An automatic system for accurate preparation of gas mixtures

Hebertty V. Dantas [a], Mayara F. Barbosa [a], Pablo N.T. Moreira [a], Roberto K.H. Galvão [b], Mário C.U. Araújo [a,*]

[a] Universidade Federal da Paraíba, Departamento de Química, Laboratório de Automação e Instrumentação em Química Analítica/Quimiometria (LAQA), Caixa Postal 5093, CEP 58051-970, João Pessoa, PB, Brazil
[b] Instituto Tecnológico de Aeronáutica, Divisão de Engenharia Eletrônica, CEP 12228-900, São José dos Campos, SP, Brazil

ARTICLE INFO

ABSTRACT

This paper presents a novel automatic system for preparation of gas mixtures with suitable accuracy for quantitative applications. The system is managed by a purpose-built software, which controls the opening of gas admission valves in order to achieve the desired partial pressures. A piston-driven diaphragm pump is used to force the homogenization of the mixture by closed-loop circulation. The proposed system was tested by preparing binary mixtures of nitrogen with methane, ethane and propane. As a result, good correlation ($R^2 > 0.99$) was obtained between the programmed molar fractions of the mixture components (as set by the user in the system management software) and the corresponding analytical signals measured by a gas chromatograph. A recovery study involving gas mixtures with certified composition was also carried out. On the overall, good recovery was obtained, with percent values of 98.5 ± 2.3, 100.5 ± 4.6, and 98.9 ± 6.4 for methane, ethane and propane, respectively. Such findings indicate that the standard additions were properly introduced and suitably mixed with the gas samples, thus corroborating the correct operation of the proposed system.

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1. Introduction

Gas chromatography (GC) is a widely used method for determining the composition of complex mixtures of chemical species in gaseous phase [1–4]. In the course of a GC analysis, the components of the mixture are separated on the basis of differences in the rate at which they are carried through a stationary phase by a mobile gas phase [5]. A simpler and less costly alternative consists of the use of multivariate instrumental techniques, which may be of value to carry out the analysis in a faster and non-destructive manner, with less chemical waste. Examples reported in the literature include voltammetric analysis [6] and middle or near-infrared spectrometry [7–9].

It is worth noting that such techniques require the use of multivariate calibration to handle the mutual interference of the gas analytes, in order to compensate for the lack of a separation process [10]. For this purpose, gas mixtures with certified composition can be acquired from specialized suppliers in order to build the calibration model. However, these mixtures are costly and may not have a range of analyte concentrations that is wide enough to encompass the composition of subsequent samples to be analyzed. Alternatively, calibration samples could be prepared in the analytical laboratory itself by mixing individual gases. However, the precise manipulation of gases entails difficulties associated to physico-chemical features such as relative volume, diffusion and effusion, expansion and compressibility. In particular, rigorous

control and monitoring of pressure, temperature and flow rate are required [11].

Gas mixing methods can be divided in static and dynamic types [12]. Static methods basically consist of adding the mixture components into a diluting volume. In contrast, dynamic methods involve the combination of different gases in a continuous manner by adjusting the associated flow rates. The main difficulties [13] that arise in the preparation of gas mixtures for use in chemical analyses are: (i) memory effects of component gases caused by adsorption or desorption processes on the inner surface of vessels, tubes and connections, as well as the trapping of small gas amounts in connections, tube deformities and manometers; (ii) difficulty in establishing and maintaining the homogeneity of the sample, because differences in volatility or density of the component gases may cause stratifications in the mixture; (iii) difficulty in ensuring the same operational conditions in the gas transportation, introduction, mixture and sampling phases.

In this context, the present paper proposes a novel automatic system to prepare gas mixtures with suitable accuracy for quantitative applications, such as multivariate calibration of spectrometric methods. The proposed system is based on a simpler architecture that was employed in [14] for near-infrared screening of natural gas. That architecture was useful to facilitate the introduction of natural gas samples into an NIR spectrometer, as well as the simulation of adulterations by mixing the samples with different other gases. However, the control of the gas concentrations in the mixture was not accurate enough for quantitative purposes. The improvements described herein consist of the introduction of a pump to homogenize the gas mixture by forced circulation, the inclusion of automatically controlled solenoid valves and the

* Corresponding author.
E-mail address: laqa@quimica.ufpb.br (M.C.U. Araújo).

development of a system management software to control the gas introduction process in order to achieve the desired partial pressures in a precise manner.

The proposed system is tested by preparing binary mixtures of nitrogen with methane, ethane and propane. In this case, the programmed molar fractions of the mixture components (as set by the user in the system management software) are compared with the resulting analytical signals measured in a gas chromatograph. A recovery study involving gas mixtures with certified composition is also presented.

2. Experimental

2.1. Samples

Methane (99.9 %), ethane (99.0 %), propane (99.5 %), nitrogen (99.9 %) and three mixtures of these gases, with certified composition, were acquired from Linde Gas. The certified mixtures were designed in order to simulate the composition of natural gas samples. All gas contents indicated herein are expressed in % mol/mol.

2.2. Proposed system for automatic preparation of gas mixtures

Fig. 1 illustrates the main elements of the proposed system. The computational interface with a purpose-built software (a) acquires pressure readings from a digital manometer (b) and controls a set of solenoid valves (c) as well as a piston-driven diaphragm pump (d). Other components indicated in the system diagram include threaded connections (e), rigid connections (thin solid lines), flexible hoses (thick lines), hose packed with polymer spheres (thick line with cross marks), manual needle valves (f), flow retention valves (g), gas intake pipe (h) and automatic sample injector for GC analyses (i). The flow retention valves (g) are used to prevent reversions in the gas flow. Gas outputs (j) with needle valves (f) are available in various parts of the system for safety purposes and manual purge operations. The piston-driven diaphragm pump (d) is used to force the homogenization of the gas mixture by closed-loop circulation within the system. Up to five different gases can be mixed together, in addition to a diluent (typically nitrogen).

2.3. System management software

A purpose-built software for system management was implemented in the Borland Delphi platform. In addition to the monitoring of pressure readings and control of the pump and solenoid valves, the software has a graphical user interface for the design of gas mixtures, which includes the calculation of partial pressures associated to the desired molar fractions. The main functions of the system management software are illustrated in Fig. 2.

2.4. Chromatographic analysis

The mixtures prepared in the proposed system were analyzed in a gas chromatograph (GC-2014, Shimadzu) using a 30-meter capillary column (GC-GASPRO) with internal diameter of 0.32 mm. The GC injections were performed in split mode (1:100) at a temperature of 240 °C by using a sampling valve (Valco E60) with a 25 μL loop. Helium was used as carrier gas with a flow rate of 1.4 mL/min. All analyses were carried out in isothermal mode with the column temperature at 90 °C. A flame ionization detector (FID) was employed with temperature set at 250 °C. The total analysis time per run was 10 min.

2.5. Procedure

The operation of the system involves four steps: cleaning, introduction of the component gases, homogenization, and chromatographic analysis.

For cleaning purposes, the pump is activated and a solenoid valve is opened to aspire external air into the system. This valve is then closed and the air is circulated in a closed loop within the system. Afterwards, a solenoid valve is closed to interrupt this loop and the external connection is opened in order to expel the air from the system. After this preliminary cleaning procedure, the system is purged with nitrogen. The time involved in the overall process is approximately 6 min.
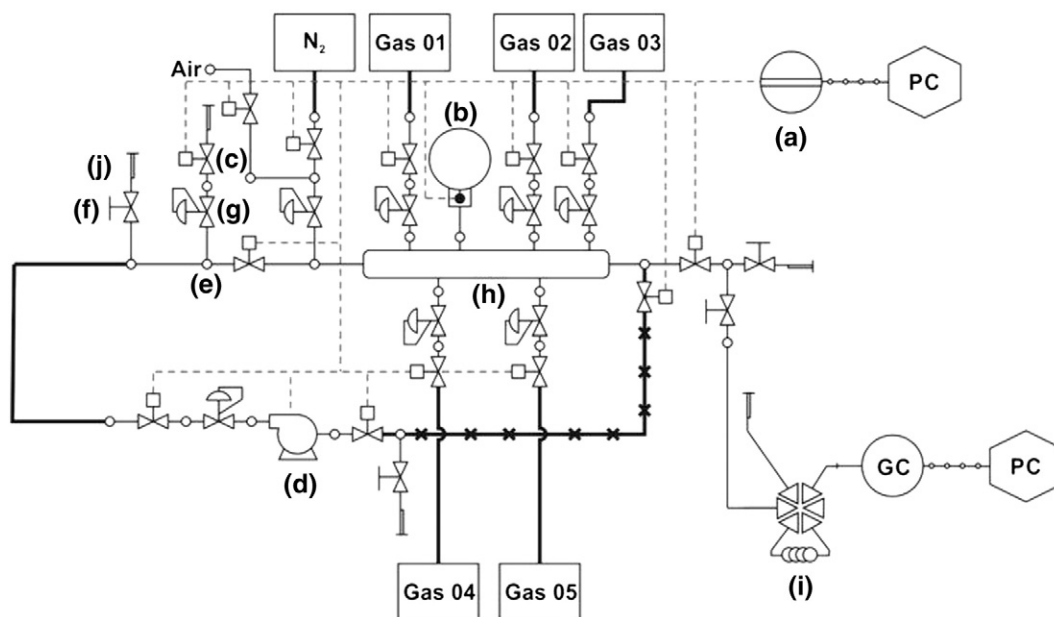

Fig. 1. Schematic diagram of the proposed system. (a) Computational interface; (b) digital manometer; (c) automatically controlled solenoid valve; (d) piston-driven diaphragm pump; (e) threaded connection (3/8″ BSP-brass); (f) needle valve; (g) flow retention valve; (h) gas intake pipe; (i) automatic sample injector; (j) purge gas output. Thin solid lines indicate rigid connections, whereas thick solid lines indicate flexible stainless steel hoses. The thick line with cross marks indicates a hose packed with polymer spheres. Dashed lines indicate electrical signal connections with the computational interface.