CHROM. 16,772

MASS FLOW CONTROL AND TEMPERATURE PROGRAMMING IN GAS CHROMATOGRAPHY

I. PRECISE DIGITAL MASS FLOW CONTROLLER

STANISLAV WIČAR

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Leninova 82, 611 42 Brno (Czechoslovakia)

SUMMARY

A new design of a digital flow controller, characterized by a separated flow meter and electronically driven valve, is described. The controller operates under microcomputer control and guarantees a long-term flow-rate stability of ±0.01 ml/min within a 0–50 ml/min range. For the carrier gas, the back-pressures range from 0 to 1 MPa gauge. Owing to the very short operation period and, consequently, short response times, the controller is especially suitable for flow-rate programming.

INTRODUCTION

Maximum accuracy and repeatability of gas chromatographic (GC) data are the most important parameters for instrument designers, and the column temperature and the stability of the carrier gas flow are important factors in this context. For quantitation, the stability of the flow of auxiliary gases, *e.g.*, hydrogen and air, is also important.

Most existing gas chromatographs are equipped with mechanical flow controllers. For the carrier gas, mass flow controllers of the Moore type[1] (Moore Products, Philadelphia, PA, U.S.A., or Brooks Instrument Division, Emerson Electric, Hatfield, PA, U.S.A.) are commonly used. These controllers provide a constant mass flow-rate in the column over a wide range of back-pressures if the gas supply is kept at a constant pressure. The flow-rates of auxiliary gases are normally set by precise needle valves situated between constant-pressure sources of these gases and the detector inlet.

In recent years, electronic flow controllers have appeared on the market. The most important feature of these new devices is the much better flow repeatability than that attainable by classical mechanical controllers. A typical representative of this kind of equipment is the Hewlett-Packard electronic flow controller[2,3], designed for use with the Model 5880A gas chromatograph. This controller operates much like a piston pump: the gas from a pressurized source flows through an opened inlet

valve into a metering volume during the first phase. Then the inlet valve is closed and the pressure in the volume, P_1, is measured at an appropriate moment just before the end of the second phase. At the beginning of the third phase, the outlet valve is opened and the gas flows to the column under pressure P_2. At the end of this phase the output is closed and the whole process is repeated. The controller is programmed to keep the $(P_1 - P_2)V/RT$ value constant and, provided that the gas behaves ideally, a constant mass flow results, independent of the kind of gas used. The disadvantages of such a system are evident: the pressure sensor has to handle small changes to high pressures and there is essentially no flow sensor to monitor explicitly the instantaneous value of the flow rate.

In order to study the dynamic phenomena that accompany temperature programming in GC, a different principle of digital mass flow controller design was utilized. The new controller is characterized by a separate flow meter, which can be used for independent flow measurements.

THE FLOW METERING SYSTEM

Of the methods used for the measurement of flow in GC, only a few are well suited for electronic conversion. Further, regarding the intended application of the flow meter, the response time of the latter has to be considered. This is why the popular commercially available heat-convection flow meters were abandoned.

When cheap semiconductor pressure sensors had become available, the classical method, based on monitoring the pressure changes brought about by the laminar flow of gas through a capillary or porous medium, became attractive. The flow meter used in this study belongs to this category of devices.

For a steady laminar flow of ideally compressible gas through a capillary, the mass flow-rate is given by the expression

$$F = \frac{\pi r^4}{16 \, RT \, \eta L} (P_1^2 - P_2^2) \tag{1}$$

where F is the mass flow-rate, r and L are the radius and length of the capillary and R, T, η, P_1 and P_2 are the gas constant, absolute temperature, gas viscosity and the absolute pressure at the inlet and outlet of the capillary, respectively.

For metrological reasons, it is more convenient to rewrite the $P_1^2 - P_2^2$ term in eqn. 1 by introducing the pressure difference $\Delta P = P_1 - P_2$:

$$P_1^2 - P_2^2 = \Delta P(2P_2 + \Delta P) \tag{2}$$

and to measure the pressure difference ΔP instead of the inlet pressure P_1.

TM 510/01 and TM 610/01 pressure sensors (Tesla, Rožnov, Czechoslovakia) were used. They consist of a circular silicon diaphragm soldered to an invar tube of 1.5 mm I.D. Four piezoresistors, made by diffusion technology, are placed on the outer side of the diaphragm to form an open tensometric bridge. One pair of resistors is located on the diaphragm periphery and the other pair is positioned near its centre (Fig. 1). Under the influence of external pressure, the diaphragm deforms itself and the peripheral resistors change their values opposite to those of the central ones.
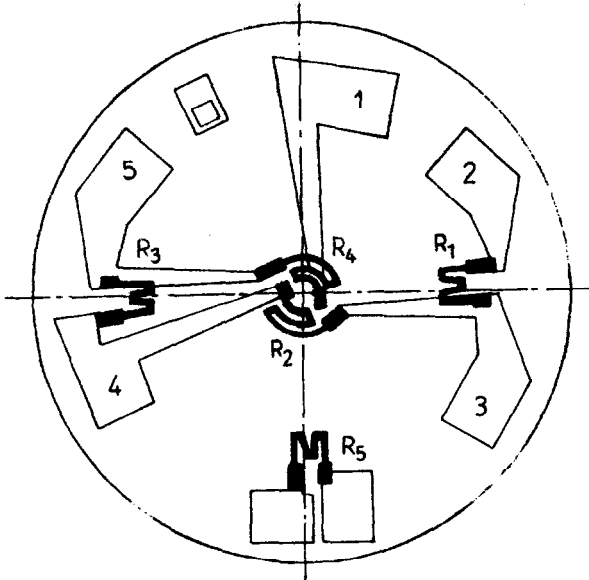
Fig. 1. Tensometric diaphragm. R_1–R_4 = piezoresistors; R_5 = uncontacted resistor; 1–5 = user accessible contacts.

Before soldering, the inner side of the diaphragm is precisely etched to the desired thickness with hydrofluoric acid, thus attaining the desired sensitivity of the sensor. Finally, a small board is fastened to the invar sensor body, and the diaphragm chip is contacted in the usual way in integrated-circuit technology. The sensors are delivered as semiconductor components, and it is left to the user to install them in the particular device.
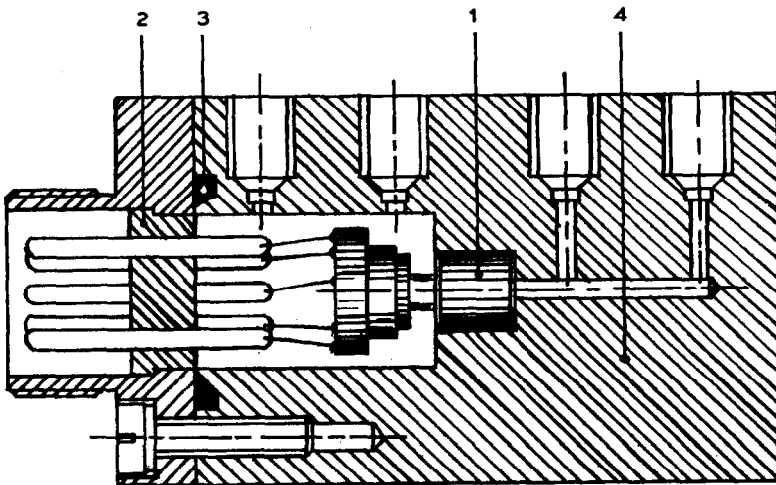

Fig. 2. Differential manometer body. 1 = Pressure sensor; 2 = hermetic connector; 3 = silicone rubber O-ring; 4 = aluminium body.

We mounted the sensors into cylindrical aluminium bodies of 30 mm O.D., where they formed differential (TM 510/01) and gauge (TM 610/01) manometers (Fig. 2). The differential manometer is equipped with an axially oriented hermetic connector. A pair of female fittings is drilled to the body wall on each side of the diaphragm; two fittings are used to bridge the differential manometer with a stain-less-steel capillary of 0.25 mm I.D. and approximately 20 cm in length.

The gauge manometer is of similar design; the connector side of the sensor is opened to the atmosphere, and merely a pair of female fittings lead through the body wall to the·input side of the sensor. The carrier gas flow controller needs a combi-nation of one differential and one gauge manometer (see eqns. 1 and 2). The flow-rates of auxiliary gases (hydrogen, air) are measured by a single capillary–dif-ferential manometer combination; the capillary geometry is fitted to the desired flow-rate limits. In order to make the function of the controller independent of atmo-spheric pressure, an additional barometric sensor based on an evacuated TM 510/01 pressure sensor was constructed. All the sensors and capillaries are placed in a well insulated cylindrical aluminium body equipped with a heater and a platinum ther-mometer and thermostated at 45 ± 0.02°C.

The tensometric bridges were closed with potentiometers (offset compensation) and connected to galvanically separated constant-current sources of 10 mA, stabilized by MAA 723 stabilizers (Tesla). The TM 510/01 sensors are designed to operate within the pressure range 0–100 kPa, the output voltage being about 50 mV at a nominal 100 kPa pressure. With TM 610/01 sensors, the output voltage of *ca.* 70 mV corresponded to a nominal pressure of 1 MPa. The output sensor voltages were normalized to the 0–10 V level by MAA 725 operating amplifiers (Tesla).

The calibration of the manometers was carried out with the aid of a mercury U-tube manometer as a standard and an MT 100 4.5-digit electronic voltometer (Metra, Blansko, Czechoslovakia). More than 100 data points were collected for each sensor, and the proportionality constant B in the expression

$$U \text{ (V)} = BP \text{ (100 kPa)} \tag{3}$$

where U is the pressure sensor voltage and P is the pressure, was determined by the least-squares method. Typical values obtained for the differential manometers were $B = 9.320$ V/100 kPa, $\sigma_{PU} = 0.003$ and $\sigma_B = 0.002$, where σ_{PU} is the variance of individual readings, $\sigma_{PU} = [\Sigma \ (u_i - BP_i)^2/(n - 1)]$, and σ_B is the slope variance, $\sigma_B = \sigma_{PU}/\sqrt{\Sigma P_i^2}$. A similar procedure applied to the gauge manometers within the range 0–0.2 MPa yielded $B = 0.9428$ V/100 kPa, $\sigma_{PU} = 0.003$ and $\sigma_B = 0.0006$. The variances σ_{PU} are in good agreement with the precision of the mercury manometer readings.

The calibration of the flow meters was carried out with the capillary–differ-ential manometer sets having one end of the capillary open to the atmosphere. The flow was kept constant during the measurement by a non-calibrated flow controller described later. A set of bubble flow meters of various volumes was used to guarantee that the shortest time measured was not less than 1 min.

The calibration range of the carrier gas flow meter was 1–25 ml/min, and the number of data points exceeded 100 for each gas (air, nitrogen, hydrogen). The data were processed according to the equation

$$F \text{ (ml/min)} = B_F \Delta P (2P_B + \Delta P) (10^4 \text{kPa}^2) \tag{4}$$

where F is mass flow-rate, ΔP is the pressure drop on the capillary, B_F is the proportionality constant and P_B is the barometric pressure.

The volumetric data were normalized to standard conditions of 25°C and 740 mmHg. The results of the air flow calibration (B_F = 33.55 ml/min 10^4kPa^2, σ_{P^2F} = 0.052, σ_{B_F} = 0.019, where σ_{P^2F} and σ_{B_F} are defined in an analogous way as σ_{PU} and σ_B) and of the nitrogen flow calibration (B_F = 34.87 ml/min 10^4kPa^2, σ_{P^2F} = 0.052, σ_{B_F} = 0.019) were in accordance with the precision of the measuring method used. All deviations were below a level of 0.1 ml/min, and the slope corresponded to the gas viscosity.

In strong contrast to these results were the data obtained for hydrogen, B_F = 68.3 ml/min 10^4kPa^2, σ_{P^2F} = 0.20 and σ_{B_F} = 0.146, where the deviations exceeded those for nitrogen or air by a factor of four. The explanation can be found in the different diffusion coefficients for hydrogen and nitrogen. The bubble flow meter behaves like a film column used by chemical engineers to measure mass-transfer coefficients. During the flow measurement, the film of the surface-active solution present on the flow meter wall evaporates, and this process results in an increase in the effective volume. At a given temperature and flow-rate, the evaporation process is controlled by diffusion. It is therefore better to calibrate the flow meter with a high-molecular-weight gas, e.g., argon, and to calculate the calibration data for other gases using viscosity data. Another possibility would be to look for a non-volatile bubble-forming solution.

Electronically driven inlet valve

Another crucial item of the controller design is an electronically activated valve. Our valve[4] consists of an aluminium body ca. 25 ml in volume. The input female fitting continues with a copper capillary coil, the other end of which is soldered to the valve seat. The length and diameter of the inlet capillary are determined mainly by the maximum desired flow-rate. A similar capillary connects the internal volume of the valve with another female fitting drilled to the valve body and serving as the valve outlet. A magnetically driven closing element is installed inside the body, designed to close the valve tightly up to an inlet pressure of 1.2 MPa. It is formed by a plate spring fastened to the valve body at one end; the other end is covered with a thin layer of silicone rubber. The free end of the spring is pressed against the valve seat by a magnetically driven lever. Both the lever and the solenoid are installed inside the valve body. As the inner diameter of the seat (and of the capillary) is less than 0.1 mm, a small force applied to the spring closes the inlet capillary tightly. The valve is now produced commercially by Laboratorní Přístroje, Prague, Czechoslovakia.

The valve operates within the frame of a 50 msec period. Except for zero flow-rate, the valve is opened at the beginning of each period for a calculated time interval set in 2-μsec multiples. For several reasons, the valve does not open for time settings shorter than about 1 msec. Starting with this opening time, an increase in the opening time by as little as 2 μsec caused flow effects that can be observed on the flow meter.

The characteristics of the valve, represented by the dependence of the outlet

flow-rate on the opening time (within the given period) at constant inlet and outlet pressures, is a straight line, except for opening times shorter than about 5 msec and/or at high flow-rates, *i.e.*, outside the laminar flow region.

In order to follow the operation of the valve in greater detail, we start with a closed valve. The inlet capillary is pressurized to the inlet pressure P_1 while the pressure $P(t)$ inside the valve body is slowly decreasing and the gas flows through the outlet capillary to the measuring part of the controller, maintained at the outlet pressure P_2, due to the pressure difference $P(t) - P_2$. During the steady operation of the controller we may assume both P_1 and P_2 to be constant.

At the moment when the silicone rubber plug leaves the seat, a rapid non-stationary process of pressure drop formation occurs inside the inlet capillary; consequently, a small portion of gas, determined by the capillary volume and the pressures P_1 and P, flows into the valve body. Simultaneously with this transient process, the pressure drop $P_1 - P(t)$ formed across the inlet capillary is responsible for the main transport of gas into the valve body. Neglecting the non-stationary process and assuming laminar flow in both capillaries, we can write for the pressure P in the opened valve

$$\frac{dP}{dt} + \frac{\pi}{16\,\eta V}\left[\left(\frac{r_1^4}{L_1} + \frac{r_2^4}{L_2}\right)P^2 - \left(\frac{r_1^4}{L_1}P_1^2 + \frac{r_2^4}{L_2}P_2^2\right)\right] = 0 \tag{5}$$

where P_1 and P_2 are the inlet and outlet valve pressures, r_1 and r_2 and L_1 and L_2 are the inlet and outlet capillary radii and lengths, respectively, η is the gas viscosity and V is the internal volume of the valve.

The opened-valve steady state ($dP/dt = 0$) is characterized by the pressure

$$\bar{P}_1 = \left[\frac{(r_1^4/L_1)P_1^2 - (r_2^4/L_2)P_2^2}{(r_1^4/L_1) + (r_2^4/L_2)}\right]^{0.5} \tag{6}$$

After introducing the initial condition $t = 0$, $P(0) = P_i$, the solution of eqn. 5 can be written as

$$\frac{(\bar{P}_1 - P)\,(\bar{P}_1 + P_i)}{(\bar{P}_1 + P)\,(\bar{P}_1 - P_i)} = \exp(-t/H_1) \tag{7}$$

where

$$H_1 = \frac{8\,\eta V}{\pi[(r_1^4/L_1) + (r_2^4/L_2)]\bar{P}_1} \tag{8}$$

In the closed-valve state the influence of the inlet capillary disappears. Repeating the above procedure and considering that the closed-valve steady-state pressure equals the outlet pressure P_2, we obtain

$$\frac{(P - P_2)\,(P_2 + P_i)}{(P + P_2)\,(P_2 - P_i)} = \exp(-t/H_2) \tag{9}$$

where

$$H_2 = \frac{8 \, \eta \, L_2 \, V}{\pi r_2^4 P_2} \tag{10}$$

The outlet capillary together with the valve volume form a pneumatic filter which effectively eliminates the pressure and/or flow noise produced by the discrete operation of the valve. With some reservations, the H_1 and H_2 values may be looked upon as the time constants of an open and a closed valve. By decreasing the length of the outlet capillary along with the operation period of the valve, we are able to change the response time of the controller without increasing the noise level. With our arrangement we were able to operate the valve successfully up to a 20-msec period.

Control unit

A microcomputer of the 8080 type was used to control both the flow-rates and the temperatures of the column oven, injection port, detector and the flow sensor unit. Together with the carrier gas mass flow controller, two other flow controllers (hydrogen, air) were subjected to computer control.

The microcomputer consisted of a JPR 80/01 processor board (Tesla, Strašnice, Czechoslovakia), an SBC 016 dynamic memory module, an SBC 732 12-bit data acquisition system for eight differential channels (Intel, Santa Clara, CA, U.S.A.), and a specially designed Multibus-compatible PC board connecting three 8253 programmable timer/counter chips and one 8255 programmable parallel input/output port to the computer bus. All the four boards were placed in a Multibus compatible card-cage (Tesla).

A CM 7202 serial CRT display (Tesla, Orava, Czechoslovakia), interfaced by a 8251 Usart chip on the JPR 80/01, served as a console communication device. Another CRT (Tesla, B. Bystrica, Czechoslovakia), interfaced in parallel with an 8255 on the processor board, displayed all the temperatures and flow data every 2 sec. The other part of the 8255 was programmed to interface an FS 1503 high-speed paper tape reader (ZPA, Košíře, Czechoslovakia) for program transfer.

The carrier gas, hydrogen and air valves were interfaced via an 8253 timer/counter chip driven with a 2-μsec hardware clock. Three 16-bit counters of one 8253 were programmed to operate in the zero mode (interrupt on terminal count).

A Chrom 61 prototype gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) was employed. All the temperatures in the gas chromatograph were measured by standard platinum thermometers; the output voltage of each thermometer was normalized to 0–10 V (0–400°C) by an operational amplifier. A 100-W heater was installed in the injection port and another in the flame-ionization detector body, and the column oven was heated by two independent 1-kW heaters. All the heaters were switched by triacs; the triac switching unit was connected via optocouplers to the output of a 8255 C-port programmed in the set/reset mode. An additional two bits of this port were used to activate the oven-head lifting mechanism. Eight analogue channels were occupied by four temperatures, three differential manometers and one gauge manometer.

Every 10 msec, determined by the mains frequency, the processor was interrupted and the program was written accordingly to distinguish between the background and the foreground (interrupt service routine) program units.

The interrupt service routine started the A/D converter, set and checked the heater periods, maintained the heating time counters and switched the heaters on or off in accordance with the counter values. At the end of each period (1 sec for main column oven heaters and 2 sec for the other heaters) a new value calculated by the background program, was stored in the heater counters, and a request for the calculation of a new value was sent to the background program. Similar communications between the foreground and background programs took place every 50 msec, when the valve opening time for a particular valve was set.

At the end of the interrupt service routine, the A/D data were stored, analysed and a new gain was set for the next reading on a particular channel. Four ranges (1.25, 2.5, 5.0 and 10.0 V) were switched to keep the 12-bit data within 2032–4080 limits, except on both the lowest and highest ranges.

The keyboard of the serial CRT was tested for new data every 10 msec, and the data were transferred to and processed by the background program. This program concept guaranted that all the calculations had been performed in the background and no re-entrant arithmetic or conversion routines were needed.

Modified discrete PI controllers were used to calculate the triac or valve opening time, and merely a 16×16 bit fix-point multiplication routine was needed. Even the calculation of mass flow-rate from ΔP and P_2 data was written in the fix-point arithmetic to save the computing time.

The resulting automated experimental gas chromatograph is shown schematically in Fig. 3.
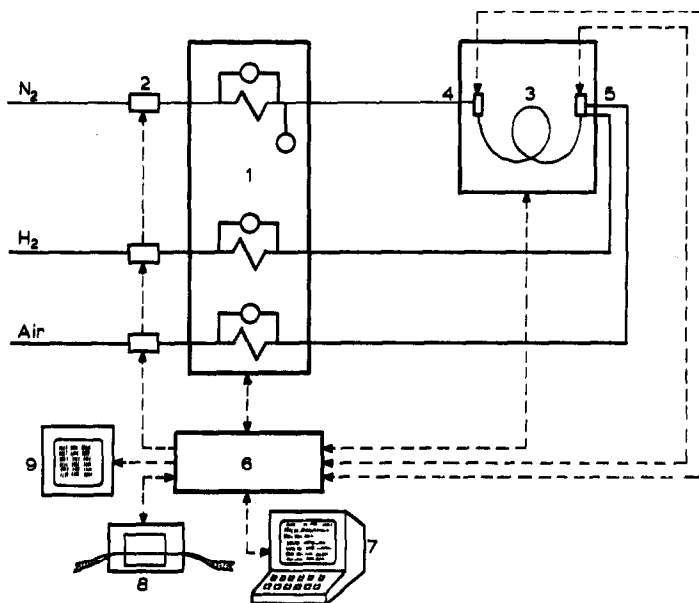

Fig. 3. Schematic representation of a microcomputer-controlled gas chromatograph. 1 = Flow metering system; 2 = inlet valves; 3 = column oven; 4 = injection port; 5 = flame ionization detector; 6 = microcomputer; 7 = serial console; 8 = paper-tape recorder; 9 = CRT.

RESULTS AND DISCUSSION

Two methods were used to determine the stability of the carrier gas flow. One was based on an independently operating flow sensor (a capillary–differential manometer combination) and the other was indirect and consisted in monitoring the column-inlet pressure variations.

The flow sensor was immersed in a double oil-bath of a U 15 ultrathermostat (VEB Prüfgeräte Werk, Medingen, G.D.R.), kept at 50°C. One end of the flow sensor was at atmospheric pressure and the other was connected in series with the controller output. The voltage of the tensometric bridge was measured by a 5.5-digit M1T 210 laboratory electronic voltmeter (Metra).

The properties of the carrier gas flow controller were tested with nitrogen and hydrogen. For nitrogen, the long-term stability (45 min) was ±0.009 ml/min at a nominal flow setting of 25 ml/min. A change in the input pressure by 400 kPa changed the flow-rate by 0.012 ml/min, and an increase in the output pressure by 78 kPa changed the flow-rate by 0.006 ml/min.

For hydrogen, the long-term stability was ±0.023 ml/min at a nominal flow of 25 ml/min. An input pressure change by 225 kPa changed the flow-rate by 0.02 ml/min, and a change in the output pressure by 297 kPa changed the flow-rate by 0.02 ml/min.

The indirect method consisted in controlling merely the pressure difference across the capillary of the carrier gas flow meter. A packed column was installed in the chromatographic oven, and the oven temperature was kept at 60°C. As a consequence of the constant pressure difference across the flow meter capillary, a constant inlet-column pressure should be displayed. The method is equivalent to constant inlet-pressure control, except that no direct information on the inlet-column pressure is sent to the controller. The inlet-column pressure sensor data, measured by an MT 100 digital voltmeter, were sampled every 10 sec for a 30-min period, and the difference between the maximum and minimum inlet pressures served for the flow stability determination.

At a nominal flow-rate of 13.14 ml/min of nitrogen, the inlet pressure was 108.85 kPa gauge. During the following 30-min sampling period, the maximum and minimum inlet pressures were 108.9 and 108.8 kPa gauge, respectively. Using the first pair of flow-rate and inlet pressure data for the determination of the overall column permeability, we calculated the flow-rate values corresponding to both the maximum and minimum inlet pressures; these were 13.15 and 13.13 ml/min, respectively, which corresponded to maximum long-term flow-rate fluctuations of ±0.01 ml/min.

REFERENCES

1 L. Guild, S. Bingham and F. Aul, in D. H. Desty (Editor), *Gas Chromatography 1958*, Academic Press, New York, 1958, pp. 226–241.
2 K. B. Augenblick, M. A. Casale, J. E. Cusack and A. J. Murphy, *Hewlett-Packard J.*, Jan. (1983) 35.
3 R. A. Nalepa and M. A. Casale, *F.R.G. Pat.*, 30 03 821 (1980).