APPLICATION BRIEF 000401

Battery drum pack gas analysis through a multi-valve, multi-column GC system

Author: Thermo Fisher Scientific Inc.

Keywords: Gas analysis, TRACE 1310 GC, TRACE 1310 Auxiliary Oven, Li-battery

Goal

The purpose of this application brief is to report a multi-column, multi-valve gas chromatographic solution for the analysis of gases producing Li-battery swelling.

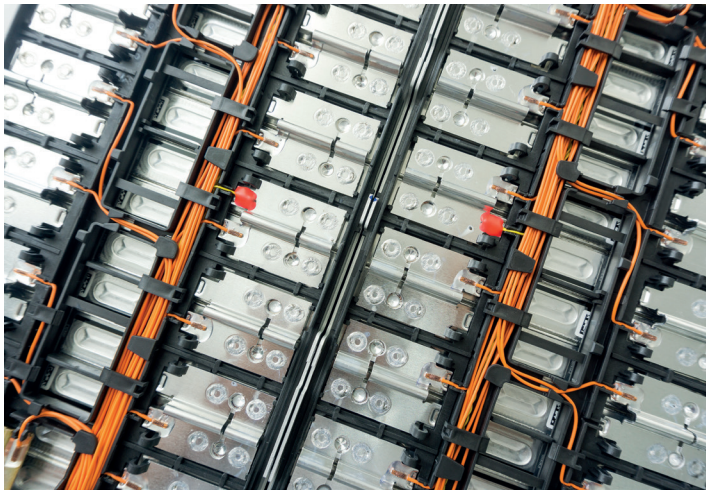
Introduction

Initial charge/discharge processes in batteries produce a variety of gas components that have an impact on battery performance after long-term use. Additionally, some flammable gases create a security risk. Therefore, the gas composition produced by batteries provides important information about possible deterioration and the performance of different battery formulations.

However, there are two main difficulties in analyzing the composition of battery gas. Firstly, the gas composition produced by batteries is highly complex. There are three categories:

- Permanent gases such as hydrogen, methane, carbon monoxide, carbon dioxide, etc.
- Short-chain hydrocarbons (C2-C5)
- Other volatile compounds

These components are difficult to fully separate on a single gas chromatographic column for systematic analysis, and



a multi-column GC configuration is required. Secondly, in many cases, in addition to the qualitative identification of the gases produced by the battery, the concentration of the produced gases is required.

In this work, a multi-valve, multi-column GC equipped with two detectors was used to analyze samples from a battery drum package and detect permanent gases and light hydrocarbons up to C6+. The components in the sample were quantitatively measured by the external standard method.

Experimental

A Thermo Scientific™ TRACE™ 1300 Series GC gas chromatograph equipped with a Thermo Scientific™ iConnect SSL injector and an iConnect FID detector was connected to a Thermo Scientific™ 1310 Auxiliary Oven housing a 10-port and two 6-port switching valves and an iConnect TCD detector.

The following capillary columns were used and connected as shown in the schematic diagram (Figure 1):

- Thermo Scientific™ TracePLOT TG-BOND Q GC column, 30 m, 0.53 mm i.d., 20 µm th. (P/N 26004-6090)
- Agilent® J&W® CP6938, PLOT Moleseive, 25 m, 0.53 mm i.d.
- Thermo Scientific™ TraceGOLD™ TG-WaxMS A GC column, RT-12454, 30 m, 0.32 mm i.d., 1 µm th. (P/N 26087-2970)
- Restek® Al_2O_3, 25 m, 0.32 mm i.d., 8 µm th.
- Thermo Scientific™ TraceGOLD™ TG-1MS GC column 30 m, 0.32 mm i.d., 3.0 µm th. (P/N 26099-4840)

Sampling method: 1 mL of gas was injected through the SSL injector using a gas-tight syringe.

A gas standard mixture in nitrogen was used as the external standard. Its composition is reported in Table 1.

Two detectors were configured for a simultaneous detection of the permanent gases (TCD channel) and the light hydrocarbons (FID channel).

The operative conditions of the system are reported in Table 2.

Table 1. Gas standard mixture composition

Compound	Conc. (%,V/V)
Methane	5.99
Ethane	5.13
Ethylene	2.99
Propane	7.93
Cyclopropane	0.51
Propylene	3.01
Isobutane	2.72
Butane	2.07
Propandiene	0.95
Acetylene	0.12
trans-Butene	1.54
Butene	1.00
Isobutylene	0.80
cis-Butene	1.23
Isoprene	0.11
Pentane	0.14
1,3-butadiene	1.53
Propyne	0.47
trans-2-pentene	0.20
2- Methyl-2-butene	0.15
1-pentene	0.10
cis-2-pentene	0.14
Hexane	0.10
Hydrogen	14.93
Oxygen	0.53
Carbon monoxide	1.50
Carbon dioxide	3.00
Nitrogen bulk gas	

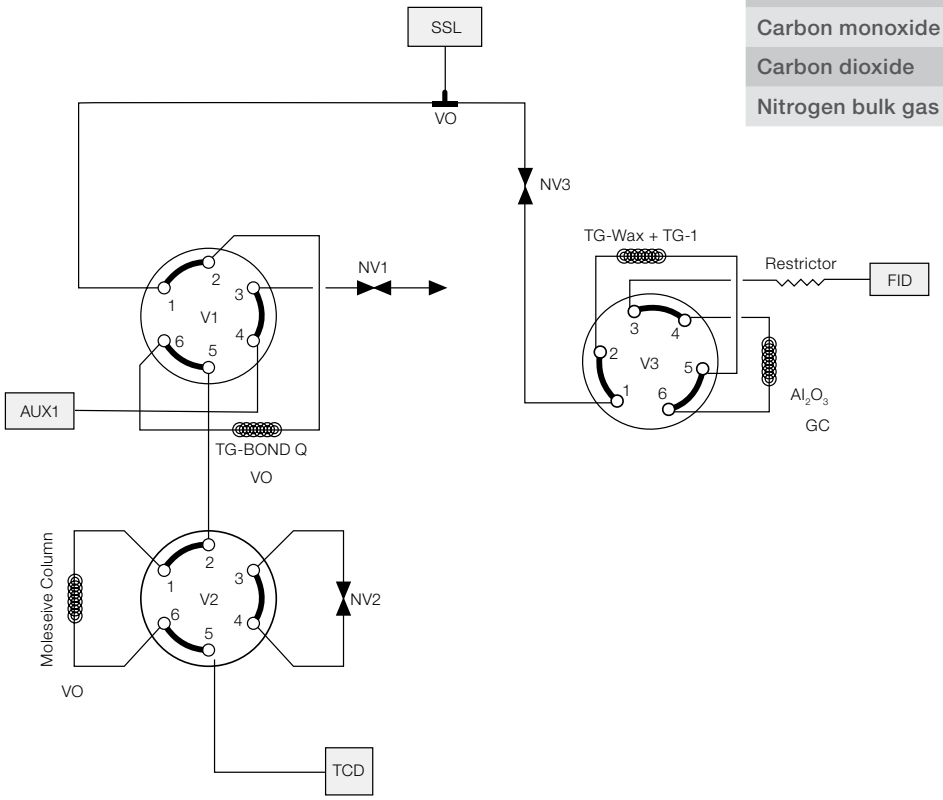


Figure 1. Valve diagram of the multi-column GC configuration

Table 2. Operative conditions of the configured GC system

Carrier gas (Argon)	
Flow mode	Constant pressure
Front SSL	123 kPa
Carrier AUX	78 kPa
Detector TCD (Aux-Left)	
Temperature	200 °C
Filament temperature	300 °C
Reference flow	1 mL/min (Ar)
Detector FID (Back)	
Temperature	250 °C
Ignition threshold	1.0 pA
Air	350 mL/min
H_2	35 mL/min
Make up gas (N_2)	30 mL/min
GC oven	
Initial temperature	60 °C
Initial time	1.20 min
Ramp 1	15 °C/min
Final temperature 1	100 °C
Final time 1	1.00 min
Ramp 2	30 °C/min
Final temperature 2	180 °C
Final time 2	1.00 min
Auxiliary oven	
Temperature	70 °C

Results

A gas sample of 500 µL was taken with a 1 mL gastight syringe directly from the battery drum pack and injected manually into the GC system for separation and detection. A single injection allowed for qualitative and quantitative determination of H_2, O_2, N_2, CO, CO_2, C1-C5, and C6+ in the battery drum pack gas.

The switching valves were activated at a specific timing to cut the fraction and divert the sample components onto the appropriate columns for their separation. Components H_2, O_2, N_2, CO, and CO_2 were then measured by the TCD, while the components of C1-C5 and C6+ were detected by the FID.

The six-port valve V3 allowed the backflush of the heavier compounds, detected as C6+, while the C1-C5 were separated onto the alumina (Al_2O_3) column. The six-port valve V1 allows the backflush of heavier gases preventing contamination of the molecular sieve column. The system configured with backflush operation effectively shortened the analysis time and extended the life of the alumina and MolSieve columns.

Five samples from two separate batches were analyzed and the components quantified against the external standard mixture.

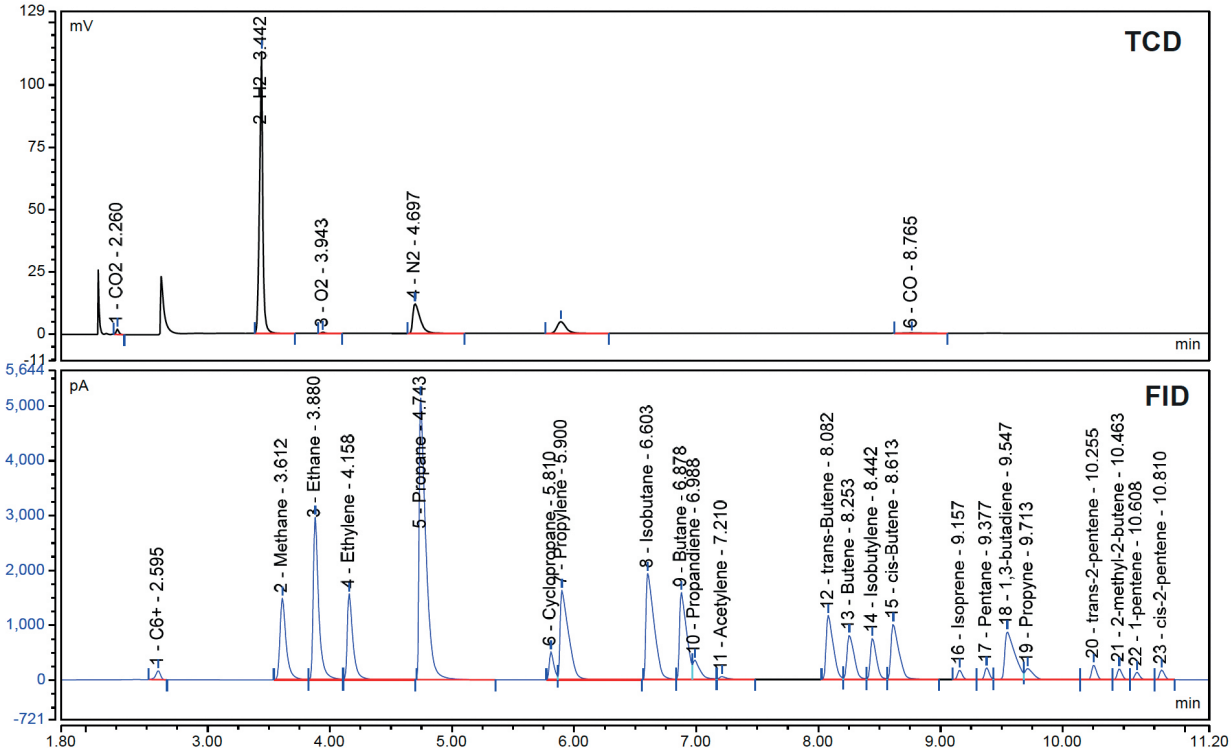


Figure 2. Chromatographic separation of the gas standard mixture. See Table 1 for composition.

First batch – Sample 1:

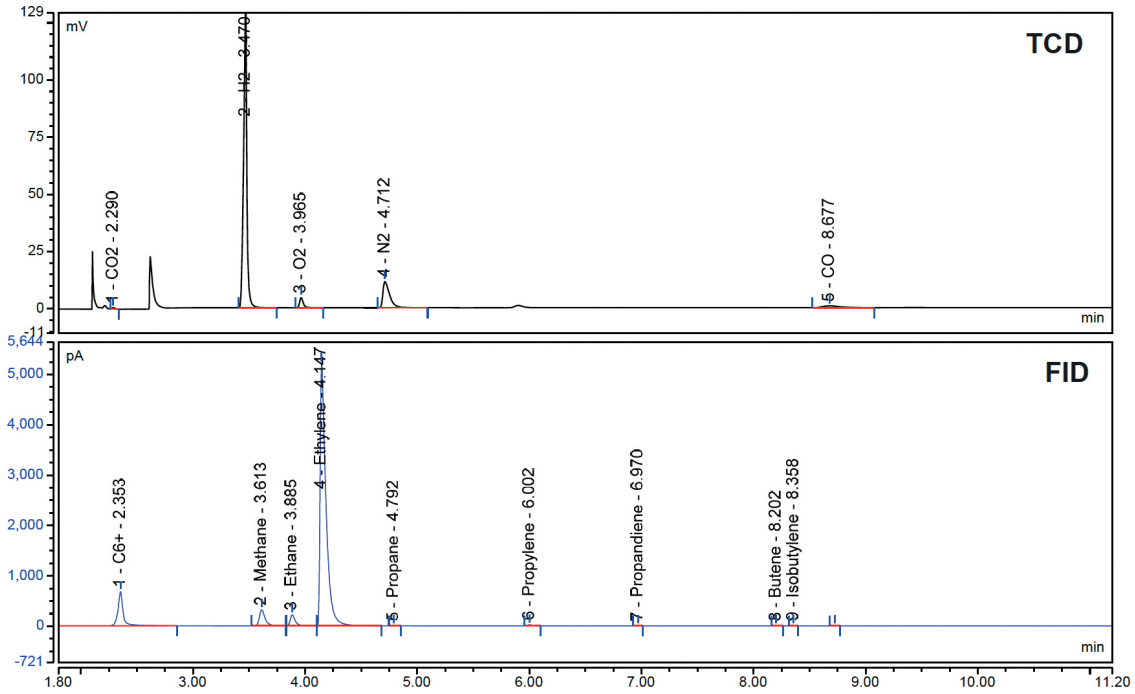


Figure 3. Chromatographic separation of Batch 1 – Sample 1

Table 3. Quantitative results for Batch 1 – Sample 1

Peak	Compound	Detector	Retention time (min)	Area (mV*min)	Height (mV)	Amount (%, V/V)	Corrected amount (%)
1	CO_2	TCD (Aux-Left)	2.290	0.014	0.59	0.80	0.94
2	H_2	TCD (Aux-Left)	3.470	4.40	138.1	18.66	22.13
3	O_2	TCD (Aux-Left)	3.965	0.17	4.66	5.42	6.43
4	N_2	TCD (Aux-Left)	4.712	0.80	11.44	38.90	46.13
5	CO	TCD (Aux-Left)	8.677	0.13	0.81	7.40	8.77
1	C6+	FID (Back)	2.353	35.69	679.3	0.40	0.47
2	Methane	FID (Back)	3.613	19.33	322.1	1.33	1.58
3	Ethane	FID (Back)	3.885	11.57	225.7	0.41	0.49
4	Ethylene	FID (Back)	4.147	310.9	5211.3	10.96	13.00
5	Propane	FID (Back)	4.792	0.13	3.13	0.003	0.00
6	Propylene	FID (Back)	6.002	0.97	24.32	0.023	0.03
7	Propandiene	FID (Back)	6.970	0.073	1.98	0.013	0.02
8	Butene	FID (Back)	8.202	0.09	2.40	0.002	0.00
9	Isobutylene	FID (Back)	8.358	0.041	1.17	0.0007	0.00

First batch – Sample 2:

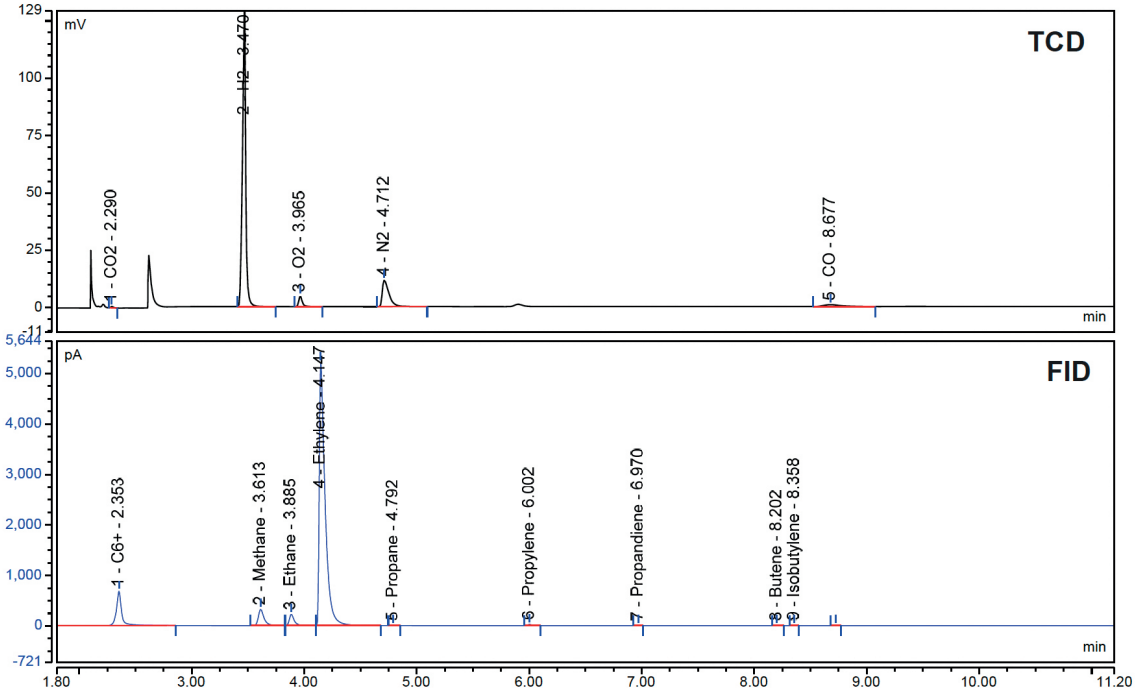


Figure 4. Chromatographic separation of Batch 1 – Sample 2

Table 4. Quantitative results for Batch 1 – Sample 2

Peak	Compound	Detector	Retention time (min)	Area (mV*min)	Height (mV)	Amount (%, V/V)	Corrected amount (%)
1	CO_2	TCD (Aux-Left)	2.272	0.01	0.56	0.77	0.88
2	H_2	TCD (Aux-Left)	3.452	3.97	128.0	16.84	19.25
3	O_2	TCD (Aux-Left)	3.948	0.17	4.60	5.44	6.22
4	N_2	TCD (Aux-Left)	4.698	0.89	12.46	43.87	50.16
5	CO	TCD (Aux-Left)	8.702	0.13	0.78	7.17	8.20
1	C6+	FID (Back)	2.355	33.48	634.3	0.37	0.42
2	Methane	FID (Back)	3.613	20.34	341.1	1.40	1.60
3	Ethane	FID (Back)	3.887	11.95	234.97	0.43	0.49
4	Ethylene	FID (Back)	4.148	315.8	5287	11.14	12.73
5	Propane	FID (Back)	4.795	0.11	2.78	0.003	0.00
6	Propylene	FID (Back)	6.007	1.01	24.89	0.024	0.03
7	Propadiene	FID (Back)	6.975	0.05	1.48	0.01	0.01
8	Butene	FID (Back)	8.207	0.06	1.79	0.001	0.00
9	Isobutylene	FID (Back)	8.365	0.03	0.87	0.0005	0.00

First batch – Sample 3:

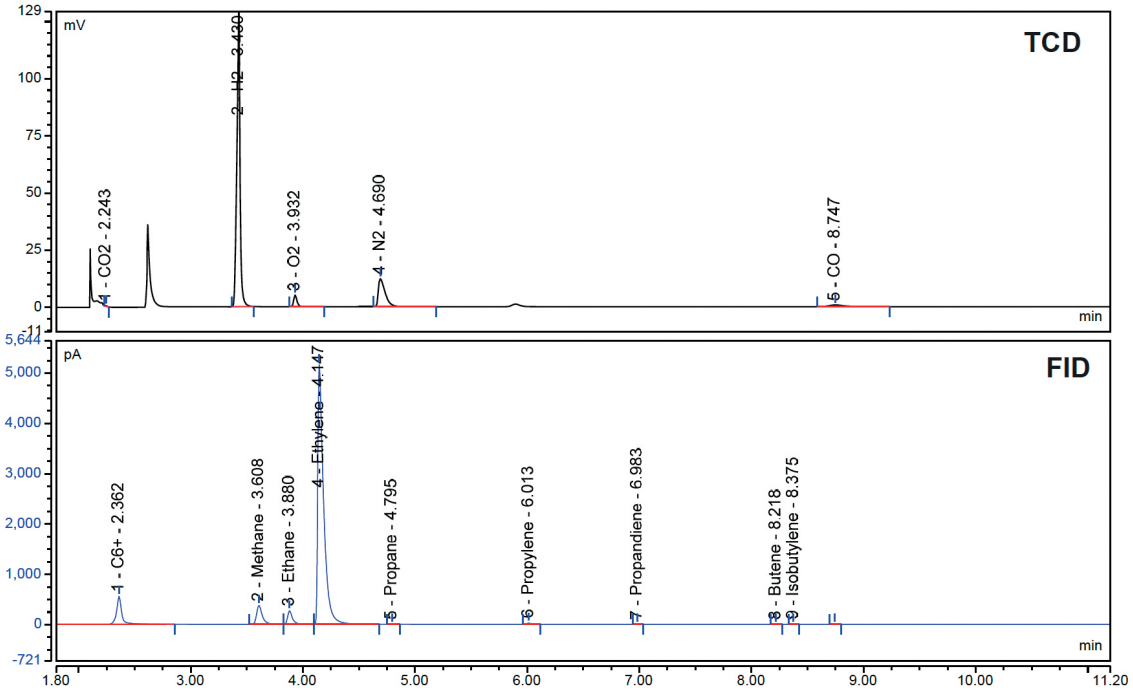


Figure 5. Chromatographic separation of Batch 1 – Sample 3

Table 5. Quantitative results for Batch 1 – Sample 3

Peak	Compound	Detector	Retention time (min)	Area (mV*min)	Height (mV)	Amount (%, V/V)	Corrected amount (%)
1	CO_2	TCD (Aux-Left)	2.243	0.006	0.31	0.31	0.36
2	H_2	TCD (Aux-Left)	3.43	4.21	133.58	17.85	20.22
3	O_2	TCD (Aux-Left)	3.932	0.19	5.15	6.06	6.87
4	N_2	TCD (Aux-Left)	4.690	0.88	12.28	43.36	49.11
5	CO	TCD (Aux-Left)	8.747	0.13	0.78	7.40	8.38
1	C6+	FID (Back)	2.362	29.63	560.10	0.33	0.37
2	Methane	FID (Back)	3.608	22.48	375.73	1.55	1.75
3	Ethane	FID (Back)	3.880	13.90	269.77	0.50	0.56
4	Ethylene	FID (Back)	4.147	308.43	5162.0	10.88	12.32
5	Propane	FID (Back)	4.795	0.16	3.86	0.004	0.00
6	Propylene	FID (Back)	6.013	1.07	26.50	0.025	0.03
7	Propadiene	FID (Back)	6.983	0.09	2.28	0.015	0.02
8	Butene	FID (Back)	8.218	0.10	2.60	0.002	0.00
9	Isobutylene	FID (Back)	8.375	0.04	1.11	0.0007	0.00

Second batch – Sample W:

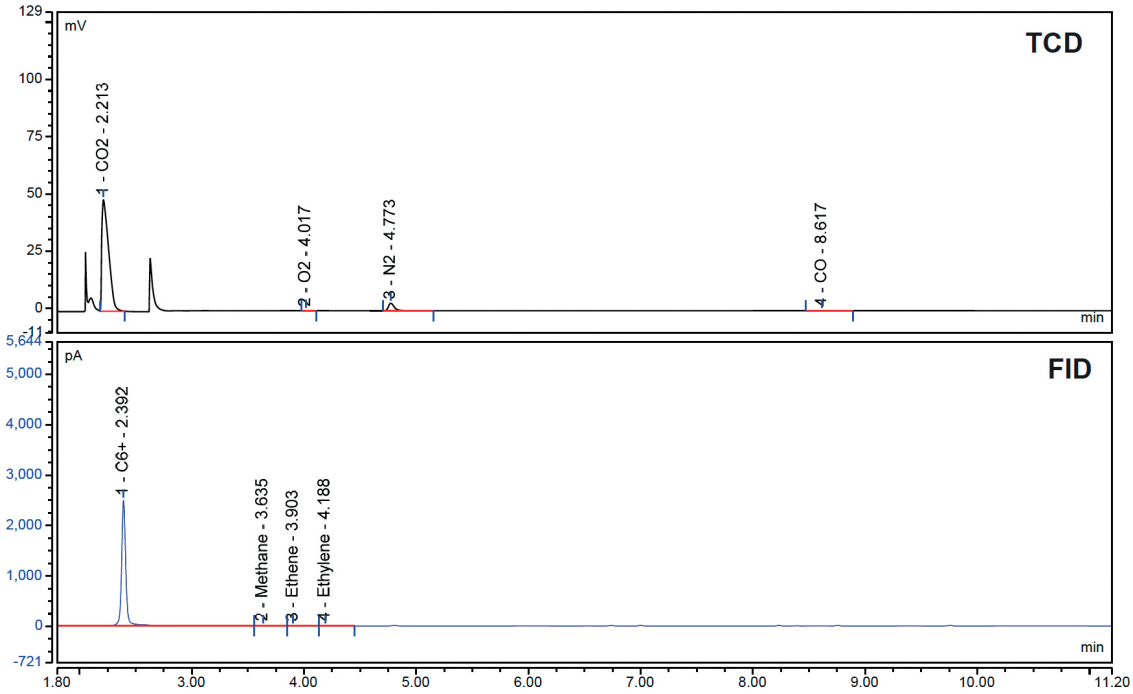


Figure 6. Chromatographic separation of Batch 2 – Sample W

Table 6. Quantitative results for Batch 2 – Sample W

Peak	Compound	Detector	Retention time (min)	Area (mV*min)	Height (mV)	Amount (%, V/V)	Corrected amount (%)
1	CO_2	TCD (Aux-Left)	2.213	3.41	48.67	79.65	92.93
2	O_2	TCD (Aux-Left)	4.017	0.006	0.15	0.10	0.12
3	N_2	TCD (Aux-Left)	4.773	0.20	3.31	4.81	5.61
4	CO	TCD (Aux-Left)	8.617	0.02	0.13	0.52	0.60
1	C6+	FID (Back)	2.392	113.32	2495.9	0.59	0.70
2	Methane	FID (Back)	3.635	0.49	3.94	0.017	0.02
3	Ethane	FID (Back)	3.903	0.37	5.25	0.007	0.01
4	Ethylene	FID (Back)	4.188	0.34	7.20	0.006	0.01

Second batch – Sample E:

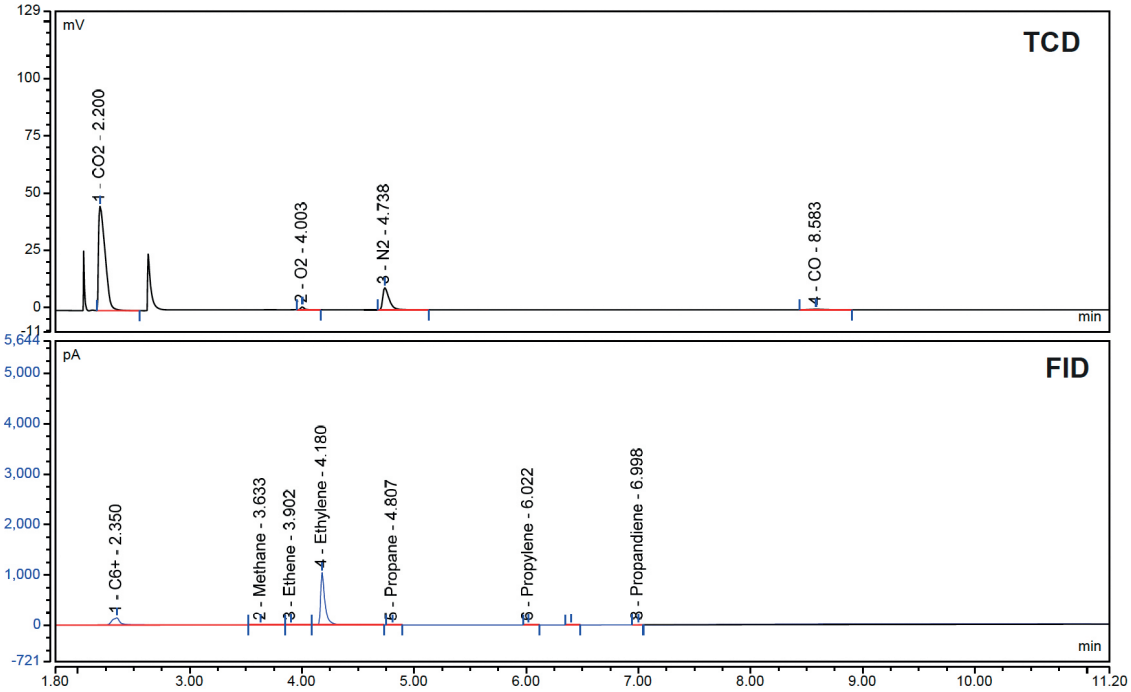


Figure 7. Chromatographic separation of Batch 2 – Sample E

Table 7. Quantitative results for Batch 2 – Sample E

Peak	Compound	Detector	Retention time (min)	Area (mV*min)	Height (mV)	Amount (%, V/V)	Corrected amount (%)
1	CO_2	TCD (Aux-Left)	2.200	3.09	45.53	72.10	80.04
2	O_2	TCD (Aux-Left)	4.003	0.05	1.24	0.87	0.97
3	N_2	TCD (Aux-Left)	4.738	0.63	9.60	15.25	16.93
4	CO	TCD (Aux-Left)	8.583	0.04	0.24	0.97	1.08
1	C6+	FID (Back)	2.350	13.57	142.90	0.07	0.08
2	Methane	FID (Back)	3.633	0.37	3.70	0.01	0.01
3	Ethane	FID (Back)	3.902	0.22	4.29	0.004	0.00
4	Ethylene	FID (Back)	4.180	46.36	1040.1	0.80	0.89
5	Propane	FID (Back)	4.807	0.02	0.43	0.0003	0.00
6	Propylene	FID (Back)	6.022	0.03	0.66	0.0003	0.00
7	Propandiene	FID (Back)	6.998	0.02	0.32	0.0003	0.00

Conclusion

The configured multi-valve, multi-column TRACE 1300 series GC system is a robust solution to detect the complex gas mixture from batteries swelling in less than 10 minutes, characterizing the aging and performance.

- The backflush configuration not only shortens the analysis time but avoids heavier compounds to damage the separation columns.
- A single injection allows qualitative and quantitative analysis of drum pack gas components, with the detection of both permanent gases and light hydrocarbons up to C6+.

Find out more at **thermofisher.com**

ThermoFisher SCIENTIFIC