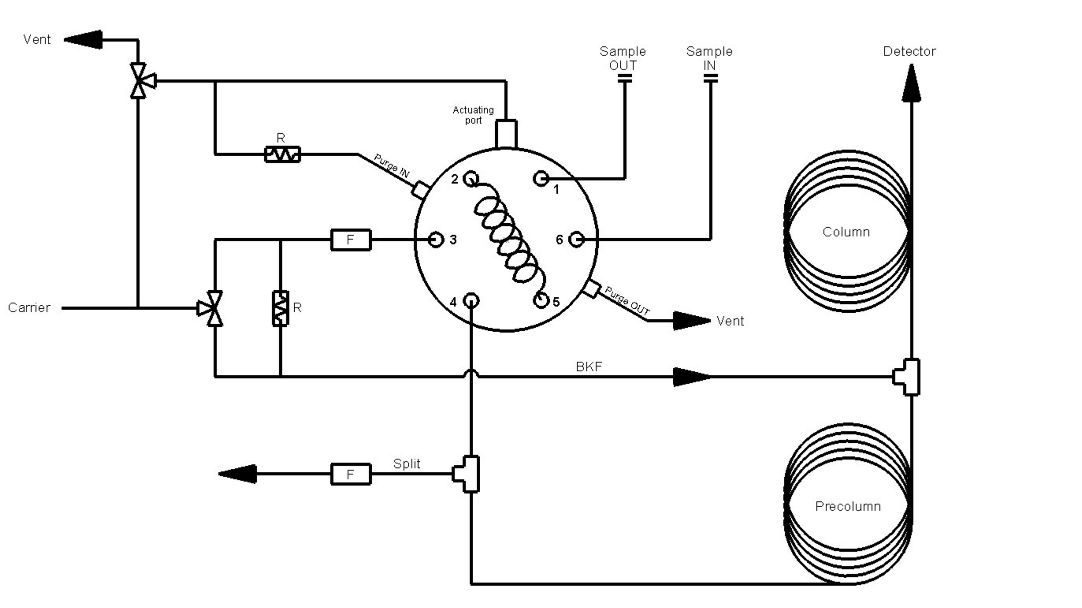
The GSV module is provided with all the electronics and pneumatics built in the module (Figure 3), including the parts necessary for the back-flush option.

The GSV is a thermostatted (up to 150 °C) 6 ports membrane valve. The valve has a constant purge of helium in order to avoid any possible air diffusion through the membrane, particularly critical when used in combination of oxygen sensitive detectors.

The channels in contact with the sample are fully surface deactivated in order to prevent corrosion or absorption phenomena, especially for sulfur components at low concentration levels.

Two charcoal filters, one on the carrier line and the other on the split line, can be replaced without any intervention on the valve connections.

FIGURE 3. GSV module pneumatics



The performances of the new GSV module have been evaluated using a certified gas mix (from S.I.A.D. S.p.A)[1]. The composition of the tank is described in the following table:

TABLE 1. Gas mix

Gas	% Volume/Volume
Oxygen	1.08
Hydrogen	2.99
Methane	2.99
CO2	3.00
CO	3.00
N2	3.02
Helium	Remaining part

The column used is:

Thermo TG-Bond Msieve 5A
30 m, 0.53 mm, 50 um.

The precolumn is:

Thermo TG-Bond Q, 15m, 0.53 mm, 20 um.

Such a precolumn has been chosen in order to allow a precise back-flush cut of unwanted portion of the mix. The diaphragm valve is from AFP ™ [2] company and is equipped with a 250 loop made by SilcoNert™ [3] coated stainless steel tube.

Results

The loop has been loaded in continuous way with gas mix through the "Sample in" port of the module with a flow of 5 ml/min. The sampling occurred automatically whenever the GC was ready to inject.

The chromatograms obtained with the FID and TCD are presented in Figure 4. The method used is listed in the Table 2. The back-flush valve was actuated after 1.6 minutes in order to preserve the molecular sieve column, avoiding the entrance of CO2. The back-flush time optimization requires few trials: it starts with an early reverse flow actuation; then the actuation start time is incremented until the last eluting peak before the undesired component is acquired in the chromatogram.

The duration of Sampling valve activation was 0.5 min, long enough to transfer completely the components from the loop into the column, considering the low dead volumes of the module.

FIGURE 4. Standard gas mix chromatograms.

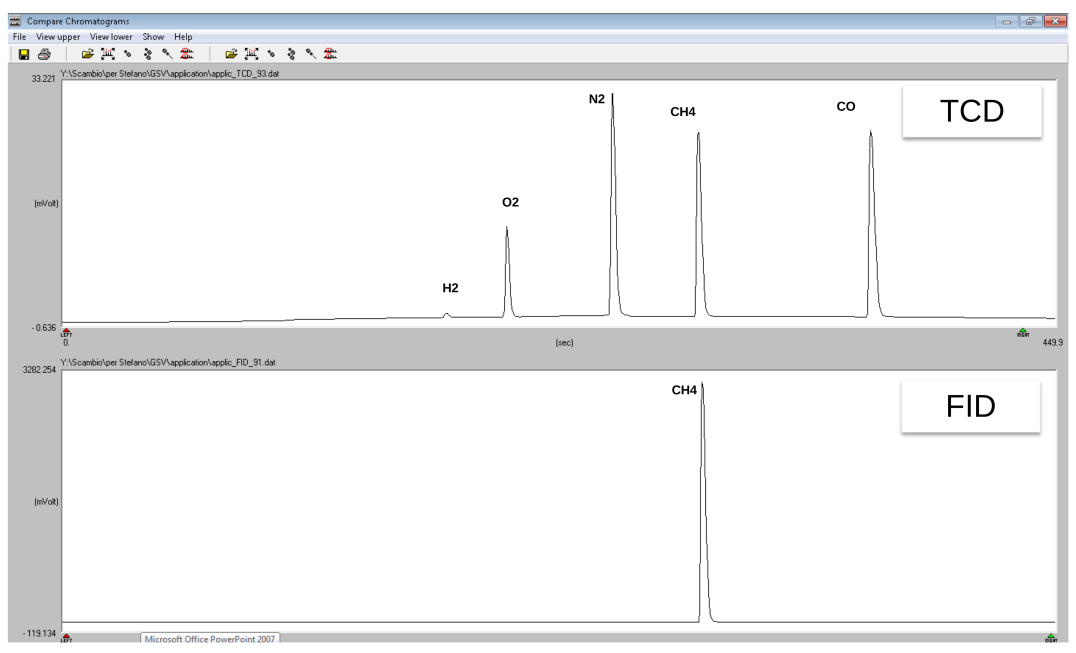


TABLE 2. GC analytical method

Oven Method	FID - Front Method
Initial temperature: 30.0 C	Temperature: 250 C
Initial hold time: 2.00 min	Ignition threshold: 1.0 pA
Number of ramps: 1	Air flow: 350.0 mL/min
Ramp rate: 20.0 C/min	Hydrogen flow: 35.0 mL/min
Final temperature: 100.0 C	Makeup gas flow: 40.0 mL/min
Ramp hold ti 2.00 min	TCD - Back Method
GSV - Front Method	Temperature: 100 C
S/SL mode Split	Filament power on: Yes
Temperature enable: On	Filament temperature: 150 C
Temperature: 120 C	Reference gas enable: On
Split flow enable: On	Reference gas flow: 1.0 mL/min
Split flow: 5.0 mL/min	Carrier source: Front
GSV inj start time: 0.00 min	Acquire data: Yes
GSV inj duration: 0.50 min	Signal process: Standard Peaks
Carrier mode: Constant Flow	Negative polarity: No
Carrier flow 5.000 mL/min	Prep-run - TCD (Back): Autozero

The repeatability of peak areas, tested over 25 injections, showed in Table 3, demonstrates a good precision of the system.

The repeatability of retention times for the analyzed gases shows a very stable pneumatic control.

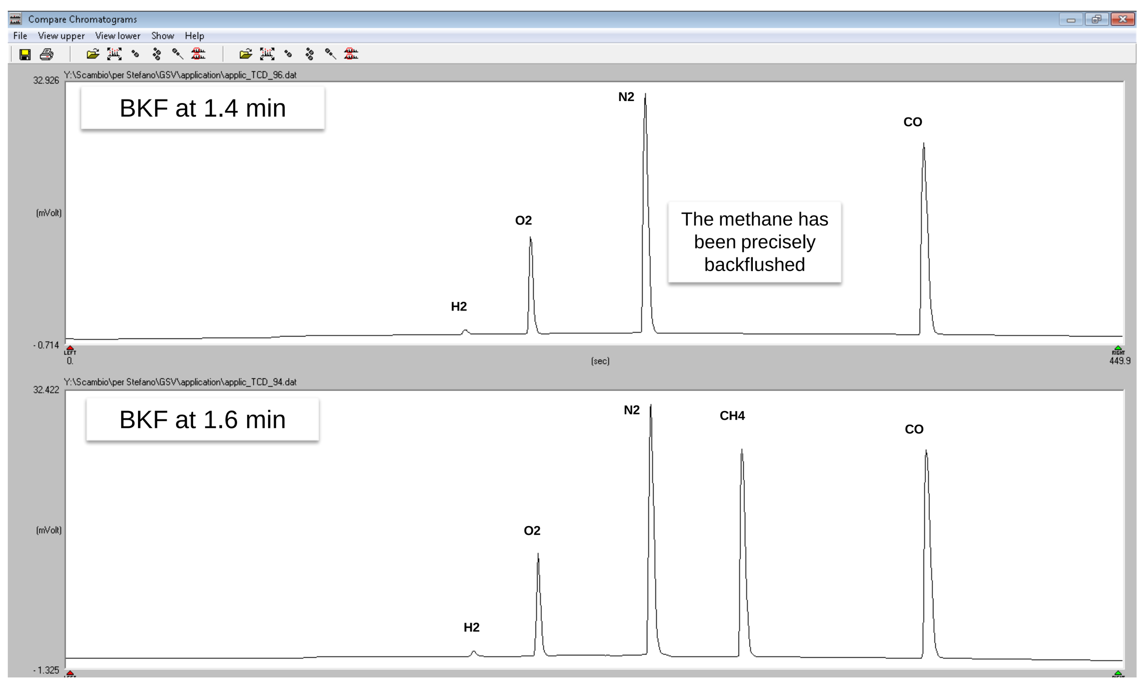
TABLE 3. Peak area and retention times repeatability

area	H2	O2	N2	CH4	CO
inj1	13266	250735	759165	660911	780563
inj2	13125	248391	749634	653404	772619
inj3	13225	247587	748704	652229	771518
inj4	13175	249261	752844	655866	775850
inj5	13197	248333	749910	653122	773409
inj6	13182	248458	750457	654182	774973
inj7	13200	249554	753400	656871	776464
inj8	13159	248388	750503	654086	774620
inj9	13091	247615	748039	652954	771570
inj10	13107	247545	749047	653151	771920
inj11	13195	249232	754607	658199	777982
inj12	13019	245449	743166	647715	765810
inj13	13169	246423	746294	650646	769293
inj14	13191	249165	753737	657913	778070
inj15	13126	247865	750023	654019	773525
inj16	13091	247573	748145	652019	770972
inj17	13161	249634	754156	656949	777327
inj18	13140	247480	749380	653754	773162
inj19	12986	247612	747750	651951	770890
inj20	13210	249962	754972	658039	778727
inj21	12985	246524	743554	648850	767180
inj22	13153	249329	752502	656392	776874
inj23	13328	251266	758369	660696	782013
inj24	13213	250395	755861	658918	779669
inj25	13077	247541	749738	653407	773632
sd	81	1401	4013	3376	4060
RSD%	0.6	0.6	0.5	0.5	0.5

RT	H2	O2	N2	CH4	CO
inj1	2.898	3.355	4.150	4.800	6.105
inj2	2.898	3.355	4.150	4.798	6.103
inj3	2.900	3.357	4.150	4.798	6.103
inj4	2.895	3.352	4.147	4.795	6.100
inj5	2.898	3.355	4.148	4.797	6.102
inj6	2.897	3.353	4.150	4.798	6.103
inj7	2.898	3.355	4.150	4.798	6.103
inj8	2.900	3.357	4.152	4.800	6.105
inj9	2.898	3.355	4.150	4.798	6.103
inj10	2.898	3.355	4.150	4.798	6.103
inj11	2.898	3.355	4.150	4.797	6.100
inj12	2.902	3.357	4.150	4.798	6.100
inj13	2.897	3.353	4.148	4.797	6.100
inj14	2.898	3.355	4.150	4.798	6.102
inj15	2.897	3.353	4.150	4.798	6.102
inj16	2.900	3.357	4.152	4.798	6.103
inj17	2.897	3.353	4.148	4.797	6.100
inj18	2.898	3.355	4.150	4.797	6.102
inj19	2.898	3.355	4.150	4.797	6.100
inj20	2.900	3.355	4.152	4.798	6.102
inj21	2.897	3.353	4.150	4.797	6.102
inj22	2.898	3.355	4.150	4.798	6.102
inj23	2.897	3.353	4.148	4.797	6.100
inj24	2.897	3.353	4.148	4.795	6.098
inj25	2.898	3.355	4.150	4.797	6.100
sd (min)	0.001	0.001	0.001	0.001	0.002
RSD%	0.05	0.04	0.03	0.03	0.03

The efficiency of the embedded back-flush system has been tested using the same gas mix, but changing the back-flush activation time (from 1.6 minutes to 1.4 minutes). The result highlights that a selective cut of the Methane peak can be obtained, as showed in Figure 5

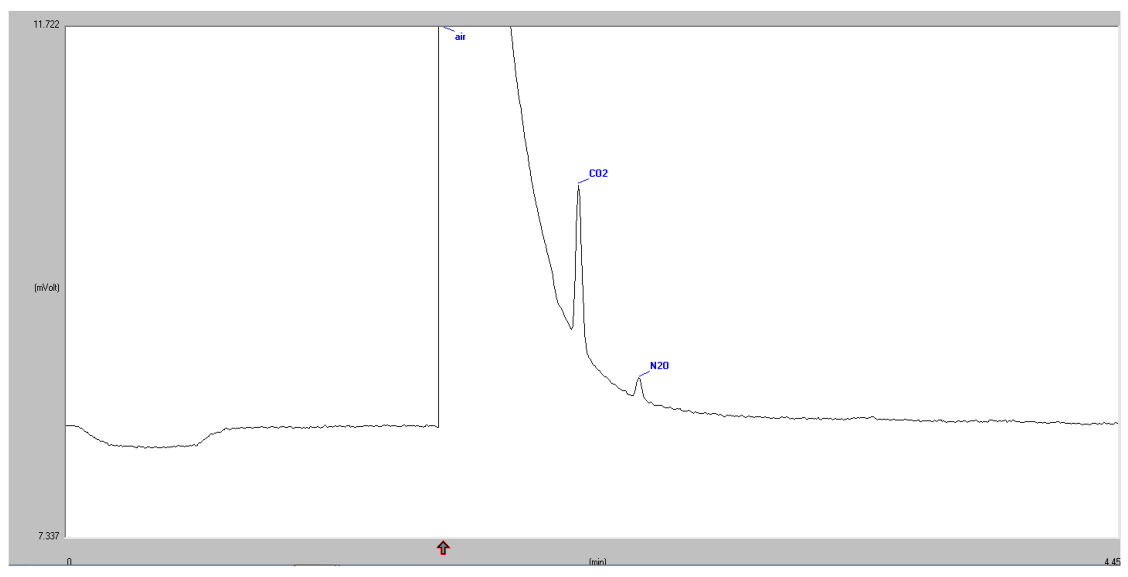
FIGURE 5. Selectivity of the back-flush cutting.



Using different detectors, columns and larger sampling loops, this on-line ambient monitoring can be used for various applications like continuous air pollution evaluation.

In Figure 6 an example of ambient air analysis performed using an ECD detector and TG-Bond Q phase column for the quantification of sub ppm levels of N_2O (greenhouse gas) is showed.

FIGURE 6. Continuous ambient air monitoring.



Conclusion

The new GSV module, easily installable on the TRACE 1300 series GC, has demonstrated to be a robust and reliable device for the detection and analysis of permanent gases or volatile compounds. The embedded back-flush capability allows to protect the column from unwanted components, reducing the analysis time and preserving the column lifetime.

1. SOCIETA' ITALIANA ACETILENE E DERIVATI S.I.A.D. S.p.A. (Bergamo, Italy)
2. Analytical Flow Products part of Norgren Ltd (Lichfield, Staffordshire, WS13 6SB)
3. Restek Corporation (110 Benner Circle • Bellefonte, PA)