A RECORDING CHROMATOGRAPH BASED ON JANÁK'S PRINCIPLE

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In 1953 JANÁK[1] presented a gas chromatographic analytical method, which differed considerably from the previously used techniques. The new method did not follow the existing practice of measuring the concentrations of the separated components in the carrier gas by means of a suitable detector, but measured the volume of the separated, pure components. The carrier gas was pure carbon dioxide, which, after being passed through the column, was absorbed in a nitrometer filled with potassium hydroxide solution. The volume of the non-absorbed, chromatographically separated sample was measured and recorded as a function of time.

Considering its great accuracy and the ease with which it can be employed, it is surprising that the method has not become more widely adopted. The unpopularity of the method may be put down partly to the drawbacks attached to it. For example, the method is very cumbersome. During analysis the gas volume in the nitrometer must be read at given intervals. The separation of the components is often difficult to observe; one moment's inattentiveness may invalidate the determination. Moreover there are some systematic errors, which can be ruled out only by applying empirical correlation factors; these include the "wall effect", which is caused by KOH solution adhering to the wall of the nitrometer, and the effect of the vapour tension of the solution. As will be made clear in the present paper, all these drawbacks can be overcome in a fairly simple way.

The assets of the method—great accuracy at higher percentages, and the fact that calibration can be dispensed with—make it very attractive, and several investigators have tried to eliminate the drawbacks without sacrificing the advantages.

JANÁK[2] designed an apparatus in which the gas bubbles ascending through the KOH solution collect under a bell suspended on a balance. The displacement of the balance arm is recorded photographically.

VAN DER CRAATS[3] started from an entirely different principle. He washed the gas issuing from the column with a countercurrent of KOH solution, and measured the pressure rise in a partly evacuated collecting vessel.

LEIBNITZ[4] used a nitrometer. The level of the KOH-solution in the nitrometer is kept constant by means of a piston which, via a relay system, is actuated by a contact near the meniscus of the solution. The piston travel is recorded mechanically.

JANÁK[5] constructed a variant of LEIBNITZ's device. He maintained a constant pressure in his fully closed system by withdrawing the KOH solution by means of a piston system operated by a mercury manometer.

VÉLUT[6] described a device in which the nitrometer pressure was kept constant by displacing the KOH-gravity feed vessel. The displacement was recorded.

In addition, a patent application[7,8] was filed for a device in which the carbon dioxide is absorbed in conformity with VAN DER CRAATS's principle, but in which the pressure of the gas is kept constant by means of a piston system.

None of these devices, however, fully satisfied our demands; what we needed was a reliable, accurate and fully automatic instrument that could be operated by an unskilled laboratory technician. On the basis of LEIBNITZ's principle we designed and constructed a device which is suitable for routine analysis of permanent gases and satisfies all our requirements.

PRINCIPLE

The sample, which should not be appreciably soluble in KOH solution, is passed through the column with a stream of carrier gas (very pure carbon dioxide) and collected in a nitrometer fitted with a short stem and containing concentrated KOH solution (see Fig. 1). The carrier gas dissolves in the solution; the sample gas ascends and collects over the liquid, producing a pressure rise, which causes the liquid level to fall. (The system burette–nitrometer–overflow is in fact a sensitive pressure indicator.)

The falling meniscus breaks a contact, which actuates a motor-operated piston-burette. The burette enlarges the volume over the solution by a volume equal to that of the amount of gas fed in, e.g. until the contact is just closed again, so that the original pressure is restored.
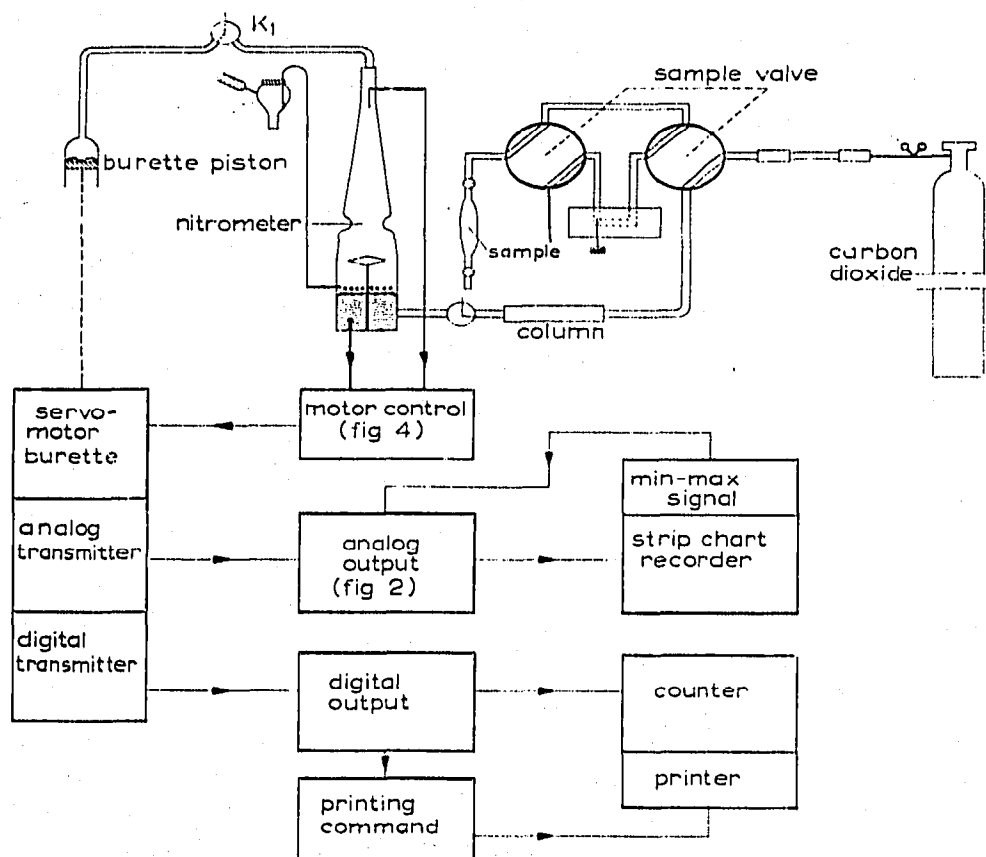

Fig. 1. Block diagram of the chromatograph.

The position of the motor-operated burette, which, as made clear above, is a measure of the amount of component that has issued from the column, can be recorded both on an analog recorder (Fig. 2) and on a digital printer. The whole device is thermostated.
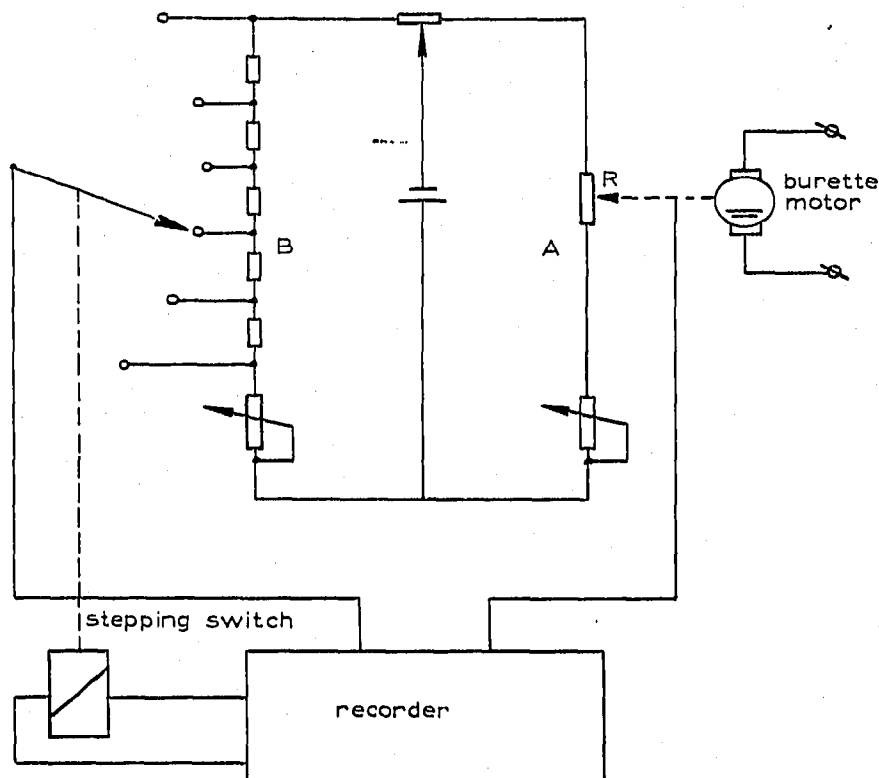

Fig. 2. Analog output circuit.

Discussion

We have found that the instrument satisfies all our requirements. Systematic errors have been eliminated and, as the KOH solution remains at a constant level, the wall effect has been ruled out. At the thermostatically controlled constant temperature the vapor pressure of the KOH is a constant, for which allowance is made in calibrating the instrument. Differences in solubility between the permanent gases in the KOH solution are very small if the concentration of the solution is 46 % and the temperature is adjusted to 35 °C. The instrument is fully automated and operation is therefore simple. After the sample introduction, no further operations are required, so that, as far as ease of handling is concerned, the device is comparable to, say, a katharometer chromatograph. The result of the analysis (in percent) can be read directly from an analog recorder and from a digital printer.

PROCEDURE

The sample is introduced into a sample-feeding system fitted with a six- or eight-way valve and left there for a few moments to adopt the thermostat temperature. The sample compartment is connected with the atmosphere via a capillary and the sample is thus measured at atmospheric pressure.

The volume of the components after leaving the column is also measured at atmospheric pressure and at the same temperature, which eliminates correction for barometer reading and temperature. The volume of the sample compartment is *ca.* 3 ml and can be varied over a limited range (see below).

The sample is fed to the column with a stream of carrier gas consisting of very pure carbon dioxide (> 99.998 % CO_2). The carbon dioxide is purified in the device described by KEULEMANS[9]. In principle, the column can be packed with any suitable material (except molecular sieves). The carrier gas that has left the column is fed to the nitrometer, where the carbon dioxide dissolves and the insoluble components ascend. However, all gases are more or less soluble in KOH; for permanent gases the differences in solubility have been found to decrease with increasing concentration of the KOH solution. The velocity with which the gas bubbles ascend depends on the viscosity of the liquid. The concentration up to which the viscosity remains reasonable is *ca.* 46 %. To avoid deposition of potassium carbonate at these high concentrations, it is essential to keep the temperature of the KOH over 30°C and to introduce the gas under mercury (Fig. 3). To prevent the gas bubbles from adhering to the mercury surface, the surface is covered with a thin layer of mercuric oxide. In addition, a continuous stream of KOH solution is fed to the nitrometer from storage flask A, via a restriction R. After use, the KOH solution is discharged via overflow B and replaced by fresh solution, which, to avoid foaming, must not contain any Ca or Ba. If traces of these metals should still be present, foaming can be suppressed by adding a small amount of EDTA.

The motor-operated burette is a commercial piston burette (Metrohm E 274) equipped with a Honeywell balancing motor. The motor is operated by means of a platinum contact in the nitrometer stem. When the falling meniscus of the KOH solution in the nitrometer breaks the contact, the motor is started. When the level of the KOH solution rises again upon displacement of the piston, the contact closes and the motor stops. In the course of one analysis this starting–stopping sequence is repeated a great many times. During continuous operation the piston moves at the rate of *ca.* 0.07 ml/sec, which is fast enough for the increase in volume to be reflected in a "peak". The smallest displacement of the piston needed for accurate recording of the "tail" and the blank is 0.003 ml. This is achieved by rapidly braking the motor after the contact has been closed. The principle of this method of motor control is outlined in Fig. 4.

Coil 1 of the two-phase motor is continuously energized with 110 V AC; coil 2 is fed via thyratrons V 1 and V 2. As long as contact C is open (*i.e.* the level of the KOH solution is under the contact point) the current passes via V1 and V 2, because their control grids connect with the cathode via R 1 and R 2. The current passing through R 4 energizes the diode circuit D 3, and thus renders thyratron V 3 nonconducting. When the KOH solution reaches contact C, in other words, when C is closed, the thyratrons V 1 and V 2 are opened via the two diode circuits D 1 and D 2. As the current has now stopped flowing through R 4, V 3 will become conducting (g 3 via R 3 to k 3) and a direct current is passed through motor coil 2. This arrangement permits the motor to be stopped within 40 msec.

The amount of energy needed for operating the circuit is very small, so that undesirable gas evolution at electrode C is avoided.

To restore the burette to its original position, the rotation of the motor can be reversed by means of switch S. This switch is coupled to valve K_1, which serves to vent
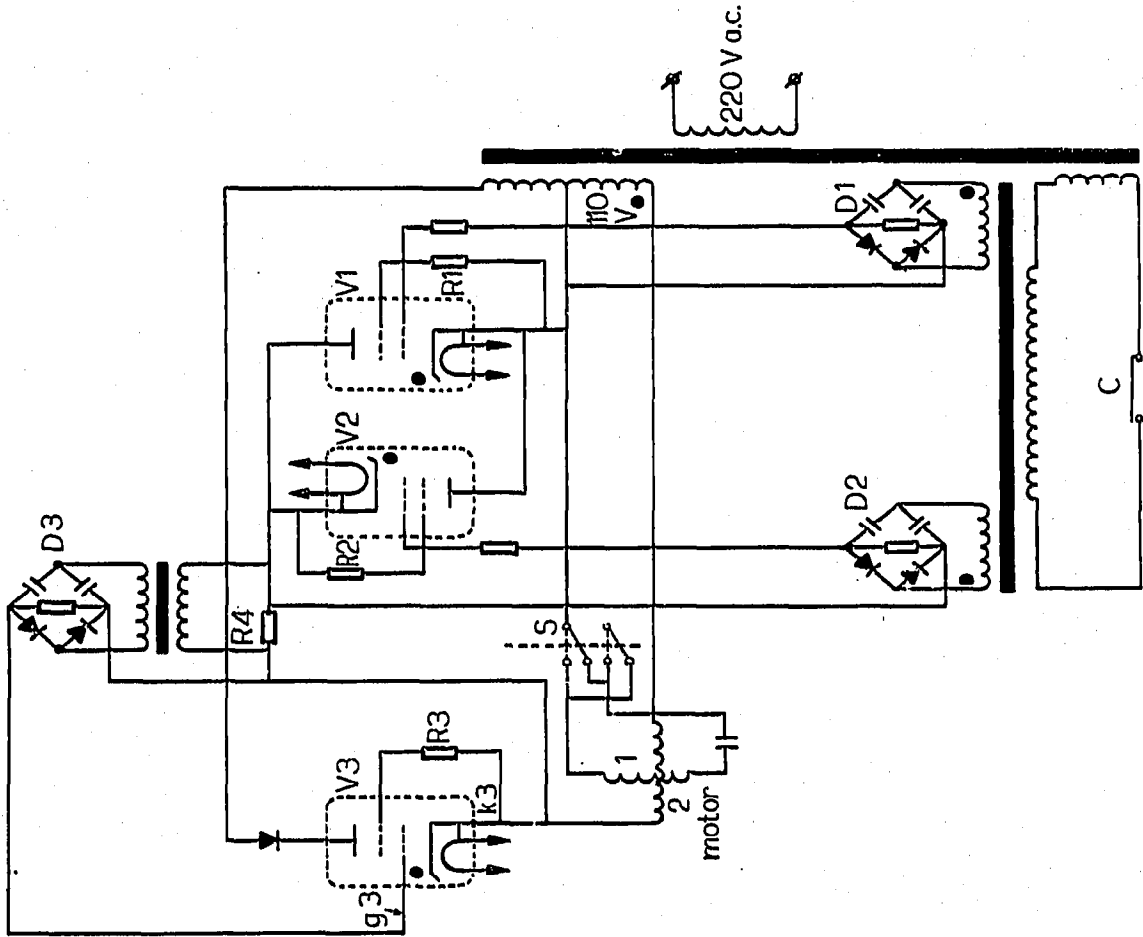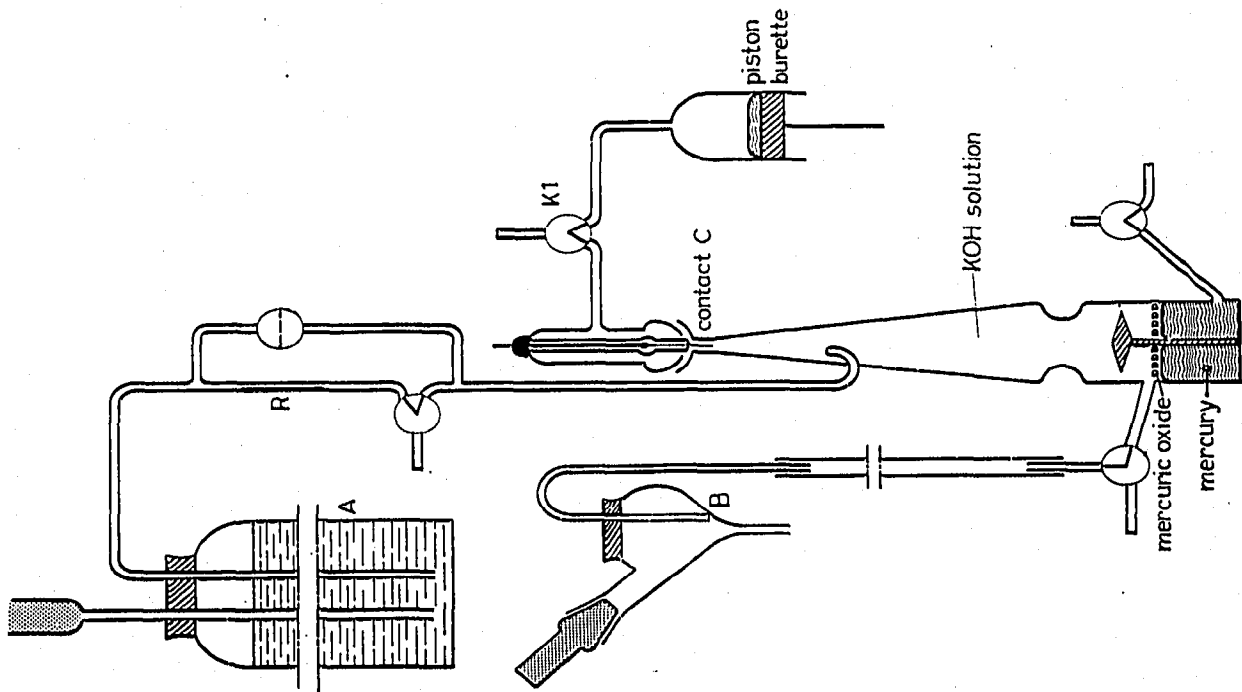
Fig. 4. Motor control circuit.

Fig. 3. Nitrometer.

the gas that has collected in the burette. Microswitches in the burette keep the burette within the measuring range.

Besides the burette drive pulley, the motor shaft also drives two gear wheels. One of these is directly coupled to a ten-coil potentiometer which delivers the analogous output signal. The principle of the analogous output can be seen in Fig. 2. Potentiometer R which, as shown above, is coupled to the piston, carries a constant weak current (branch A). Consequently, the voltage taken from the potentiometer is a measure of the volume of the gases that have collected in the nitrometer. This voltage is fed to an mV recorder, so that an integrated chromatogram is recorded on the recorder chart. To improve the reading accuracy and to facilitate reading, the relation between the voltage taken from the potentiometer and the recorder input voltage is so adjusted that 0.1 % of the total sample volume corresponds to 1 mm on the recorder. As the diagram width of the conventional recorders is no more than 250 mm, a second branch B has been incorporated in the circuit. Via this branch a compensating voltage equal to full-scale deflection of the recorder can be applied when the recorder pen has reached the edge of the diagram. This is done automatically by means of a stepping-switch controlled by the recorder pen. The number of opposing millivolts can be read from a digital indicator tube.

The digital measuring circuit is arranged on the other motor-driven gear. This gear carries a disc provided with 100 slots. A lamp over the disc intermittently illuminates a photoresistance under the disc when the latter is being rotated. A counter is energized via a amplifier circuit. The transmission ratio between burette and counter disc is such that 0.1 % of the total sample volume corresponds to 1 counting impulse (one illumination of the photo-resistance).

After elution of a peak, the pulses collected on the counter are printed on a strip chart, after which the counter is zeroed. The printing device becomes operative in response to a signal from a printing command circuit; this signal is given when no counting signals have been received over an adjustable time interval. The printed digits directly give the composition of the sample in 0.1 %.

As the ratio of the transmission from the burette to the digital measuring circuit can only be adjusted discontinuously (the adjustment being determined by the number of teeth on the gearwheels) provision has been made also for a fine adjustment. To this end the sample volume has been made adjustable. By means of a screw that can be fitted in the sampling space of a conventional six- or eight-way sampling valve, the sample volume can be varied over a limited range. The absolute amount of sample need not be known, because the (unknown) sample volume is always taken equal to 100 %, so to 1000 mm in the analog output and to 1000 counts in the digital output.

RESULTS

To determine the accuracy of the method, a number of analyses were performed on a mixture of permanent gases under the following conditions:

Column: inner diameter 8 mm, length 5.5 m.
Column packing: silica gel Ee (Gebr. Herrmann, Cologne, Ehrenfeld, Germany) washed with 3 N HCl and activated with a stream of carbon dioxide for 4 h at 250 °C. Fraction 0.35–0.42 mm.

TABLE I

ANALYSES OF PURE GASES

	Analog				Digital			
	H_2 mm	O_2 mm	N_2 mm	Ar mm	H_2 pulses	O_2 pulses	N_2 pulses	Ar pulses
Mean	1002.0	1005.5	1005.1	1001.5	601.1	603.6	603.6	601.3
φ	5	5	5	5	5	5	5	5
s	1.5	1.2	0.8	1.8	1.5	1.2	1.4	1.2
$s_{tot.}$	2.0 = 0.20 vol. % φ = 20				1.7 = 0.28 vol. % φ = 20			

s = standard deviation.
φ = degrees of freedom.

Gas flow rate: *ca.* 50 ml/min.
Temperature: *ca.* 35°C.

At the time of the analyses we had at our disposal only a burette giving 600 pulses for the total volume.

(1) A series of pure gas samples was analyzed. The total deflection of the recorder pen and the printed total number of pulses were considered to correspond to 100 % concentration (see Table I). The figures listed in Table I show that the accuracy of the analysis of a gas mixture is *ca.* 0.20 % by volume (standard deviation $s_{tot.}$). It is only when a greater accuracy is desired that the differences in solubility between the various gases become important.

(2) We then prepared 12 gas mixtures of known compositions. Each mixture contained 2 or 3 components in different ratios, and was analyzed in duplicate by means

TABLE II

RELATIVE AND ABSOLUTE DEVIATION (ANALOG METHOD)

		90 %	60 %	40 %	30 %	10 %	Mean
H_2	s	0.17	0.20	0.05	0.11	0.14	0.16
	φ	3	7	3	3	3	19
Δ_{mean}		—0.05	—0.12	+0.02	+0.20	+0.10	+0.01
CH_4	s		0.08		0.27	0.14	0.17
	φ		3		3	7	13
Δ_{mean}			0.00		+0.10	+0.02	+0.05
CO	s		0.13		0.17	0.28	0.20
	φ		3		3	3	3
Δ_{mean}			—0.32		—0.02	—0.07	—0.14
Ar	s		0.13		0.32	0.15	0.22
	φ		3		3	3	9
Δ_{mean}			+0.27		—0.02	+0.12	+0.12
Mean	s	0.17	0.16	0.05	0.23	0.18	0.18
	φ	3	16	3	12	16	50
Δ_{mean}		—0.05	—0.06	+0.02	+0.06	+0.04	+0.01

Δ = absolute systematic deviation (vol. %).
φ = degrees of freedom.
s = standard deviation (vol. %).

of the chromatograph. The sample volumes were equal to those in the first test series. The standard deviation and the deviation from the calculated percentage are represented in Tables II and III. These tables show that the absolute systematic deviation (Δ) is insignificant; this also holds for the differences between the accidental errors (s) for the various gases.

TABLE III

RELATIVE AND ABSOLUTE DEVIATION (DIGITAL METHOD)

		90%	60%	40%	30%	10%	Mean
H$_2$	s	0.17	0.26	0.15	0.23	0.20	0.22
	φ	3	7	3	3	3	19
Δ_{mean}		—0.15	+0.02	+0.17	+0.30	+0.02	+0.07
CH$_4$	s		0.13		0.21	0.28	0.23
	φ		3		3	7	13
Δ_{mean}			—0.17		—0.12	—0.02	—0.10
CO	s		0.15		0.13	0.35	0.23
	φ		3		3	3	9
Δ_{mean}			—0.37		—0.12	—0.05	—0.18
Ar	s		0.13		0.25	0.10	0.17
	φ		3		3	3	9
Δ_{mean}			+0.33		—0.07	—0.15	+0.03
Mean	s	0.17	0.20	0.15	0.21	0.26	0.22
	φ	3	16	3	12	16	50
Δ_{mean}		—0.15	—0.03	+0.17	0.00	—0.04	—0.03

(3) Finally, one sample of coke oven gas was analyzed a few times on the chromatograph. The results of this analysis are compiled in Table IV.

Table V is derived by combining the figures in Tables I, II, III and IV. The results

TABLE IV

ANALYSES OF ONE SAMPLE OF COKE OVEN GAS

	Analog (%)					Digital (%)				
	H$_2$	N$_2$+O$_2$+Ar	CO	CH$_4$	Total	H$_2$	N$_2$+O$_2$+Ar	CO	CH$_4$	Total
1	61.7	4.2	4.5	25.9	96.3	61.8	4.2	4.5	25.8	96.3
2	61.8	4	4.6	25.7	96.3	62.0	4.2	4.5	25.8	96.5
3	61.6	4.1	4.7	25.8	96.2	61.8	4.2	4.5	26.0	96.5
4	62.0	4.3	4.6	25.8	96.7	62.0	4.2	4.7	25.8	96.7
5	62.1	4.1	4.6	25.5	96.3	62.0	4.2	4.7	25.6	96.5
6	62.1	4.2	4.7	25.4	96.4	62.0	4.2	4.4	25.5	96.2
7	61.8	4.1	4.7	25.8	96.4	61.8	4.3	4.7	25.8	96.6
8	62.3	4.3	4.7	25.8	97.1	62.1	4.3	4.8	25.8	97.0
9	62.5	4.3	4.7	25.8	97.3	62.3	4.3	4.7	26.0	97.3
Mean	61.9	4.20	4.64	25.72	96.55	61.98	4.23	4.62	25.79	96.62
s	0.29	0.09	0.07	0.17		0.17	0.05	0.12	0.16	
φ	8	8	8	8		8	8	8	8	
s_{mean}		0.18					0.13			
φ_{mean}		32					32			

TABLE V

ACCURACY

	Analog method	Digital method
s	0.185 vol. %	0.210 vol. %
φ	102	102

of the analog and digital methods do not differ significantly. It may be taken that if use is made of the burette giving 1000 counts per analysis, the accuracy of the digital method will be slightly greater, because in this case the influence of the rounding-off errors will be relatively smaller.

ACKNOWLEDGEMENTS

SUMMARY

This paper describes a gas chromatograph developed on the basis of JANÁK's principle, which permits rapid and accurate determination of the permanent gases in a gas mixture of arbitrary composition. The analytical result is fed both to an analog recorder and to a digital printer. At 102 degrees of freedom, the standard deviation is 0.185 vol. % for the analogous and 0.210 vol. % for the digital measurement. The systematic error lies within the statistical error.

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