Universal system of gases and vapors composition measurement at atmospheric pressure based on quadrupole mass spectrometer

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This paper describes a system that measures gases at atmospheric pressure using a residual gas analyzer with a quadrupole mass spectrometer. A specially designed gas introduction system made it possible to measure gas mixtures at pressures slightly above and below atmospheric pressure. Additionally, the system can measure gases released when heating liquid and solid samples. Quantitative analyses of gas mixtures can be carried out with good accuracy, with detection limits down to the ppm level.

Introduction

Recently, there has been increased interest in measuring the composition of gas mixtures at atmospheric pressure. This is due to environmental pollution problems [1-3] and the successful use of these measurements in medicine. For example, they are used to test for Helicobacter pylori [4-5], and they hold the prospect of determining various diseases through patient exhalation [6-7]. Currently, two competing methods are used to determine the composition of gases: optical methods and mass spectrometry-based methods. The optical method is more economical but can only analyze a limited number of gas molecules, depending on the spectrometer used. When using a quadrupole mass spectrometer, an important advantage, in addition to the high detection limit, is the ability to obtain the complete gas composition in a single measurement. This paper presents a gas composition measurement system developed in our laboratory that uses a residual gas analysis (RGA) system based on a quadrupole mass spectrometer and a leak valve for gas injection into a high-vacuum chamber.

Materials and Methods

Figure 1 shows a schematic diagram of the gas analysis system and photos of the working prototype. The main components of the system are: a turbomolecular station (HiCube) from Pfeiffer with a 60 l/s turbomolecular pump (1); an all-metal leak valve that allows annealing up to 450 °C and an adjustable gas inlet with a residual pressure of up to 10^{-4} Torr (the limit pressure for operating the used mass spectrometer) (2); and a quadrupole mass spectrometer that operates in the mass range of 2 to 200 a.m.u. with electron impact ionization by electrons emitted from a heated tungsten filament (model RGA 200) from Stanford Research Systems (3) [8]. The electron energy was 70 V, and the electron current was 2.5 mA. The spectrometer, which is equipped with a Faraday cup, has a detection limit of 5×10^{-11} Torr for the residual concentration of gas molecules. The mass resolution exceeds 1 a.m.u.

The residual pressure in the chamber is controlled by a cold cathode ion gauge. The inlet system for the measured gas consists of a KF25 cross (5), which is connected via a valve to a mechanical pump (6) and a nitrogen cylinder (7). The nitrogen cylinder is used to ventilate the inlet chamber (5), and a special adapter connects a vessel (cylinder, etc.) to the inlet chamber through a valve. Heating tapes are used to heat the high-vacuum part of the system and the inlet chamber. The heating temperature is limited to 100 °C (80 °C at the turbomolecular pump flange). The pressure in the low-vacuum part of the system is controlled by thermocouple-type sensors, which allow operation at atmospheric pressure, slightly higher pressure, and lower than atmospheric pressure.

The gas analysis system was developed to measure the composition of gases emitted by solid-state materials, such as silicate glasses, when heated to approximately 500 °C. We have also developed a special adapter to heat the analyzed sample, which connects to the inlet cross via the KF25 flange. This part of the system consists of a quartz tube connected to the KF25 cross via a T-adapter (KF16) (Figure 1c). As will be shown below, this chamber can also be used to analyze the vapor of some liquids with relatively low vaporization temperatures. The quartz tube is placed in a graphite cup. A ceramic heater was used for heating and a digital controller with thermocouples was used for control. One thermocouple was in contact with the quartz tube and another was in direct contact with the powder (liquid) sample.

To obtain a high vacuum in the analysis chamber, it was annealed at a temperature of about 80 °C for 24 hours using a belt heater. The gas inlet chamber (cross) of the low vacuum part of the system was annealed at 80 °C for approximately four hours. This is necessary to remove water adsorbed to the inner surfaces of the chamber and adapters when changing adapters or analyzing experimental samples with water vapor. Note that the protocol for analyzing water-containing gases includes rapidly desorbing water at 80 °C for at least 30 minutes between measurements.

The standard protocol for analyzing a gas mixture (or vapor, in our case) involves pumping the sample inlet chamber down to approximately 1-2 mTorr. Then, the mechanical pump is closed, and the valve is opened to allow

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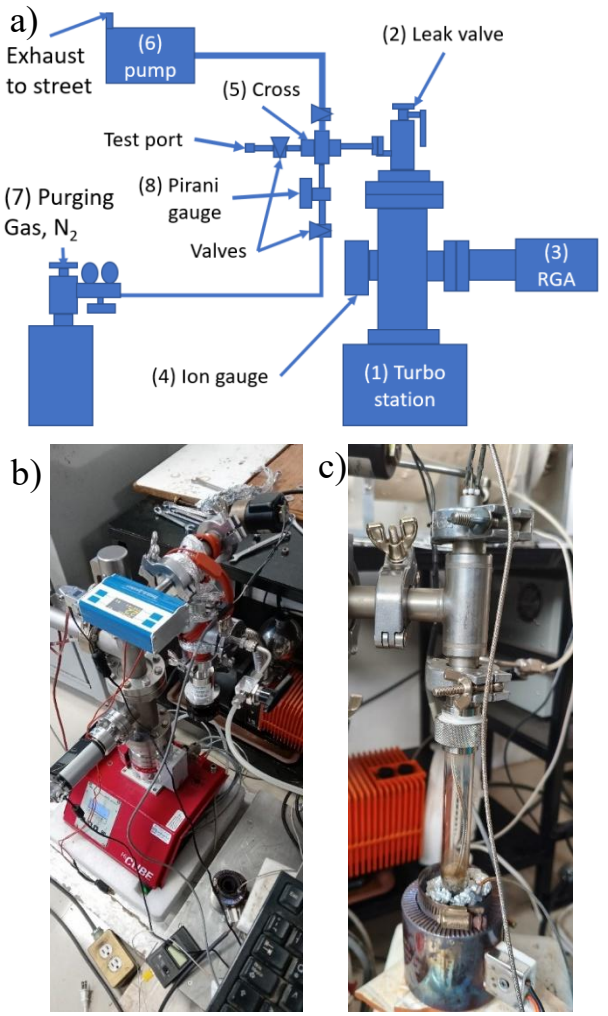

Figure 1. Schematic diagram (a) and photo (b) of the experimental setup for gas measurement, and the assembly for heating solid and liquid samples connected to the inlet chamber (c).

the measured gas mixture to enter. The inlet chamber pressure typically varies from 500 to 1,100 Torr. The pressure is measured by a Pirani vacuum gauge and controlled by a valve on the gas cylinder. In the case of evaporation from a liquid or solid, the pressure is controlled automatically. If another gas was analyzed previously, the mixture to be analyzed is introduced into the sample chamber three times, after which the system is evacuated with the mechanical pump to the residual pressure. When analyzing gas vapors containing water vapor, heating to a temperature below 100 °C is required to prevent water vapor adsorption on the internal walls of the inlet chamber. After completing the analysis, replace the connection between the gas cylinders or the quartz tube used to analyze vapor from liquids and gases emitted from solid samples. Then, ventilate the filling chamber with dry nitrogen. The same ventilation is required when studying different but similar gas mixtures to avoid the "memory" effect. After ventilating with nitrogen, evacuate the inlet chamber to approximately 1-2 mTorr before introducing the gas mixture.

Quantitative analysis of gas mixtures using a mass spectrometer is carried out as follows. First, the main fragments of the molecules of the analyzed gases are determined in the measured mass spectrum. Then, the mass spectrometer is switched to measure the partial pressures of these fragments over time in a mode called P-T. Once the signals of all analyzed fragments had stabilized, the mass spectrometer was switched back to mass spectrum measurement mode. The final measurements of the gas mixture composition were then made. Repeating this procedure demonstrated excellent reproducibility in analyzing gas mixtures at a constant pressure in the analyzed chamber. The intensity of the gas molecules and their fragments was recalculated, and the composition of the gas mixture was determined using the manufacturer's Analyze Utility. The Analyze Utility uses a multiple linear regression algorithm to automatically calculate the composition [9]. Since each gas molecule has its own probability of ionization by electron impact and its own probability of detection (i.e., the instrument's transmission coefficient), the concentration calculations require corrections in the form of sensitivity factors for each gas. These sensitivity factors are determined during the mass spectrometer calibration process using pure gases.

Results and discussion

Gas analysis

Figure 2 shows a portion of the mass spectrum obtained before and after the annealing of the high-vacuum chamber of the gas measurement system. The initial measurements were taken with the leak valve closed after approximately 24 hours of pumping. The initial mass spectrum of residual gases consists of hydrogen, water, nitrogen, and carbon dioxide molecules. Pumping down for 72 hours decreased the nitrogen and carbon dioxide molecules. After baking-out for 24 hours at ~80 °C, the ion gauge measured a pressure of 7×10^{-9} Torr. The main residual gas was hydrogen (>90%), which is typical of vacuum systems based on turbomolecular pumps. These pumps have a low compression rate for hydrogen, consequently resulting in a low pumping speed for this gas. Annealing primarily removes nitrogen and residual

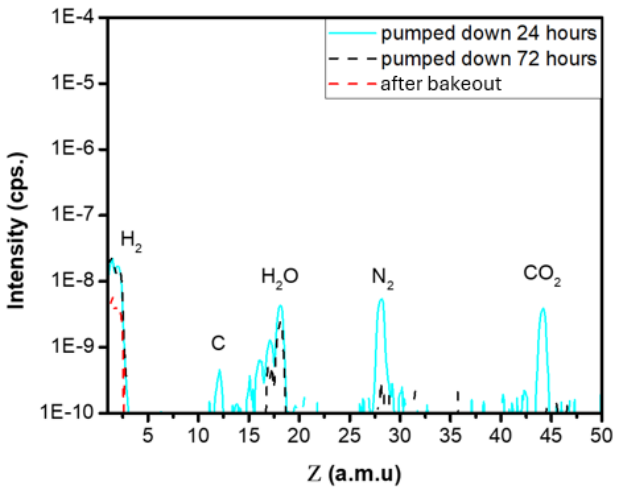

Figure 2. Mass spectra (2-47.5 a.m.u.) of residual gases in the high-vacuum chamber of the gas analyzer before and after bake-out for 24 hours at 80°C.

water and carbon dioxide vapor. However, note that subsequent gas analyses with high percentages of these gases (H_2O and CO_2) result in an increase in their background level. This level requires subsequent annealing to lower it to that shown in Figure 2. In other words, the strip heater should be part of the gas measurement system and ready for regular use. Additionally, gas mixtures containing water vapor and carbon dioxide require a temporary pause between measurements to restore the background level.

Of course, all of this is necessary for measurements with the maximum detection limit of these gases, which is 1 ppm, as shown in Figure 2. These additional processes are not necessary when determining the main components of a gas mixture. To lower the background level of hydrogen in the high-vacuum section, an additional getter pump is required, such as a Non-Evaporable Getter (NEG) [10].

To test the possibility of quantitatively analyzing gas mixtures, we used a 50:50 industrial gas mixture of carbon dioxide (CO_2) and methane (CH_4) from Infra Company in Mexico. Figure 3 shows the experimental mass spectrum obtained from measuring this mixture. This mass spectrum was obtained after establishing a stable ratio of the residual atmosphere components in Pressure-Time (P-T) mode. This mass spectrum was obtained by averaging several measurements. It shows the main peaks for each gas molecule, as well as the detected impurities. As mentioned earlier, gas concentrations should be calculated considering the probability of ionization by electron impact and the transmission coefficient of each molecule. Data on the ratio of the main molecular fragments appearing in the mass spectrum for each gas were taken from [9] and are shown in the form of color-coded histograms in Figure 3. The ratio of intensities does not coincide for all fragments due to various factors, such as different electron energies used to ionize gas molecules, different electron-optical system configurations in mass spectrometers, and interference between fragments of different gas molecules (e.g., CO and N_2).

The quantitative analysis in this study was performed according to the previously described procedure. The

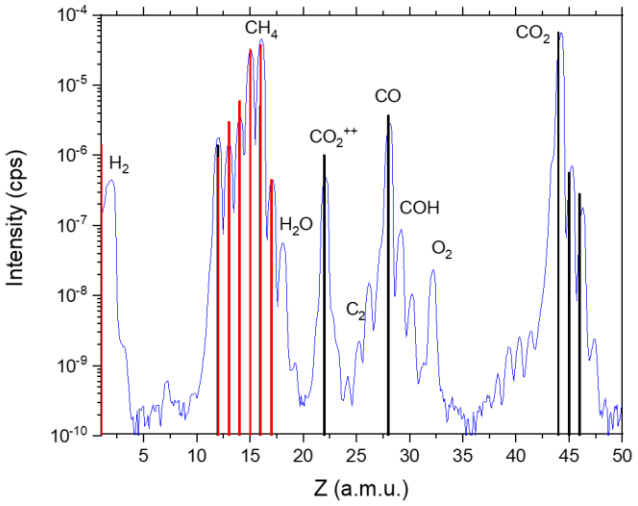

Figure 3. Fragment of mass spectrum of CO_2 (50%) - CH_4 (50%) gas mixture from Infra (Mexico). Ratio of intensities of molecule fragments (histogram peaks) are taken from [10].

Analyze program can calculate the composition of a mixture if all detected components are included in the preinstalled library. Without calibration, as we do not have pure methane and carbon dioxide gases in our laboratory, we obtained the mixture composition averaged over five measurements. The relative percentage of each gas is given in brackets: H_2O (0.3%), O_2 (0.2%), CO_2 (42.25%), and CH_4 (56.5%).

As an alternative method, we employed a calculation method used in secondary ion mass spectrometry (SIMS). We divided the intensities of the main peaks, averaged over 12 measurements (16 a.m.u. for methane, 44 a.m.u. for carbon dioxide, 18 a.m.u. for water, and 32 a.m.u. for oxygen), by sensitivity factors taken from the Pfeiffer catalog: 1.6 (CH_4), 1.4 (CO_2), 1.0 (H_2O), and 1.0 (O_2). These factors reflect the probability of electron impact ionization, normalized to the probability of nitrogen molecule ionization, which is taken as the unit. The intensity of each specified signal was then normalized to the sum of all intensities. The resulting relative concentrations are given below, along with the error calculated as the root mean square deviation for five independent measurements. The relative percentage of each gas is given in brackets. The concentrations are as follows: H_2O (less than 0.04%), O_2 (0.06 ±%), CO_2 (49.9 ± 2%), and CH_4 (50.1 ± 2%). Thus, the experimental concentration ratio was CO_2:CH_4 = 49.9%:50.1%, which practically coincides with the gas mixture data sheet. The root means square deviation for the main components, CO_2 and CH_4, was ~4%, a typical value for experimental error in quadrupole mass spectrometers.

Calculations for hydrogen, nitrogen, and argon are impossible due to interference with fragments of the measured gases' molecules (fragments are indicated in the figure). The data obtained are insufficient to estimate the experimental error since the full composition of the measured mixture of gases is unknown (measured by any other method). However, the obtained concentration of the main gases suggests an error of less than 10%.

Analysis of gases released from liquid and solid samples during heating.

We used ethyl alcohol (commercial) as an example for the analysis of liquid vapors. Note that we used alcohol purchased at a supermarket rather than the ultra-pure alcohol typically used in technological processes for surface cleaning. Two grams of alcohol were poured into a quartz tube (Figure 1c) and heated to around 60 °C. Then, the leak valve was opened to create a vacuum level of around 5×10^{-5} Torr in the analysis chamber. The pressure in the inlet chamber was between 700 and 800 Torr. Figure 4 shows a fragment of the mass spectrum of alcohol vapor. The resulting mass spectrum differs slightly from those reported in the literature due to additives and a higher water content in "commercial" alcohol compared to "laboratory" alcohol. The obtained mass spectrum is rather saturated; only some fragments of the alcohol molecule are labeled in the figure. The formation of fragments and the ratio of their intensities primarily depends on the energy of the electrons used to ionize the evaporated molecules. Therefore, mass spectra may differ for different systems in terms of the ratio of fragments.

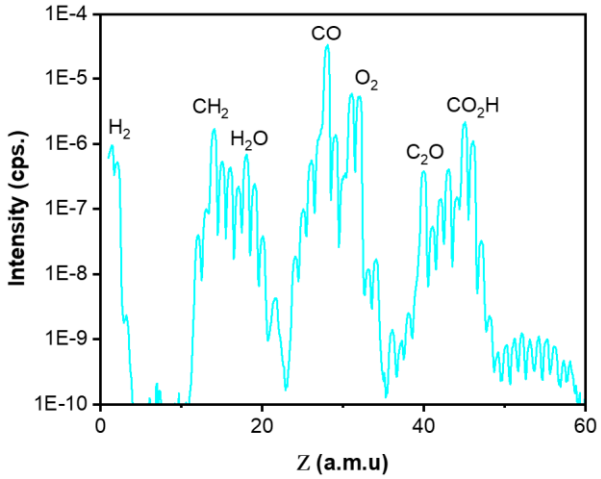

Figure 4. Mass spectrum fragment of ethyl alcohol vapor.

One purpose of developing this system was to study gases emitted from solids when heated to a certain temperature. The results of gas emission from borosilicate (Pyrex) and aluminosilicate (obsidian) glasses hydrated in deionized water vapor at 200°C for several days are given below. This was done to determine the composition of a surface layer several microns thick in the glass that is saturated with bound hydrogen (presumably in the form of silicon hydroxide). Previous experiments have shown that heating such hydrated glasses to temperatures above 350°C results in hydrogen emission from the glass. In this case, we used the developed gas measurement system to determine the composition of gases emitted from the glasses to calculate the percentage of hydrogen (H_2) emitted relative to water molecules (H_2O) and other gases, if any were present.

The experimental glass samples were obtained by crushing them in a 5-ton press into a coarse powder. The glass samples, which weighed about 20-30 g, were placed in special ceramic dishes and put into a high-vacuum nipple (CF 2-3/4"). About 1 g of deionized water was then added to the nipple. The nipple was then closed with a flange, tightened with bolts, and sealed with a copper gasket (see details in our previous paper [11]). Annealing was carried out in a conventional furnace with a digital temperature controller and a conventional atmosphere.

Figure 5 (a and b) shows the mass spectra of borosilicate (a) and aluminosilicate (obsidian) (b) glass powders heated to 500 °C, as determined by a thermocouple installed on the surface of a quartz tube. Before acquiring the spectra, the samples were heated for 12 hours at 200 °C to remove adsorbed water from the surfaces of the glass samples and the inner surface of the quartz tube in which the samples were placed. Mass spectra (the composition of the emitted gases) were measured at temperatures above 500 °C after about ten minutes of preliminary annealing. Preliminary studies have shown that a thin layer saturated with "internal" water forms on the surface during the glass hydration process. Therefore, at first, an increased yield of water molecules from the glass surface is observed after the beginning of annealing. Over time, after about 20 minutes of annealing, the relative percentage of emitted hydrogen (H_2)

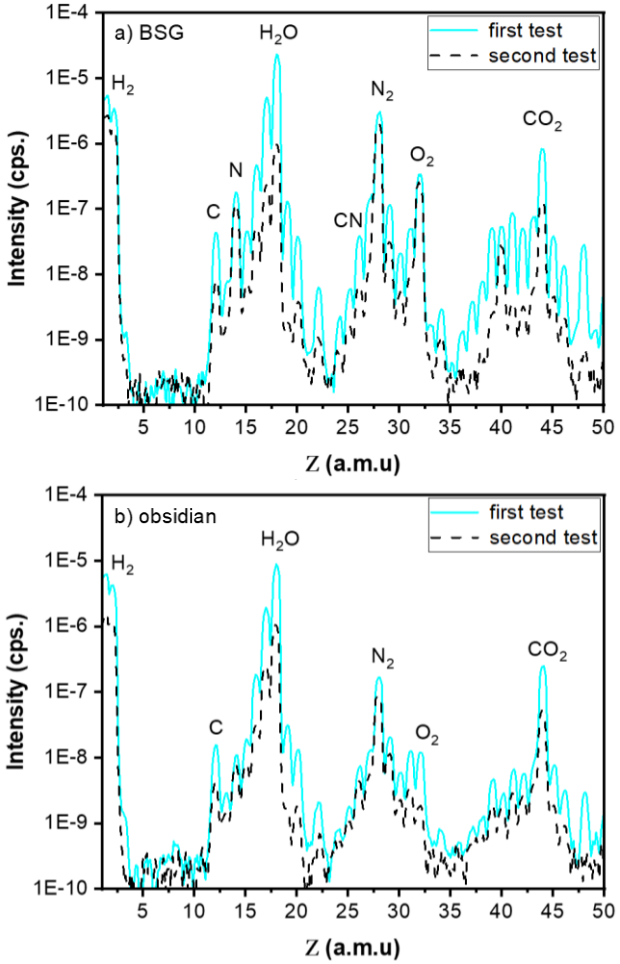

Figure 5. Fragments of mass spectra of gases emitting from hydrated borosilicate (a) and aluminosilicate (b) glasses obtained by heating to 500°C. Each figure shows spectra obtained after 10 min (first test) and after 20 min of sample heating (second test).

begins to exceed the yield of water molecules, as shown in the comparison of spectra in Figure 5(a, b). Before taking the spectrum again, the low-vacuum part of the system (the cross and gas tubes) was evacuated by a mechanical pump to a pressure of around 1-3 mTorr. Then, the pressure in the sample injection chamber was expected to be around 700-800 Torr. After opening the leak valve, the measurement was carried out.

The obtained result is obviously affected by the desorption of water molecules from the inner surfaces of the tubes and adapters used to transport the gas sample to the leak valve through the cross and adapters (Figure 1). In the future, we plan to modify this part of the setup by reducing the length of the tubes and the number of adapters. We also plan to use an additional heating element to maintain the temperature of the latter near 100 °C and prevent the adsorption (and subsequent desorption) of water molecules on the inner surface of the cross and tubes.

Another solution to the desorption problem, which we intend to test in future research, involves using "heavy water," which contains the heavy hydrogen isotope deuterium (making up 99.9% of its composition). Hydration in this water vapor will enable us to distinguish between

hydrogen emitted from the sample surface and hydrogen from the inner walls of the vacuum system.

Conclusions

We managed to build a universal gas analyzer based on a residual gas analyzer with a quadrupole mass spectrometer and a leakage valve. This analyzer is suitable for analyzing gas mixtures and studying the emission of gases released when heating liquid and solid materials. The analyzer can work with various gas pressures, from slightly above atmospheric pressure (as in the case of a CO_2 and CH_4 mixture) to several hundred Torr. The detection limit for some special gases can reach the ppm level. The range of measured masses covers almost the entire spectrum of existing gases. The quantitative analysis of gas mixtures is performed automatically by considering the probability of ionization by electron impact of the measured gas molecules. For most gases, correction factors determined by experiments are published in specialized literature.

As with commercial gas analyzers, however, complete quantitative analysis of gas mixtures is difficult due to fragmentation of gas molecules during ionization. Therefore, it is only possible for mixtures of simple gases, such as oxygen, nitrogen, and carbon monoxide.

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