

4.1 Installation of a New Gas Chromatograph at Izaña GAW Station (Spain) to Measure CH₄, N₂O, and SF₆

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Abstract

We have installed a new GC at Izaña Global GAW Station (Tenerife, Spain) with two detectors: a FID (to measure CH₄; this compound has been measured at Izaña with another GC-FID since 1984) and an ECD (to measure N₂O and SF₆). Each detector has associated a set of precolumn, maincolumn, and 10-port-2-position valve to allow for backflushing. Additionally, there is a 4-port-2-position valve to avoid the flow of O₂ through the ECD. Routinely continuous background measurements (with this new GC) started on June 14, 2007. In this presentation, the setup of the GC system, injection procedures and associated chromatograms, integration methods, sampling and traceability strategy, and data processing procedures are described. We also obtain the power spectrum of the chromatograms (noise plus signal) and briefly discuss the sources of uncertainty in peak integration. Finally, we briefly study the response functions of the detectors, associated uncertainties, and repeatabilities.

4.1.1 System configuration, time sequences and chromatograms

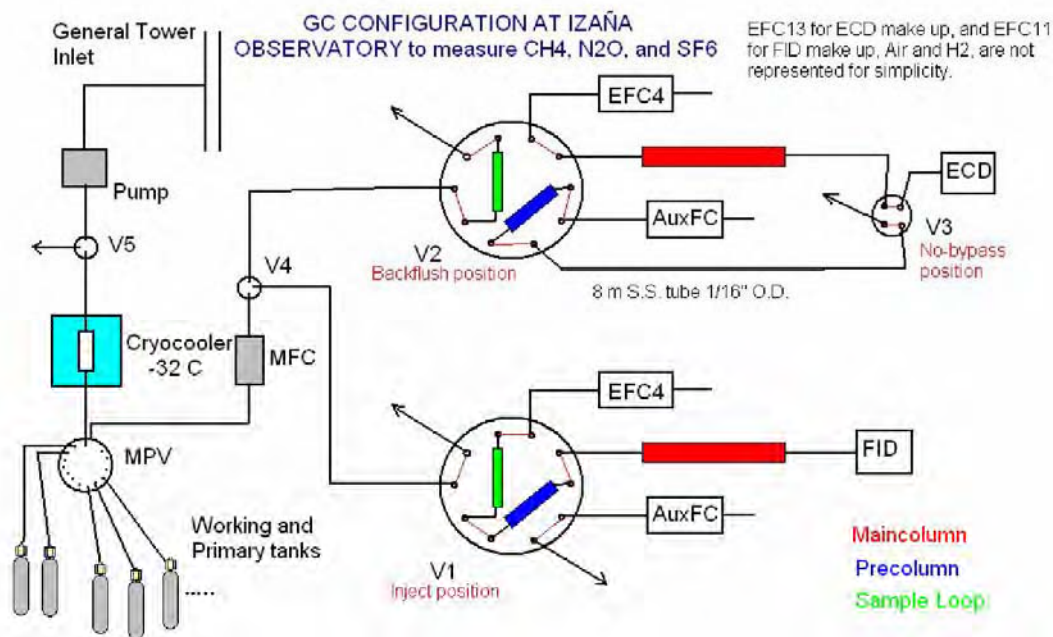


Figure 1. GC configuration scheme. For valves V1, V2, and V3, the depicted positions of the valves are indicated in red colour.

We have installed a GC Varian 3800 with two detectors (ECD and FID) at Izaña Observatory. Figure 1 shows the GC system configuration. The general ambient air inlet, which is situated on top of the building tower (30 m height) and provides ambient air for all instruments that analyze it, is a 8 cm I.D. stainless steel pipe and has a high flow rate. A tube branches from the general air inlet toward a pump that provides ambient air to the GC. Valves V4 and V5 are 3-port-2-position valves. MPV is a Valco multiposition valve with 1 outlet and 16 inlets connected to the ambient air inlet, the working tanks and the laboratory standards. MFC is a mass flow control. Valves V1 and V2 are 10-port-2-position valves, with positions inject and backflush as showed in Figure 2. EFC4s are electronic flow controls that regulate flow maintaining a prescribed pressure above ambient. AuxFCs are auxiliary flow controls (with values fixed by analogical controls). Valve V3 is a 4-port-2-position valve, with positions bypass and no-bypass. There are a few meters of PTFE tube at the vent of V5 and at the loops outlets to prevent any diffusion from the laboratory.

The Ar/CH₄ carrier flowing through the vents of EFC4 and V3 is conducted out of the laboratory. For ECD safety, AuxFC allows carrier flow even if the GC is turned off (EFC4 does not). The electronic and battery that controls V3 (bypass valve) are configured in such way that V3 commutes to bypass position in the case that the GC is turned off (e.g. AC supply interruption) and therefore the very hot ECD is not damaged by carrier flow interruption.

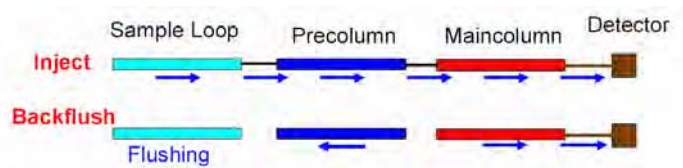


Figure 2. Scheme with the connections and the flow direction (blue arrows) for two valve positions: Inject and Backflush.

Table 1. GC configuration.

	ECD	FID
Oven temperature	80 °C. Columns, loops and 8 m S.S tube 1/16" O.D.	
Sample Loop	10 ml; O.D.=1/4"	10 ml; O.D.=1/4"
Precolumn	Porapak Q 80-100 Mesh L= 2 m; O.D.=1/8"; I.D.=2.0 mm	Hayesep D 60-80 Mesh L=4 ft; O.D.=1/8"
Maincolumn	Hayesep Q 80-100 Mesh L= 3 m; O.D.=1/8"; I.D.=2.0 mm	Molesieve 13x 45-60 Mesh L=6 ft; O.D.=1/8"; I.D.=0.092"
Carrier gas	Ar/CH ₄ (95%-5%) Oxygen/Moisture Trap	N ₂ Hydrocarbon/Moisture Trap
Carrier direct flow	31.1 ml/min	52.4 ml/min (high flow)
EFC4 set pressure (above ambient)	Inject: 50.0 psi Backflush: 37.0 psi	Inject: 27.1 psi Backflush: 17.4 psi
Carrier Backflow	32.2 ml/min	28.3 ml/min
Valve Oven	80 °C. Only for V1 and V2	
DETECTOR:	ECD	FID
Temperature	380 °C	150 °C
Make up flow	0 ml/min	0 ml/min
Air flow	---	300 ml/min
H2 flow	---	30 ml/min

Table 1 provides details about the GC system configuration. The indicated flows, non corrected for T and p , have been measured with an external Varian digital flowmeter (laboratory temperature=21.3 °C, typical Izana pressure: 770 hPa). Additionally, the FID Carrier direct flow for low flow is 30.6 ml/min, which only happens in Backflush position (11.5 psi). Table 2 provides the time sequences (cycle of 7.5 minutes) for the GC-FID and the GC-ECD subsystems. 30 seconds before a sample loop injection, valve V4 stops flushing (commuting to the other loop) to allow temperature (oven) and pressure (ambient) equilibration. Valve V5 directs pumped air towards the cryocooler (flask of approximately 300 ml) whenever there is an ambient air injection and each cycle between minutes 3.15 and 6.15.

Table 1. Time sequences. For each subsystem, some events have been denoted with letters a, b, and c.

Minute	ECD	Minute	FID
0.00	Stop sample loop flushing (V4)	0.50	Start sample loop flushing
0.50 a	Inject (V2)	1.44 a	Increase of carrier flow
1.50 b	Start of ECD Bypass (V3)	1.50	Stop sample loop flushing (V4)
3.00 c	Backflush & End of Bypass	2.00 b	Inject(V1)
6.50	Start sample loop flushing	4.00 c	Backflush & Decrease of carrier flow

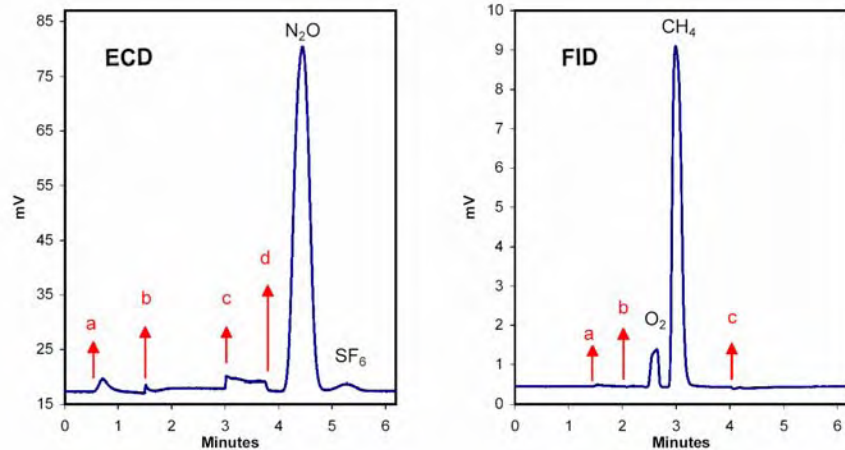


Figure 3. Obtained ECD and FID chromatograms. Events marked with red letters as indicated in Table 2.

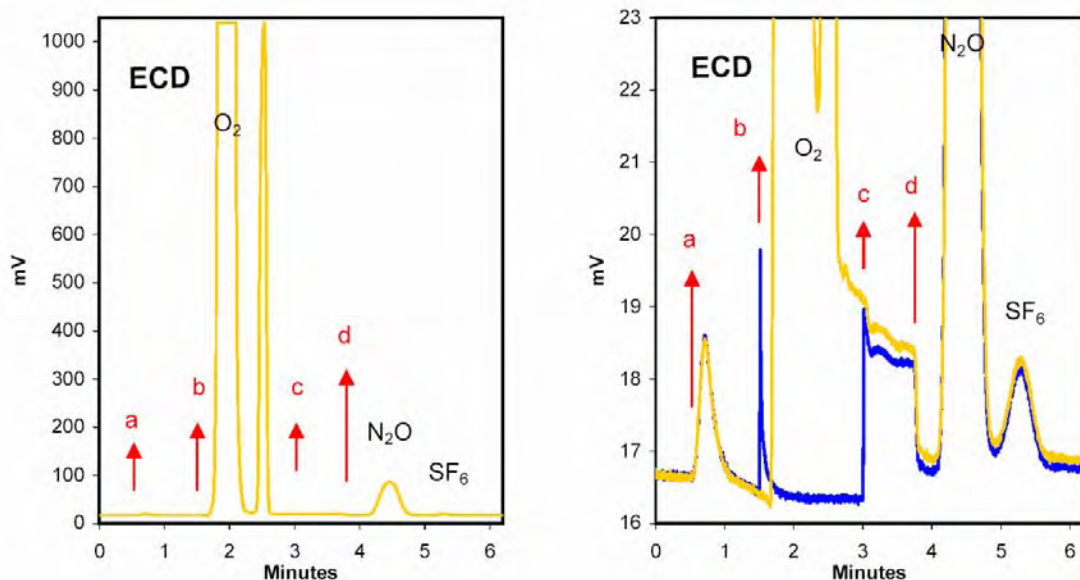


Figure 4. Yellow line: ECD chromatogram without bypass. Blue line: ECD chromatogram with the usual time sequence for valves.

Figure 3 shows the obtained ECD and FID chromatograms. Figure 4 shows ECD chromatograms with the usual bypass (to avoid the flow of O₂ through the ECD) and without bypass. As Gomez-Pelaez shows, what is detected in the ECD between times c and d, is the O₂ present in the main column (very weak tail). Abrupt decrease d happens when there is no more O₂ inside the maincolumn.

The cryocooler temperature is -32 °C. Working and laboratory standards, which are very dry (H₂O < 5 ppm), do not flow through the cryocooler, whereas ambient air does, achieving the saturation water vapour content for this temperature. The saturation water vapour pressure (e_i) at -32 °C is 0.3078 hPa (e.g. Iribarne&Godson). The relation among r_{xd} , mixing ratio (mole fraction) of compound x in dry air, and $r_{xw}(T)$, mixing ratio when water vapour is added till saturation (which depends on T), is given by:

$$\frac{e_i}{p_d} = \frac{r_{xd} - r_{xw}}{r_{xw}} \cong \frac{r_{xd} - r_{xw}}{r_{xd}} \equiv \text{relative bias}$$

The relative bias is 4.00×10^{-4} , taking into account the typical atmospheric pressure at Izana ($p= 770$ hPa). The GAW N₂O recommended Inter-Laboratory comparability is ± 0.1 ppb, which relative to 320 ppb has a value $\pm 3.125 \times 10^{-4}$. Therefore, we have to correct our ambient air measurements for this systematic error produced by dilution, and consider the associated uncertainty. Probably, in the future, we will use a more powerful cryocooler. Backflush prevents from any undesired effect of water vapour (which has a large retention time) inside the GC.

4.1.2 Data acquisition and integration methods

The sources of uncertainty in (isolated) peak integration (e.g. Dyson) are: a) Sampling frequency (to decrease time resolution, averaging from a higher resolution chromatogram, does not affect area but affects height); b) Signal digitalization (A/D converters). In our GC, $\Delta V = 0.001$ mV; c) Placement of baseline under the peak (the uncertainty for area is larger than for height).

In our system, the sampling frequency is 10 Hz, averaging from a 40 Hz signal. We think that the decrease of peak height is negligible. The area uncertainty is dominated by c), whereas for height uncertainty there is also a significant contribution of a). For CH₄ integration we use area because a FID is a mass sensitive detector and the peak is asymmetric. For N₂O and SF₆ integration we use height. We store raw chromatograms. At present, we are using the Star Varian integrator. We selected parameters to get good integration repeatability. We force a Valley Baseline between the N₂O and SF₆ peaks, which is used when necessary (rarely).

4.1.3 Chromatograms power spectrum

Figure 5 shows the power spectrum of the ECD and FID chromatograms. The integer k defines the linear frequency: $f_k = k / (n\Delta t)$ (e.g. see Press et al for the definition and properties of the power spectrum). As Figure 5 shows, these power spectra allow a clear separation between signal and noise. The ECD power spectrum has been obtained for the time interval 3.85-6.45 minutes, 10Hz, 1557 points padded till $n=2048$, and the noise threshold is identified at $k=27$ ($1/f=7.6$ s). The FID power spectrum has been obtained for the time interval 2.75-4.00 minutes, 10Hz, 750 points padded till $n=1024$, and the noise threshold is identified at $k=37$, $1/f=2.8$ s. The RMS noise estimation obtained from the power spectrum is 0.036 mV for the ECD, and 0.0022 mV for the FID. But these are not final values because: 1) we have used a Fast Fourier Transform, so padding with a constant value till the nearest and larger power of 2; and 2) we need to analyse the power spectrum of a large number of chromatograms.

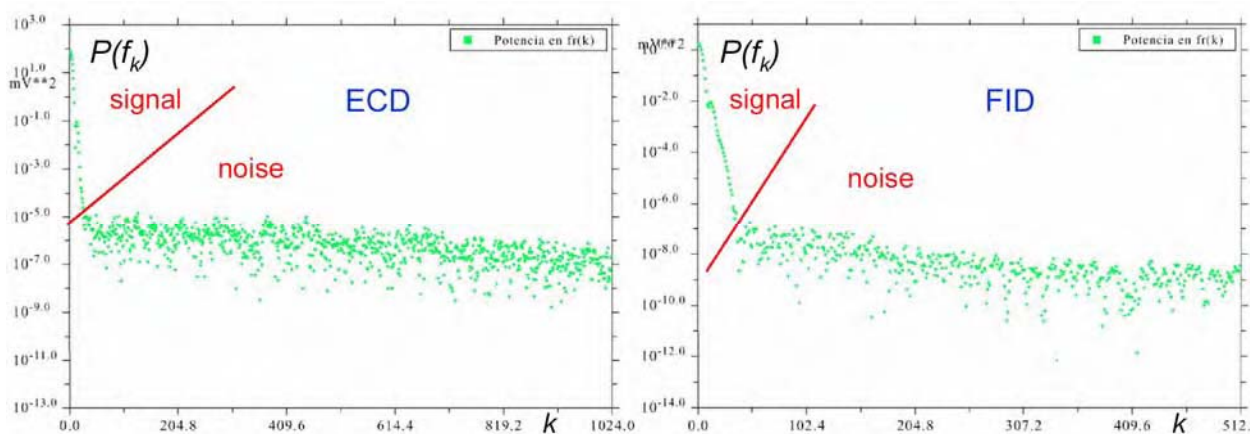


Figure 5. Power spectrum of the ECD and FID chromatograms.

4.1.4 Sampling, traceability, and calibrations

Valve V4 allows the introduction of distinct samples in the ECD and FID loops within the same run. Table 3 shows the one hour cycle we use for ambient air measurements.

Table 2. One hour injection cycle for ambient air measurements. Notation for injections: ambient air (amb), working gas for CH₄ (wch4), and two working gases for N₂O and SF₆ (wns1 and wns2).

Min:Seg	00:00	07:30	15:00	22:30	30:00	37:30	45:00	52:30
FID	wch4	Amb	wch4	amb	wch4	amb	wch4	amb
ECD	wns1	wns2	amb	amb	wns2	wns1	amb	amb

We are still not using a target gas. With Varian Star software, we have to use “Sample Lists” with cycles of 1 or 24 hours (among other inconveniences). The working gases are periodically calibrated, and the response functions of the detectors are obtained, using the sets of Izana standards (WMO Tertiaries, provided by NOAA, CCL): 5 standards for N₂O and SF₆, and 2 (3 in the near future) standards for CH₄. Within a calibration, the repeatability for a tank is around 0.3 ppb for N₂O and 0.06 ppt for SF₆. We have programmed Fortran 90 numerical codes to read run reports and write data in a more compact format, and to process calibrations and ambient measurements.

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