Invited paper

Integrated gas chromatograph

Jan A. Dziuban, Jerzy Mróz, and Jan Koszur

Abstract—A portable gas chromatograph with integrated micromachined flushed injector and thermal mass detector (TCD) has been developed. The silicon/glass injector operates in a fixed volume (2×7 μL) or electronically operated mode. An integrated, pneumatically operated, fast cross-valve is applied in the injector. The TCD detector consists of two Pt microheaters and thermoresistors packaged in a silicon/glass micromachined chip. The temperature of two capillary molecular sieve separation columns is controlled by a thick-film heater fabricated on polyimide foil. The chromatograph is equipped with two 16-bits microprocessors communicating with the external portable PC. The instrument may operate in the on-line continuous analysis mode.

Keywords—portable gas chromatograph, integrated injectors, silicon micromechanics.

1. Introduction

In this paper the results of a long-lasting research program on portable gas chromatograph are presented. The program was carried out under the auspices of the State Committee for Scientific Research. The main goal of the research was to obtain a miniature gas chromatograph (GC) with a flushed gas injector and fast, nano-dead-volume TCD. The device is equipped with appropriate software and analog/digital circuits and is capable of ensuring continuous detection of combustible atmosphere in deep coal mining industry and/or continuous monitoring of the environment (long-term air quality, drifts, emission of polluters, etc.).

2. Experiment

The portable gas chromatograph consists of two micromachined parts: a fixed or electronically adjusted gas injector and thermal-mass-detectors. Restek (USA) ID 0.32 mm Rt-Msieve 5A capillary columns, each 10 m long, are positioned in a thermally isolated chamber. A thick-film heater fabricated on elastic polyimid foil surrounds the columns and ensures proper adjustment and stabilization of the temperature (50–120°C) (see Fig. 1).

The injector consists of two Borofloat 33 glass substrates, silicon (100) deep-micromachined substrate polished on both sides, and polyimide foil coated with Teflon®. The gas circuit of the injector includes one integrated fast cross-valve (1 ms) operated pneumatically, two fixed-volume chambers (7 μL each) and two narrow channels for active and reference gas column supplying (Fig. 2). The fabrication process of the injector includes new processes of 3D-structure substrate-by-substrate assembling: selective bonding of glass and silicon substrate using polyimide foil (Fig. 3).

The TCD sensor applied in the GC has been designed and fabricated by the Institute of Electron Technology in Warsaw. In the device a thin-film Pt heater and a thermo-resistor

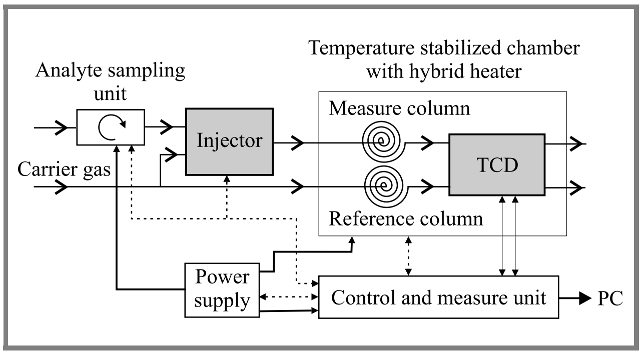

Fig. 1. Block diagram of the gas chromatograph with integrated micromachined components – gas injector and TCD sensor (grey areas).

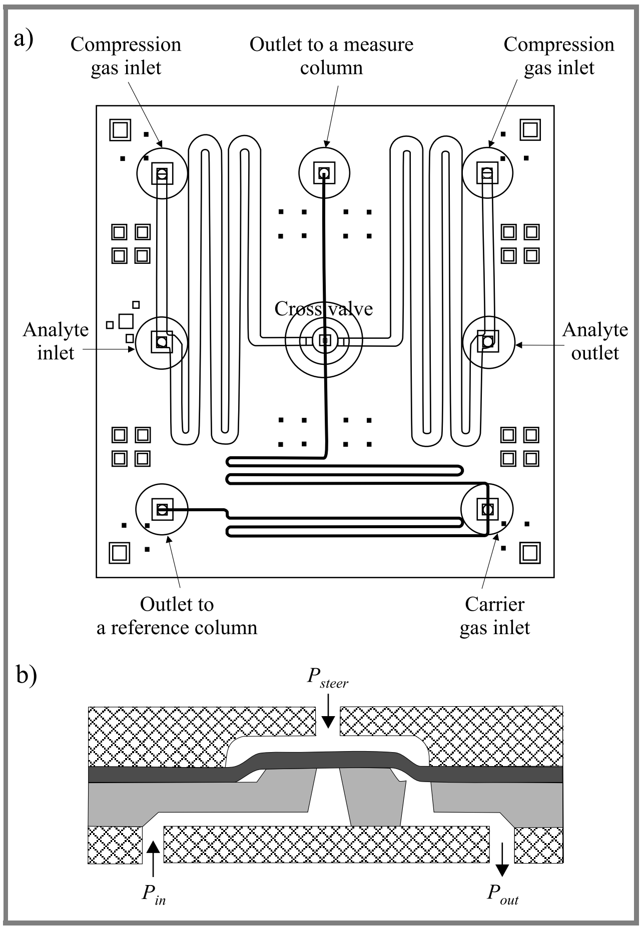

Fig. 2. The injector: (a) layout of the device; (b) cross-section of a microvalve; for $P_{steer} < P_{in}$ the microvalve is closed.

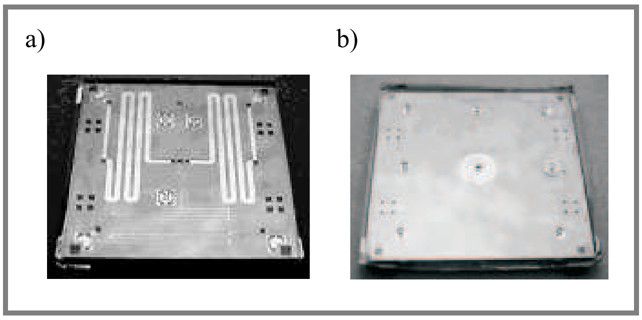

Fig. 3. The injector: (a) front-side: gas channels, fixed volume chambers and microvalve (in the middle) may be seen; (b) back-side view: analyte, carrier gas and control pressure inlets.

have been formed on a perforated membrane made of a double-layer SiO_2/Si_3N_4 system fabricated using LPCVD. The membrane extends over a gas channel formed by means of deep wet etchnig of a (100) silicon wafer. This structure is covered with a glue-bonded, 1 mm thick glass plate. The device chip is assembled with the capillaries and packaged in a metallic case, then wire-bonded connections are made (Fig. 4).

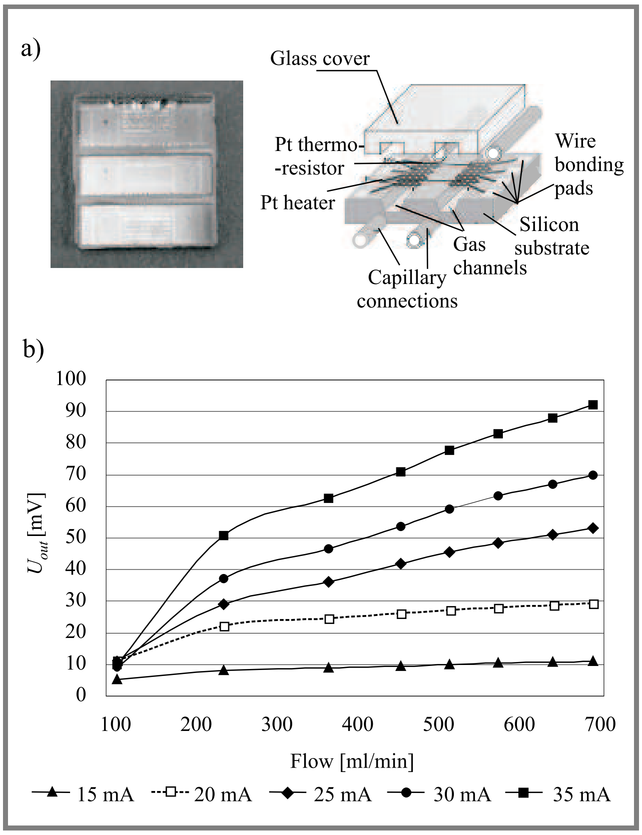

Fig. 4. TCD detector: (a) diagram (right) and view of the fabricated device (left); (b) most important characteristics – U_{out} versus N_2 flow for different levels of supply current.

In the solution reported here two independent sensors have been formed in a single chip and connected in the full Wheatstone bridge configuration in the self-calibrating mode.

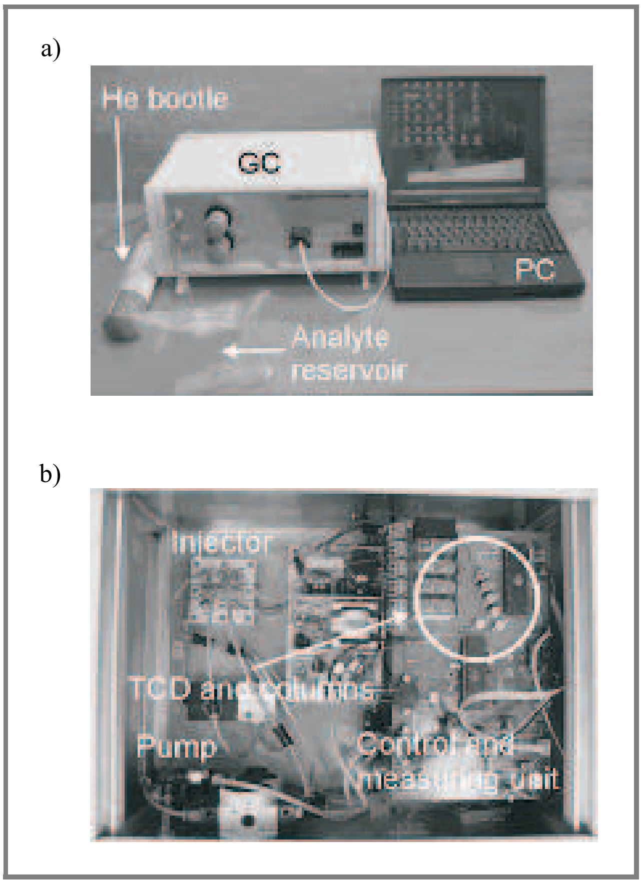

Fig. 5. Portable gas chromatograph: (a) the instrument, carrier gas bottle, and PC; (b) inside view.

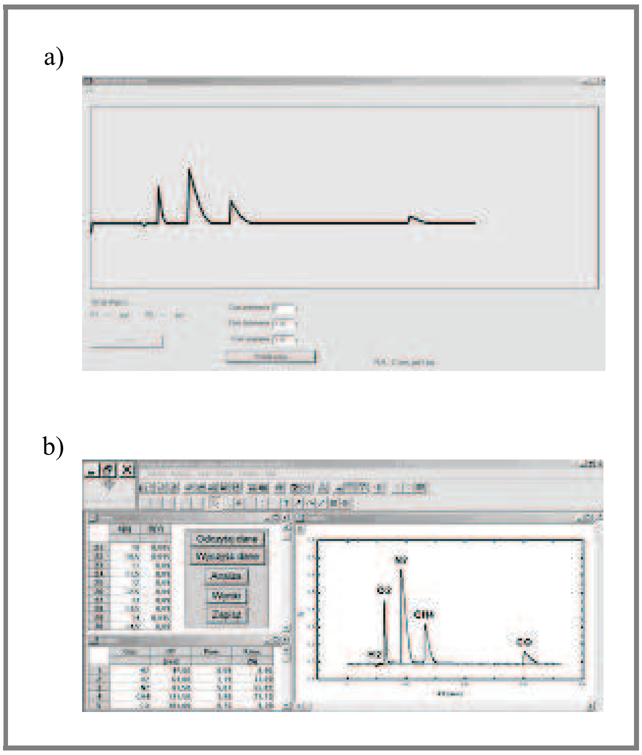

Fig. 6. Results of analysis: (a) electrical output signal and virtual control board of the GC; (b) processed chromatogram of a gas mixture and data table.

Table 1
Technical parameters of the GC reported here

Dimensions/weight: 15 cm × 45 cm × 30 cm/∼ 3.5 kg
Environmental conditions: Indoor, automatic sampling from atmosphere (build in pump) or external source of analyte
Supply: 230 $V_{(AC)}$, 50–60 Hz, 200 VA
Carrier gas: Helium carrier gas, external source, min. pressure 220 kPa
Analysis time: Depends on gas mixture and applied column, 400–700 s
Injector: Silicon/glass micromachined with polyimide membrane, the volume of injected analyte determinated by cross-valve open time or total volume of the dosage loop (14 μL $\pm$1%), possible backflush and independent temperature stabilization
Detector: Silicon/glass micromachined two-way thermo conductive detector (TCD) with four Pt micro spirals set up in auto compensating Whetsfone's bridge circuit, death volume in nL range
Chromatographic column: Depends on application (RT-Msieve 5 A, 10 m long, temperature 50–150°C)
Control unit/software: External PC laptop-type with RS 232 or USB port, specialized software under Windows98/NT/2000/XP platform, all parameters of analysis electronicaly adjusted

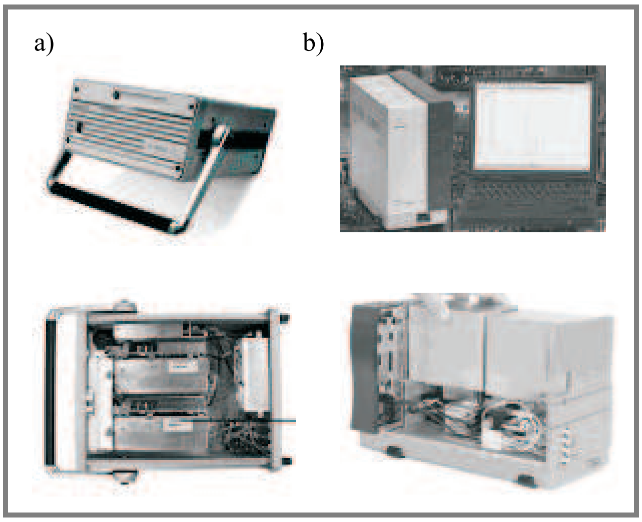

Fig. 7. The competing portable GCs: (a) Agilent 3000 Micro-GC; (b) Varian CP-4900 Micro-GC.

A printed circuit board with two 16-bit microcontrolers and specialized software designed and fabricated by the Institute of Automation and Electrification of Mining Industry – EMAG is used in the chromatograph.

The GC has been mounted in a metal box containing gas/electrical facilities (pump, pressure regulators and sensors, control valves). Both the injector and the TCD with the capillary columns enclosed in a thermally stabilized case are assembled in this box (Fig. 5).

The GC is able to operate either in the single-shot or in the continuous, automatic mode of analysis. All parameters of an analysis have to be set up by software from an external portable PC. The pressure of the carrier gas has to be adjusted manually, prior to the first analysis.

Chromatograms of gas mixtures may be observed immediately (real-time measurements), stored in memory and edited in the form table data and processed chromatograms with the description of detected gases added (Fig. 6).

Technical parameters our GC are similar to those of the well known Agillent/HP instrument (Table 1). The external view of both devices is shown in Fig. 7.

3. Conclusions

The most advantageous feature of our GC is the technical solution applied (possible only due to a complex know-how procedure). The approach resulted in technical parameters similar to those obtained by big producers of similar equipment in the world.

It is well known that the first integrated gas chromatograph was developed in the late 70's of the 20th century by Angell, Terry and Jerman [1]. After several years of redesigning, production of the portable gas chromatograph was undertaken by MTI Inc. (USA) and carried out in the late 80's and early 90's. Later the instrument became widely used under the name of Hewlett Packard (Agilent USA, http://www.chem.agilent.com).

At the moment, few projects devoted to the development of integrated gas chromatographs exist in Europe [2, 3], although many companies have been developing their own custom-designed gas meters based on the solutions used by Agilent. The lack of an independent market of key components and/or assembled portable gas chromatographs is the most important barrier blocking wider application of miniature gas chromatographs for on-line analysis in environment protection, gas systems electroengineering systems, etc.

We have built a portable (weighting aprox. 3.5 kg) gas chromatograph for continuous analysis of a gas mixture. The lowest detection level obtained is a few ppm, the average analysis time is below 6 minutes (depending on a column applied), the repetition time is 10 seconds. All parameters of the GC may be adjusted electronically, the results of the analysis may be visualized immediately. At the moment it seems that our gas chromatograph is the only European solution comparable to Agilent/HP standards.

We would like to emphasize that the GC presented here is the effect of a long-lasting cooperation between several partners from academic and research institutes in Poland (Wrocław, Warsaw, Katowice). The success of this shared efford relies heavily on programs of the State Committee for Scientific Research PBZ 2705 (basic technologies

applicable in GC fabrication) and PBZ 01915, as well as on other projects carried out by EMAG Katowice.
We hope that good scientific results reported here will be followed by technology transfer and industrial implementation of the integrated GC.

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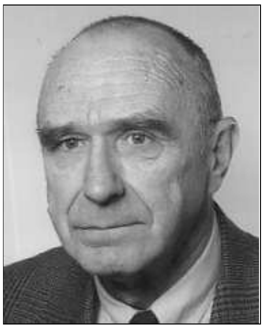

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