Journal of Chromatography, 446 (1988) 173–178
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1394

SIMPLE INSTRUMENT FOR TEACHING THE BASICS OF CHROMATOGRAPHY IN SCHOOLS

T. P. KAHN
All-Union Research, Development, and Design Institute of Chromatography, N. Syromjatnicheskaj, 5/7, 107120, Moscow (U.S.S.R.)

SUMMARY

A simple instrument has been developed to train students in gas chromatography. It contains all the components and units necessary for chromatographic analysis. The main units, such as the sample input, column-temperature control, thermal conductivity detector and flame ionization detector, feature the simplest, cheapest, yet reliable designs. The problem of the carrier gas source has been solved with due consideration of safety. A number of simple and useful experiments have been selected to illustrate chromatographic separation and detection of individual components in mixtures, such as the analysis of air, *n*-hydrocarbons, commercial gasoline and halogen-containing organic substances.

INTRODUCTION

Modern chemistry is well equipped with highly developed theories and efficient experimental techniques. Chromatography plays an important part in widening the scope of chemical composition studies, and its use in teaching chemistry in schools appears to be both important and timely. The introduction of chromatographic methods into school programmes will acquaint the students with widely used chemical analytical techniques and widen the range of experiments possible. However, school experiments must meet a number of requirements, such as simplicity, short duration, safety, instructiveness, repeatability, low cost and reliable equipment. These requirements should be taken into account both in selecting a chromatography experiment and in the design of chromatographic equipment.

A number of publications discuss simple and inexpensive chromatographic instruments for teaching purposes[1–4]. However, such chromatographs are designed only for the analysis of organic substances. In the present article a teaching chromatograph is described; it is intended to demonstrate the analysis of both inorganic gases and organic compounds with high boiling points. The design of the major components is described, as well as carrier gas sources and chromatographic methods for school experiments.

EXPERIMENTAL

Equipment

The gas chromatograph shown in Fig. 1 includes (1) an air microcompressor, (2) a glass tube filled with sodium hydroxide for drying the carrier gas, (3) a reference detector, (8) a thermal conductivity detector, (5) a sampling device, (7) a chromatographic column in the form of a glass helix of diameter 35 mm, (6) a metal cup, containing the thermostat bath inside a plastic foam container, (10) a flame ionization detector, (9) a soap-bubble flow meter and (4) an output signal measuring instrument.

Carrier gas sources. The instrument may be supplied by the following carrier gas sources: an air microcompressor, a cylinder with natural gas for home use; a hydrogen source based on intermetallic compounds; a school device for gas production. Depending on the type of chromatographic experiment to be carried out and the detector used, either a fuel gas (propane–butane mixture, hydrogen) or air is used. No gas-flow regulator is used.

Gas supply and column. The air microcompressor is electrically operated with two channels and 500 ml/min production per channel. It drives the desired separations of pentane–hexane–heptane mixtures and mixtures of gasoline and chlorine-containing organic substances, using a 1 m × 0.7 mm I.D. column packed with powdered detergent "Crystal" (sieve size 0.25–0.5 mm). The gas flow through the column is about 40 ml/min, and a vessel at the column inlet eliminates air pulsations. A cylinder of natural gas (propane–butane mixture) is used in experiments with a flame ionization detector. A full 1-l cylinder provides a gas flow of about 120 ml/min at the column outlet described above. Carrier gas sources based on intermetallic compounds are available in the form of vessels filled with metal compounds in a stoichiometric relation. Intermetallics are capable of storing hydrogen at a 1:100 volumetric ratio, without the hydrogen pressure inside the vessel exceeding 1.5 atm at room temperatures. The hydrogen output from such a vessel is a function of the temperature of the intermetallic compound. A 100-ml vessel containing $NiLa_4$ can store 20 l of hydrogen. Since variations in the carrier-gas flow are less than ± 3% in any 5-min interval (average duration of an experiment), no flow regulator is needed. Another convenient source of carrier gas is the Kipp generator, found in most school laboratories. It is charged with zinc and hydrochloric (1:1) or sulphuric (1:3) acid, the device is reliably plugged and a 50-ml burette is fitted to its upper part with a rubber stopper. The burette, filled with the same acid, provides a low positive pres-

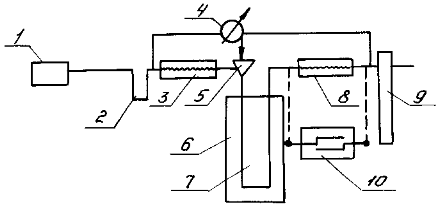

Fig. 1. Gas chromatograph. 1 = Air microcompressor; 2 = drier; 3 = reference detector; 4 = output signal meter; 5 = sampling device, 6 = temperature-control device; 7 = chromatographic column; 8 = detector; 9 = bubble flow meter; 10 = flame ionization detector.

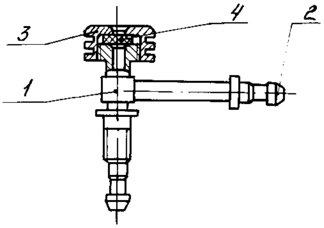

Fig. 2. Sample injector. 1 = Metal body; 2 = pipe fitting; 3 = nut; 4 = rubber diaphragm.

sure. The level of the liquid is maintained constant at about 35 cm during the experiment. The drop in hydrogen flow at the column outlet will not exceed 10% during 1 h.

Sampling device. A metal device for sample input is shown in Fig. 2. Sample introduction is by means of puncturing a rubber diaphragm (4) with a needle, or with a 1-ml hypodermic syringe; a 10-μl microsyringe can also be used.

Thermal conductivity detector. The sensor is a standard tungsten element, manufactured by the Chromatograph Plant of the Manometer Moscow Production Corporation (Moscow, U.S.S.R.). The resistance of each element is 30 ± 1 Ω. These elements are sealed into glass chambers, equipped with pipe fittings for gas input and output. The chamber volume is about 1.5 ml. The sensor is shown in Fig. 3. The reference sensor and the working element constitute two branches of a Wheatstone bridge. Their imbalance is corrected by a variable resistor.

Flame ionization detector. The detector is illustrated in Fig. 4. The copper electrodes (2) are mounted on a plate (4) and their ends cross above the outlet from the capillary (3) which constitutes the flame jet (5) terminal, with a capillary diameter of *ca.* 1 mm. The other end of the detector is connected to the chromatographic column. The detector is provided with a screw (6) to displace the mounting plate and thus vary the position of the electrodes inside the flame zone. The copper electrodes are held *ca.* 1 cm from the capillary outlet for experiments with flame ionization. The spacing between the electrodes is 0.5–1 mm. A glass cup (1) protects the flame from draughts of air.

Electric circuitry. Fig. 5 shows the circuit diagram of a simple amplifier for the flame ionization detector, with two general-purpose small signal transistors eq. BC 107, BC 108, BC 109; also shown is the amplifier and Wheatstone bridge connection to the supply circuit and measuring circuit. The detectors are powered by 1.5-V dry cells connected in series; experiments are carried out at supply voltages of 4.5, 6.0, 7.5 and 9.0 V, the sensitivity of the thermal conductivity detector being determined

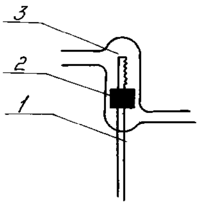

Fig. 3. Thermal conductivity detector cell. 1 = Sensing element; 2 = cup with insulator; 3 = glass enclosure.

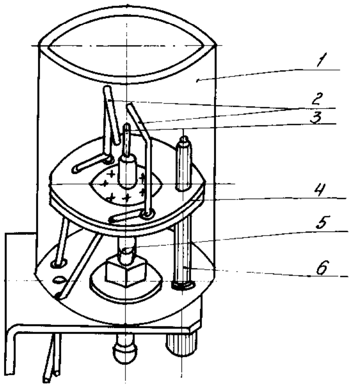

Fig. 4. Flame ionization detector. 1 = Fused-quartz cylinder; 2 = electrodes; 3 = capillary; 4 = mounting plate; 5 = injector; 6 = screw.

at 50, 100, 150 and 200 mA, respectively. At currents ranging from 100 to 200 mA, dry cells with a 3 A/h capacity provide power for several dozen experiments, the meter deflecting by not more than 5–7% during the expeirment. The output signal meter is a microammeter with a 25–0–25 μA scale. The front panel of the instrument

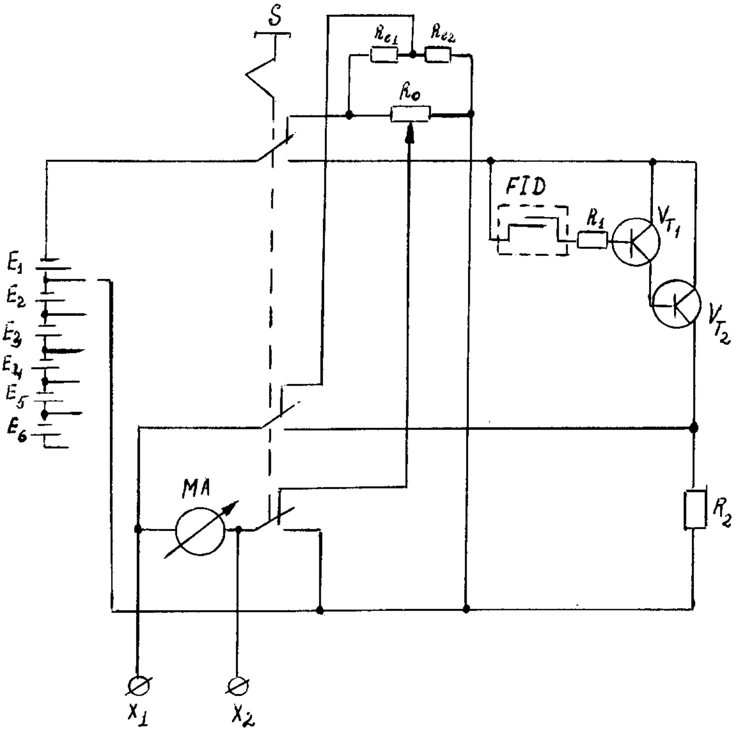

Fig. 5. Circuit diagram. E_1–E_6 = Batteries; MA = 25–0–25 mA microammeter; X_1,X_2 = clips; S = switch; R_{e_1}, R_{e_2} = thermal conductivity detector elemengs; R_0 = potentiometer; E_1,R_2 = resistors, V_{T_1}, V_{T2} = transistors; FID = flame ionization detector.

is equipped with a terminal for connection to a recorder with an input range of 0–10 mV.

RESULTS AND DISCUSSION

Analysis of the contents of nitrogen and oxygen in air

This experiment can be carried out in chemistry classes of 16- to 18-year old students to demonstrate the composition of air. The chromatograph output signal is read from the microammeter scale and is produced when a separated component emerges from the column. The profile of the signal that is recorded during the emergence of a component is in the form of a peak. Three parameters must be monitored for the elution of each component peak: the time when the meter pointer is first deflected (start of peak), the maximum pointer deflection (peak maximum) and the time taken by the pointer to return to zero (end of peak). The composition of a mixture should be carefully choosen to provide good separation and reliable readout from the meter. In an experiment to measure the content of nitrogen and oxygen in air, a 130 cm × 3.5 mm I.D. column should be used. The column is filled with molecular sieves 5A (fraction 0.25–0.5 mm) and placed in a glass of water heated to 50°C. A 0.5-ml air sample is injected with a 1.0-ml hypodermic syringe. The carrier gas used is hydrogen from a Kipp generator and is passed through the column at a rate of 25 ml/min. The exhaust gas from the chromatograph must be vented to a fume cupboard. A thermal conductivity detector is used, with the sensor filament powered by a voltage of 9.0 V. The analysis takes 2.5 min, with oxygen emerging (being eluted) in 20 s and nitrogen in 40 s. The pointer deflection is about 2/3 of the meter scale, and the air composition thus determined is 24.3% (w/w) oxygen and 75.7% (w/w) nitrogen (the actual values are 23.1 and 75.6%, respectively).

Analysis of a mixture of n-hydrocarbons and gasoline

This demonstration is recommended to illustrate the natural sources of hydrocarbons. It is performed with a 100 cm × 0.7 cm I.D. column, packed with detergent "Crystal" (sieve size fraction 0.25–0.5 mm) inside a vessel containing water at 60°C. The sample size depends on the detection technique used, this also restricts the choice of carrier gas. The experiment may be carried out in three ways. In the first version, hydrogen or natural gas is fed through the column at a rate of 100–120 ml/min, and identification is by visually observing the changes in the flame intensity at the outlet from the capillary of the injector of the flame ionization detector (Fig. 4) when the separated organic compound peak emerge. The sample volume used is 0.1–0.2 ml. In the second version, detection is by measuring the ion current in the flame with subsequent amplification and recording. In this case, the column is supplied with hydrogen. In the third version, the column is supplied with air and identification is by means of a thermal conductivity detector. In the last two cases the sample size required is about 10 μl.

The demonstration is carried out with a mixture of *n*-hydrocarbons (pentane–hexane–heptane, 1:2:4) and gasoline. The separation is carried out using air at about 40 ml/min; the detector supply voltage is 6.0 V. Visual observation shows that the flame exhibits rapid pulses to a height of up to 2–3 cm at the moment when an organic substance emerges, each flame being coloured for 20–40 s. The overall duration of the experiment in the case of the *n*-hydrocarbons is about 3 min. When analysing gasoline, three flame pulses are observed at the moments when pentane, hexane and heptane appear. These two experiments demonstrate the potential of chromatographic analysis in studies of natural substances.

Analysis of halogen-containing compounds

The copper electrodes in the flame ionization detector can be used in an interesting classroom experiment, with halogen-containing organic substances identified by the following observations. Such substances produce a greenish colour in the flame in the presence of copper, and their separation and identification can be a useful exercise in analysing reaction products, *e.g.*, in depolymerization of poly(methylmethacrylate), polyethylene, poly(vinyl chloride) during ethylene bromide synthesis, during heptane cracking, testing water chlorination, etc.

Chromatographic analysis of halogen-containing organic substances is demonstrated by using a mixture of 1,2-dichloroethane and ethyl chloride in 4:1 ratio. The chromatographic column packed with detergent described above is employed, with the water in the temperature-control vessel at *ca.* 50°C. Hydrogen or natural gas with a flow-rate at the column exhaust of 120 ml/min is used. After injecting the sample (0.1–0.2 ml) and waiting for about 20 s, the flame colour changes from blue to green due to the ethyl chloride. After 1.5 min, the flame changes colour under the influence of 1,2-dichloroethane. Detection is performed with the aid of a thermal conductivity detector at a supply voltage of 4.5 V. The sample volume is 4 μl.

CONCLUSION

A chromatograph with two detectors, thermal conductivity and flame ionization, has been developed for school use. This instrument is designed for demonstration of the chromatographic analysis of mixtures of both inorganic gases and organic substances. It can be used to familiarize students with the principles of operation of all units and components constituting a commercial chromatograph. Classroom experiments on the analysis of mixtures of saturated hydrocarbons, gasoline and halogen-containing organic compounds are presented.

REFERENCES

1 G. Hesse, *Chromatographisches Praktikum*, Vol. 6, Akademische Verlagsgesellschaft, Frankfurt-am-Main, 1978, pp. 142–150.
2 A. Wollrab., *J. Chem. Educ.*, 52 (1975) 200.
3 C. E. Bricker, M. Taylor and K. E. Kolb, *J. Chem. Educ.*, 58 (1981) 1.
4 C. D. Brabson, *J. Chem. Educ.*, 49 (1972) 71–72.