A non-invasive method for measuring relative concentration of gases (i.e argon) in double-pane windows

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Abstract. A DC electrical discharge was used to obtain information about the presence of gaseous species (i.e. argon) inside a laboratory model of a double pane window. The relative concentrations of additive gases (i.e argon) were measured by means of the optical emission in the spectral region from near ultraviolet through near infrared (NIR). Amount of argon in air can be determine using our method with precision of 10% at low concentrations and about 5% at moderate to high concentrations.

Keywords: double-pane windows, DC electrical discharge, optical emission


1. Introduction

The thermal performance of double-pane windows can be highly increased by modifying the composition of the filling gas. Typically volume of the window is filled with argon or krypton instead of air [1]. However, additive gases often escape from the window through the seal resulting in deterioration of its insulating properties. Sometimes the additive gases escape without being replaced by the air. The estimated rate of exchange with surrounding is 1 : 3, or even more in favor or argon. Since argon is escaping up to three times faster than nitrogen and oxygen without being replaced from the outside of the unit, a progressive negative deflection of the insulating glass unit will build-up over time, occasionally even leading to implosion. One of the important conclusions from the Sealed Insulating Glass Manufacturers Association (SIGMA) [2] is the need for further understanding of the process of gas migration through different sealants and different edge-seal systems. At DOE-sponsored meeting in Cincinnati [3] participants endorsed the need for design and deployment of a portable instrument for non-destructive, non-evasive determination of the relative concentration of argon or krypton in Insulated
A non-invasive method for measuring relative concentration of gases (i.e. argon) in double-pane windows

Glass (IG) units. The reliable method for quantitative determination of the rare-gas content in the window would provide the criterion in decision making process when to replace the poor performing units. Several methods for determination of the rare-gas content of the window systems have been proposed in the past [4]. However, many of them require taking the gas sample or dismantling the window itself. Clever non-invasive technique was recently developed by Glora, Reichenauer and Fricke [5] and is based on the fact that the velocity of ultrasound in the rare gases used as window filling differ from that in air. Authors claim the accuracy of sound speed measurements within 1%. This results in inaccuracies of the air content of 20% for argon-filled windows and 5% for krypton-filled windows.

In this paper we present alternative non-invasive and non-distractive method and demonstrate that relative concentration of the gas species in the window can be determined using spectroscopic techniques. The idea is based on optical diagnostics of atmospheric pressure air plasmas [6].

The method proposed in this work requires only minor modification of the window during the manufacturing process, namely the insertion of a pair of wires or in some cases only one wire (when corona discharge is employed) with leads accessible from outside the window. The approximate diameter of a wire should be 1.0 mm, the length about 3.0 mm.

2. Experiment

2.1. Discharge

The relative concentrations of argon were inferred from the ratio of the integrated emission lines from known excited states of molecular nitrogen and argon atoms. The excited states of nitrogen and argon were produced in DC electrical discharge. The experimental setup is shown in Fig. 1.

The discharge operated between two cylindrical copper electrodes tapered at their ends and separated by a gap of approximately 2.0 mm. A high voltage DC (HVDC) power supply provided negative voltage (about -3000 V) to the cathode. The power supply works as a current source with a limit set to 1 mA. Additionally, a high impedance resistor $R_{DC1}=2.0 \text{ M}\Omega$ was used to eliminate fast current oscillations. The typical voltage drop during this continuous discharge between the electrodes was in the range of 1000 V. The anode was connected to the ground via a resistor $R_{DC2}=120.0 \text{ k}\Omega$. The insertion of a $R_{DC2}$ resistor was necessary to obtain stable, uniform glow throughout the entire region between the electrodes. It was noticed that the discharge was stable only in the very narrow range of current values.

The estimated electron density $n_e$ was in the range of $5 \times 10^{10} \text{ cm}^{-3}$ at 1.0 mA current. That estimate may be subject to an error, mostly due to our inability to evaluate accurately the volume of the discharge.

The discharge was placed inside a Plexiglas box with $5 \times 10^3 \text{ cm}^3$ with BK7 glass
windows in order to simulate a double-pane window. The relative humidity inside the box during all experiment was characteristic of the laboratory environments and could vary anywhere between 40 and 70\%, temperature being 20-25°C. All experiments were conducted at atmospheric pressure. The relative strength of emission from Ar and N\textsubscript{2} showed no noticeable dependence during the experiments where humidity in the laboratory would change significantly. No changes in relative emission intensities were noticed over time as electrodes were aged and became covered by an oxide layer.

2.2. Emission measurements

The typical passive emission spectrum detected during 2.0 s from electrical discharge inside the model window filled with pure air is shown in Fig. 2. The dominant spectroscopic features belong to the second positive system of nitrogen $C^3\Pi_u(v') \rightarrow B^3\Pi_g(v'')$, $v'' - v' = 2 \ (\text{for } v' = 0, 1, 2, 3, 4)$ in the spectral range between 330 and 420 nm. For the purpose of identification of emission lines from air we used spectroscopic data from reference [7]. The sharp cutoff in emission intensity near 370 nm is due
A non-invasive method for measuring relative concentration of gases (i.e. argon) in double-pane windows.

Figure 2. Emission spectrum from DC discharge in air.
A non-invasive method for measuring relative concentration of gases (i.e. argon) in double-pane windows.

The spectrum was observed with the apparatus shown in Fig. 1. The emission was collected in the direction perpendicular to the axis of the discharge electrodes by a f/3.8 quartz lens and imaged 1:1 onto the 50 µm entrance slit of a 0.275 m Czerny Turner spectrograph equipped with 150 lines/mm grating. No bandpass filters were needed, as higher diffraction orders did not interfere with spectroscopic signatures of interest. An intensified linear diode array was used to measure the emission signal on the output of the spectrograph. The overall spectral resolution of the monochromator was estimated to 3 nm. A spectral range of 400 nm wide was recorded simultaneously during each measurement by Optical Multichannel Analyzer (OMA). In order to obtain a sufficient signal-to-noise ratio each spectrum was recorded for about 2.0 s. The two broad features in the spectrum near 580 nm and 650 nm are from fluorescent lights in the laboratory. We made no efforts to eliminate them as they are in a spectral range insignificant for our measurements. Interference from other species such as: OH, O₂, ozone, atomic oxygen and nitrogen seemed to be negligible.

3. Results

In this section we are concerned with measurements of emission spectra from discharge in air/argon mixtures at vicarious concentrations. In the course of the experiment two types of measurements were performed: (1) in the time domain with equal sampling intervals while argon gas was flowing into the model window at the rate of 25 cm³/min and at the same rate mixed gas (air/Ar) was allowed to escape through the exit port V_{out1}. (2) a second series of experiments was performed at stationary conditions when the flow of gas was interrupted with all exit valves closed. In this case a premeasured amount of argon was added to a known amount of air and intermixed with a fan.

During the first series of experiments the pressure inside the container was approximately equal to 1 atm at all times. The argon gas inflow was controlled by valve V_{in} while valve V_{out1} was opened and V_{out2} was closed. Simple calculations show that at described experimental conditions the relative concentration of Ar in the model window changes with time as:

\[
P_{Ar} = 1 - exp(-\frac{c}{V} t),
\]

where \(P_{Ar}\) is a fractional argon pressure, \(c\) is the argon flow rate, and \(V\) is the total volume of an experimental chamber. At time \(t=0\) there was no argon inside the window.

This gas-flow arrangement allowed us to record a large number of spectra for different, known Ar/air ratios without the need for repeated evacuation of the experimental chamber and refilling it with new gases. The fan placed inside the model window, rotating at 3600 revolutions/minute, assured that gases were promptly mixed. The spectra recorded at different air-to-argon concentrations are presented in Fig. 3. The very top trace corresponds to the highest concentration of argon. The lowest trace was obtained when argon concentration was minimal. The most prominent
A non-invasive method for measuring relative concentration of gases (i.e. argon) in double-pane windows

Figure 3. Series of emission spectra taken at different air/Ar ratios. The relative amount of Ar in gas mixture is decreasing from the top to the bottom of the figure. The time indicated in the figure is measured from the moment Ar started to flow into the window. Sampling time was 2 sec. for each measurement.
A non-invasive method for measuring relative concentration of gases (i.e argon) in double-pane windows

Line of argon comes from the 3p^54p electronic state and appears at 750.4 nm. The relative spectral response of the spectrograph/diode array system was not absolutely calibrated. Therefore no ratios of intensities were corrected for the spectral response of the monochromator/diode array system and are given as an arbitrary ratio specific to our experiment. The purpose of these measurements was to establish the relation between emission intensities from prominent N_2 lines and Ar lines at different nitrogen-to-argon concentrations.

The second series of measurements allowed us to verify that the relative emission intensity from molecular nitrogen and argon is not a function of time at constant Ar-to-air ratio. It also assured us that under our experimental conditions the gasses are rapidly mixed, and the concentration of Ar/N_2 is uniform throughout the volume of the model window. We measured the emission from discharge operating at the same electrical parameters as in the flow experiment for time up to 40 minutes in 2 to 5 minute intervals. These experiments provided basis for estimated errors in our measurements. Example of integrated emission line intensities from argon at fractional argon pressure P_{Ar}=0.3 atm. taken during 40 minutes are shown in Fig. 4. No significant changes in emission intensities from Ar and N_2 were observed over the duration of the experiment. Primary source of variations in integrated line intensities is our inability to subtract accurately enough the background intensity.

3.1. Discussion

We present the results from our series of measurements in the form of calibration function. The calibration function provides direct and unique information about fractional concentration of Ar inside the window. The measured ratio of emission from the Ar 3p^54p line near 750.4 nm to emission from the second positive system of nitrogen C^3Π_u(v') → B^3Π_g(v''), v'' − v' = 2 (for v' = 0, 1, 2, 3, 4) as a function of the relative concentration of the two gases is shown in Fig. 5. The emission intensity ratio is linear with increasing concentration Γ from 0.05 to 0.5. We define concentration Γ as the ratio:

\[ Γ = \frac{P_{Ar}}{P_{Ar} + P_{N_2}}, \]

where, P_{Ar} is the partial pressure of argon and P_{N_2} is the partial pressure of nitrogen. Deviation from linearity of calibration function at the smallest values Γ is attributed to the difficulties of measuring weak emissions from Ar. Large errors at lowest argon concentrations are due to difficulties to accurately subtract background radiation in the vicinity of weak argon line.

In summary we have demonstrated that one can make an accurate determination of fractional ground state population in argon/air mixtures from observed emission intensities from their excited state created in DC electrical discharge at atmospheric pressures. Our experiment is similar to optical actinometry approach used often in plasma processing and manufacturing (see for example Ref. 8).
Figure 4. Integrated emission intensities from argon line at 750 nm at fractional argon pressure $P_{Ar}=0.3$ atm. Sampling time was 2 sec. for each measurement. The time equal 0 both valves were closed.
Figure 5. The relative concentration versus relative emission intensities inferred from flow experiments. In most cases the experimental error was smaller than the size of the markers in the graph with the exception of two measurements at lowest concentrations.
4. Conclusion

Our analysis indicates that the relative concentration of argon-to-nitrogen can be inferred with an accuracy of few percent. A field-deployable instrument can use two broad-band interference filters centered at 380 and 750 nm and a pair of simple photodetectors in place of a spectrometer.

5. References


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