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DETERMINATION OF PERMANENT GASES AND LIGHT HYDROCARBONS BY SIMULTANEOUS OPERATION ON PACKED AND CAPILLARY COLUMNS WITH THERMAL CONDUCTIVITY DETECTION AND FLAME-IONIZATION DETECTION ON A SINGLE COMPUTER INTEGRATOR

F. POY* and L. COBELLI

DANI S.p.A., Via Rovani 10, 20052 Monza MI (Italy)

SUMMARY

Simple instrumentation, based on a commercial gas chromatograph equipped with one packed and one capillary column channel and two different detectors leading to a single computer integrator, is described. The simultaneous injection into both channels provides the means to perform the determination of inorganic and hydrocarbon gases of the same sample.

Methane, used as an internal standard, allows correlation between the two chromatograms, recorded on two files of the same computing integrator. Data reduction is performed by means of BASIC program. The instrumentation is suitable for routine laboratory analysis or on-lined and closed-loop application.

INTRODUCTION

The determination of the single components of a gaseous mixture containing oxygen, nitrogen, methane, carbon monoxide, carbon dioxide and hydrocarbons from C_1 to C_8, is of great interest in petrochemical plants and refineries, and in the production of natural gas.

Several gas chromatographic (GC) methods have been developed for this type of analysis[1–3]. Most of them are suitable for analysing all the components of the mixture, making use of the newest microprocessor control, multi-column switching, automatic valves, and different types of capillary column. Nevertheless, all the methods described suffer from some limitations. For example, in one case[1] the sample injection is performed in two steps, in other cases the quantitation requires special calibration and high sample volume reproducibility[2] or demands high instrumentation cost for a second integrator channel in case simultaneous introduction is desired[3].

The GC system described here permits the analysis of both inorganic gases and hydrocarbons up to C_8 with a single, unmodified commercial gas chromatograph and with a single computer integrator. The sample is injected simultaneously into two different GC channels. The single final report summarizes all qualitative and quantitative data.

EXPERIMENTAL

The GC system consists of a DANI 8500 gas chromatograph with a flame ionization detector at the end of the capillary column channel for hydrocarbon analysis, and a thermal conductivity detector at the end of a channel including three packed column and two switching column valves for the inorganic gases. Two gas-sampling valves with different sample loops are mounted. All valves are installed outside the column oven and are automatically operated by means of compressed air. The switching time programme is set on the GC control module.

The two detectors are connected to a single computer integrator, Shimadzu C-R3A, via a switching relay, timed by the computer. All analytical parameters, e.g. temperature programme, detector temperatures, sample injection, and column switching, are set on the GC control module. Analysis files, e.g. integrator parameters, calibration tables, analysis report, detector outputs, switching time, and BASIC programs, are stored in the computing memory without need for a cassette tape unit. The schematic diagram of the chromatographic system is shown in Fig. 1.

The gas-sampling loop of the capillary column channel sampling valve is 50 μl. This small amount of sample permits the use of a low split ratio (1:50). The gas-sampling loop of the packed column sampling valve is 0.5 ml. The sample volume may be optimized independently in order to ensure the correct linear detector response and to avoid column overload effects. On the first column switching valve a short Porapak column is mounted where C_2 and higher hydrocarbons are retarded and backflushed just after methane and carbon dioxide enter the main Porapak column.

When methane and other inorganic gases enter the molecular sieve column, mounted on the second switching valve, this column is isolated. Carbon dioxide is now eluted from the main Porapak column. After carbon dioxide elution, the mo-
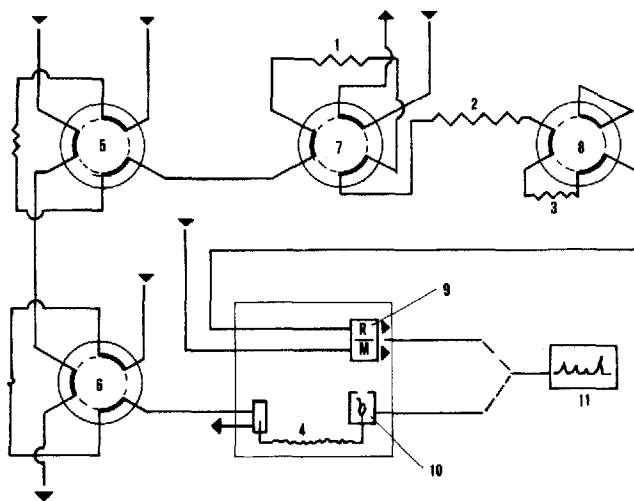

Fig. 1. Sampling valves, switching valves, columns and analytical channels of DANI 8500 GC system for permanent gases and light hydrocarbon analysis. 1 = Precolumn; 2 = Porapak Q; 3 = molecular sieve 5A; 4 = capillary column; 5 and 6 = sampling valves; 7 and 8 = column switching valves; 9 = thermal conductivity detector; 10 = flame ionization detector; 11 = computer integrator.
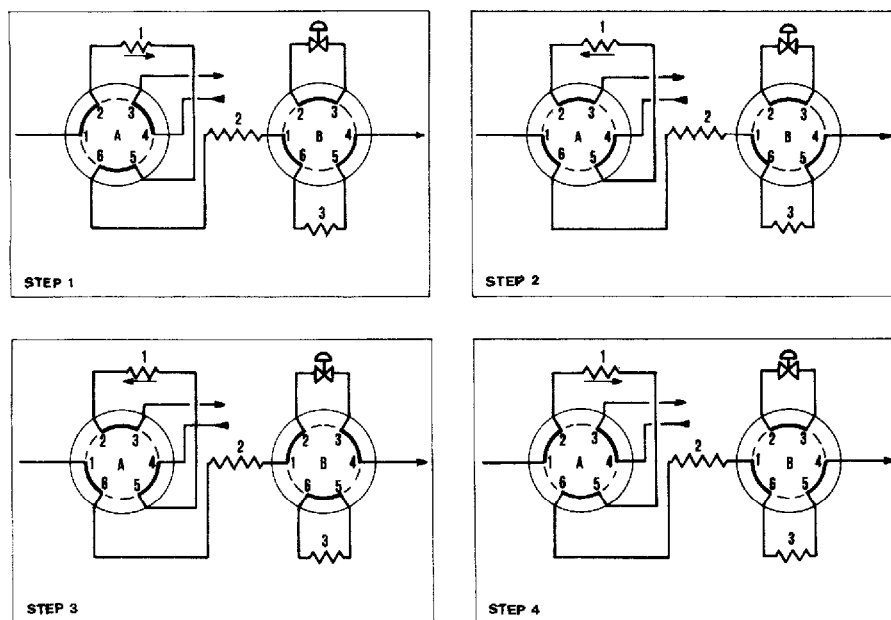
Fig. 2. Configuration of the column switching valves and organization of the columns during the different steps of a complete analytical run.

lecular sieve column is again included in the analytical cycle for the elution of oxygen, nitrogen, methane and carbon monoxide. A schematic diagram of the valves actuation and column organization during the analytical cycle sequence is shown in Fig. 2.

At the beginning of the analysis, the sample, which purged ahead of both gas-sampling loops, is injected into both analytical channels by simultaneous switching of the sampling valves. At the starting time the column oven is kept at 50°C and the integrator input is connected to the thermal conductivity detector. The carrier gas flow-rate of capillary column is adjusted to produce elution of methane 20 s after the carbon monoxide peak. After the elution of carbon monoxide, the column oven is programmed to 200°C at a rate of 10°C/min, and the input of the integrator is switched to the flame ionization detector.

Fig. 3 shows a complete chromatogram of a mixture containing inorganic gases and hydrocarbons up to C_6.

The detector response is ingegrated on two different files of the computing integrator, and at the end of the analysis a BASIC program produces the correlation of data obtained from both the capillary flame ionization detection (FID) and packed thermal conductivity detection (TCD) column systems. Methane, which appears in both channels, is used as internal standard.

The sum of components is normalized to 100% by volume. The calculation is expressed by the following formula:

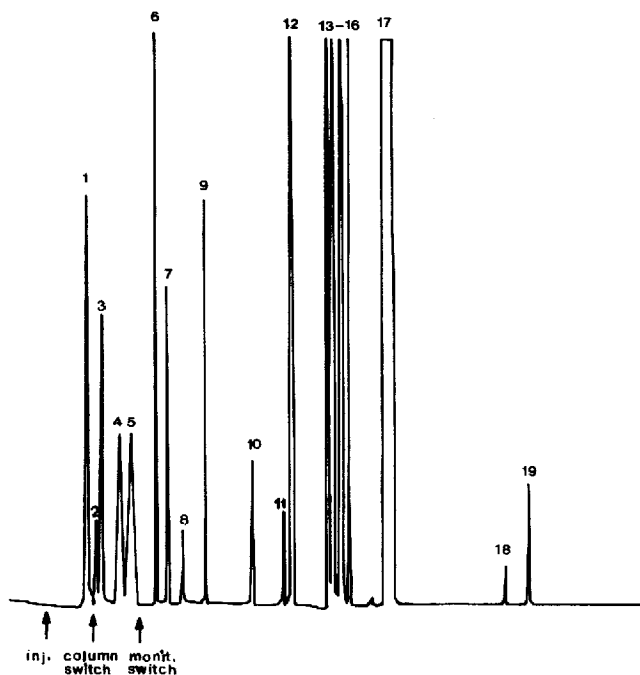$$\Sigma\left(\frac{A_i}{C_i} + \frac{C_x}{A_x} - 1\right) \cdot K = 100$$

Fig. 3. Typical chromatogram of permanent and hydrocarbon gases, with a single recording computer, obtained from a DANI 8500 gas chromatograph. Columns: 1 = stainless steel, 50 cm × 3 mm I.D., Porapak Q; 2 = stainless steel, 1.50 m × 3 mm I.D., Porapak Q; 3 = stainless steel, 1 m × 3 mm I.D., molecular sieve 5A; 4 = fused silica, 50 m × 0.32 mm I.D., Al₂O₃, KCl (Chrompack). Carrier gas, hydrogen. Flow-rate: packed columns, 25 ml/min; capillary column, 2 ml/min; split, 50 ml/min. Oven temperature programme: 50°C for 4 min, then 10°C/min to 200°C, then 200°C for 7 min. Peaks: 1 = CO_2; 2 = O_2, 3 = N_2; 4 = CH_4(TCD); 5 = CO; 6 = CH_4(FID); 7 = C_2H_6; 8 = C_2H_4; 9 = C_3H_8; 10 = C_3H_6, 11 = iso-C_4H_{10}; 12 = n-C_4H_{10}; 13–16 = C_4H_8 isomers; 17 = 1,3-butadiene; 18 = iso-C_5H_{12}, 19 = n-C_5H_{12}.

where A_i is the TCD area of component i, C_i is the TCD area of methane, A_x is the FID area of component x, C_x is the FID area of methane, K is the normalization constant. This procedure allows quantification even if different amounts of sample are injected.

The analytical cycle is automatic from the injection up to the final report, and the instrument is suitable for on-line operation or in a closed-loop system, provided the sample is available at the input of the sampling valves as a continuous stream.

RESULTS AND DISCUSSION

The capillary column used (Chrompack, 50 m × 0.32 mm I.D., Al₂O₃, KCl) described by De Nijs and De Zeeuw[4] has two main advantages.

(1) The retention time of methane at the initial temperature programme is long enough to permit the previous elution of all inorganic gases coming from the packed column.

(2) It provides the separation of all saturated and unsaturated C_4 hydrocar-

TABLE I

STATISTICAL DATA OBTAINED FROM TEN RUNS

Calculated by the internal normalization method.

Compound	t_R	R.S.D. (%)	Concentration	
			%	R.S.D. (%)
CO_2	2.11	0.5	5.3	0.8
O_2	2.58	0.3	1.1	0.7
N_2	2.58	0.3	4.4	0.6
CH_4	3.77*/5.54**	0.25*/0.15**	5.0	0.8
CO	4.33	0.25	4.9	0.7
C_2H_6	6.91	0.15	2.2	0.6
C_2H_4	8.05	0.12	0.6	0.7
C_3H_8	9.05	0.10	2.1	0.8
C_3H_6	10.28	0.12	1.9	0.6
iso-C_4H_{10}	11.73	0.10	0.4	0.8
n-C_4H_{10}	12.13	0.10	7.4	0.5
iso-C_4H_8	13.05	0.10	6.7	0.5
C_4H_8	13.95	0.10	4.83	0.5
2-trans-C_4H_8	14.27	0.10	10.80	0.4
2-cis-C_4H_8	14.66	0.10	4.7	0.7
1,3-Butadiene	16.28	0.09	38.8	0.8
iso-C_5H_{12}	21.05	0.08	0.4	0.6
n-C_5H_{12}	22.18	0.08	1.0	0.8

    * Packed column.
   ** Capillary column.

bons. This separation is not required in the case of a natural gas analysis, but it is of paramount importance in the petrochemical industry. However, this column is not suitable for the determination of hydrocarbons with more than eight carbon atoms.

The simultaneous injection into both analytical channels as already stated[4] provides two advantages.

(1) There is a guarantee that the quantitative data refer to a homogeneous sample, resulting in greater reliability, not only when standard or calibration mixtures are injected, but also when actual samples are analysed.

(2) It is possible to perform the quantification by using the relative response factor, thus eliminating the need for repeatable sample volume injections and frequent recalibration.

The use of a single computing integrator saves money and simplifies the reading of the analytical data and results.

It is clear that from such a detailed report, a simple post-chromatographic calculation may provide the calorific value, the specific gravity, and the Wobbe index of the analysed gas mixture.

Statistical data from ten consecutive automatic analyses are given in Table I.

CONCLUSION

The instrumentation described may be used for the analysis of gases, oil con-

densate and complex gas mixtures coming from pilot plants without any change.

The final report provides all the required physical and chemical parameters of the analysed gas mixtures.

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