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Nondestructive Method of Measuring Relative Concentration of Gases (*e.g.* Argon) in Double-Pane Windows

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A DC electrical discharge was used to obtain information on the presence of gaseous species (*e.g.* argon) inside a laboratory model of a double-pane window. The relative concentrations of additive gases (*e.g.* argon) were measured using the optical emission in the spectral region from near ultraviolet to near infrared (NIR). The amount of argon in air can be determined using our method with a precision of 10% at low concentrations and approximately 5% at moderate to high concentrations.

1. Introduction

The thermal performance of double-pane windows can be markedly increased by modifying the composition of the filling gas. Typically, 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 air. The estimated rate of exchange with the surroundings is 1:3, or even higher in favor of argon. Because argon escapes up to three times faster than nitrogen or oxygen without being replaced from 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 obtained by the Sealed Insulating Glass Manufacturers Association (SIGMA)(2) is the need to further understand the process of gas migration through different sealants and different edge-seal systems. At the DOE-sponsored meeting in Cincinnati,(3) participants

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endorsed the need to design and deploy a portable instrument for nondestructive, non-evasive determination of the relative concentration of argon or krypton in insulated glass (IG) units. A reliable method of quantitative determination of the rare-gas content in the window should be used to determine when to replace the poorly performing units. Several methods of determining the rare-gas content of the window systems have been proposed in the past;(4) however, many of them require collecting a gas sample or dismantling the window itself. A clever noninvasive technique was recently developed by Glora *et al.*(5) based on the fact that the velocity of ultrasound in the rare gases used as window filling differs from that in air. The authors claim that the accuracy of the sound speed measurements is within 1%. This results in inaccuracies of the air content of 20% for argon-filled windows and 5% for krypton-filled windows. Sparklike Ltd. based in Helsinki is marketing an instrument capable of measuring argon concentration in gas-filled window units with accuracy of 1% at concentrations greater than 90%. It works by creating a spark and analyzing the emission spectrum. However, its accuracy drops to 5% when the gas concentration falls to 80% and becomes unusable at gas concentrations below 50%.(6) In this paper, we present an alternative idea and demonstrate that the relative concentration of the gas species in the window can be determined using DC discharge.(7) Using the method described in this paper, we were able to measure the argon concentration down to 5%.

The method 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 each wire should be 1.0 mm, the length being about 3.0 mm.

2. Experimental Details

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 $R_{DC1} = 2.0$ MΩ 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 $R_{DC2} = 120.0$ kΩ. The insertion of a R_{DC2} resistor was necessary to obtain stable, uniform glow throughout the entire region between the electrodes. Test observations confirmed that the discharge was stable only in a very narrow range of current values.

The estimated electron density n_e was in the range of 5×10^{10} cm^{-3} at 1.0 mA current. This estimate may be subject to a fairly large error, mostly because of our inability to accurately evaluate the volume of the discharge.

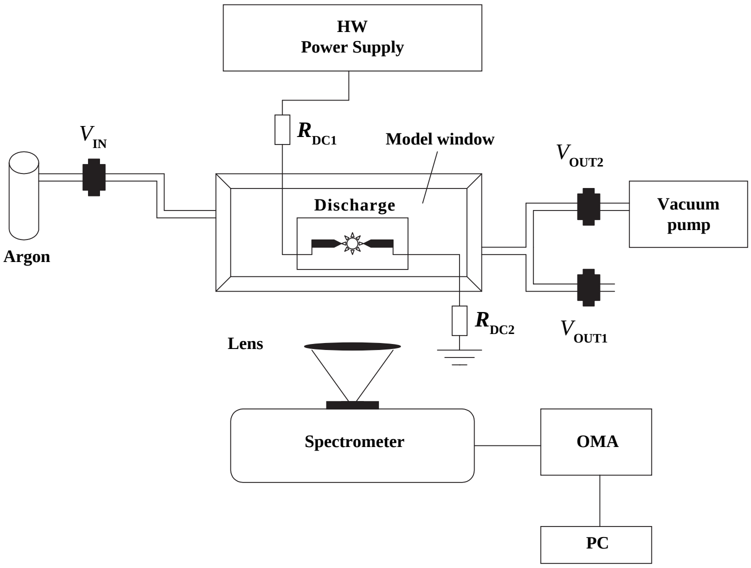

Fig. 1. Schematic of experimental configuration used for emission measurements together with details of discharge design.

The discharge was placed inside a Plexiglas box of 5×10^3 cm^3 with BK7 glass windows to simulate a double-pane window. The relative humidity inside the box during all experiments was characteristic of the laboratory environment and could vary anywhere between 40 and 70%, the temperature being 20–25°C. All experiments were conducted at atmospheric pressure. The relative strength of emission from argon and N_2 showed no noticeable dependence during the experiments where humidity in the laboratory would change significantly. No changes in relative emission intensities were observed over time as the electrodes aged and became covered with an oxide layer.

2.2 *Emission measurements*

The typical passive emission spectrum detected within 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 $C\,^3\prod_u(v') \rightarrow B\,^3\prod_g(v'')$, $v''-v' = 2$ (for $v' = 0, 1, 2, 3, 4$) in the spectral range between 330 and 420 nm. For the purpose of identifying emission lines from air, we used spectroscopic data from ref. 8. The sharp cutoff in emission intensity near 370 nm is due to absorption in the glass window. The spectrum was observed using the apparatus shown in Fig. 1. The emission was collected in the direction perpendicular to the axis of the discharge electrodes using an f/3.8 quartz lens and imaged 1:1 onto the 50 µ entrance slit of a 0.275 m Czerny Turner spectrograph equipped with 150 lines/mm grating. No bandpass filters

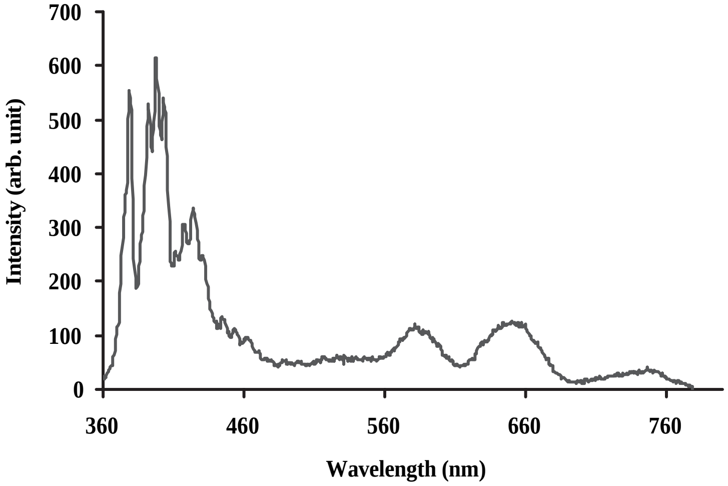

Fig. 2. Emission spectrum from DC discharge in air.

were required, 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 be 3 nm. A spectral range 400 nm wide was recorded simultaneously during each measurement using an Optical Multichannel Analyzer (OMA). 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 and 650 nm are from fluorescent lights in the laboratory. We made no effort to eliminate them because they are in a spectral range that is not significant for our measurements. Interference from other species such as OH, O_2, ozone, atomic oxygen, and nitrogen appeared to be negligible.

3. Results

In this section, we are concerned with measurements of emission spectra from discharge in air/argon mixtures at various concentrations. In the course of the experiment, two types of measurement were performed: (1) in the time domain with equal sampling intervals while argon gas was flowing into the model window at a rate of 25 cm^3/min, and at the same rate, mixed gas (air/argon) was allowed to escape through the exit port V_{out1}, and (2) a second series of experiments was performed under 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 using valve V_{in} while valve V_{out1} was opened and V_{out2} was closed. Simple calculations show that under the described experimental conditions, the relative concentration of argon in the model window changes with time as

$$P_{\mathrm{Ar}} = 1 - \exp\left(-\frac{c}{V}t\right), \tag{1}$$

where P_{Ar} is fractional argon pressure, c is argon flow rate, and V is 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 of various predetermined argon/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/min, ensured 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 the argon concentration was minimal. The most prominent 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 relationship between emission intensities from prominent N_2 and argon 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 argon-to-air ratio. It also assured us that under our experimental conditions the gasses are promptly mixed, and the concentration of argon/N_2 is uniform throughout the volume of the model window. We measured the emission from discharge operating under the same electrical parameters as in the flow experiment for time up to 40 min in 2 to 5 min intervals. These experiments provided the basis for estimated errors in our measurements. Examples of integrated emission line intensities from argon at fractional argon pressure $P_{\mathrm{Ar}} = 0.3$ atm taken over 40 min are shown in Fig. 4. No significant changes in emission intensities from argon and N_2 were observed over the duration of the experiment. The primary source of variation in integrated line intensities is our inability to subtract the background intensity accurately enough.

4. 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 the fractional concentration of argon inside the window. The measured ratio of emission from the argon $3p^54p$ line near 750.4 nm to emission from the second positive system

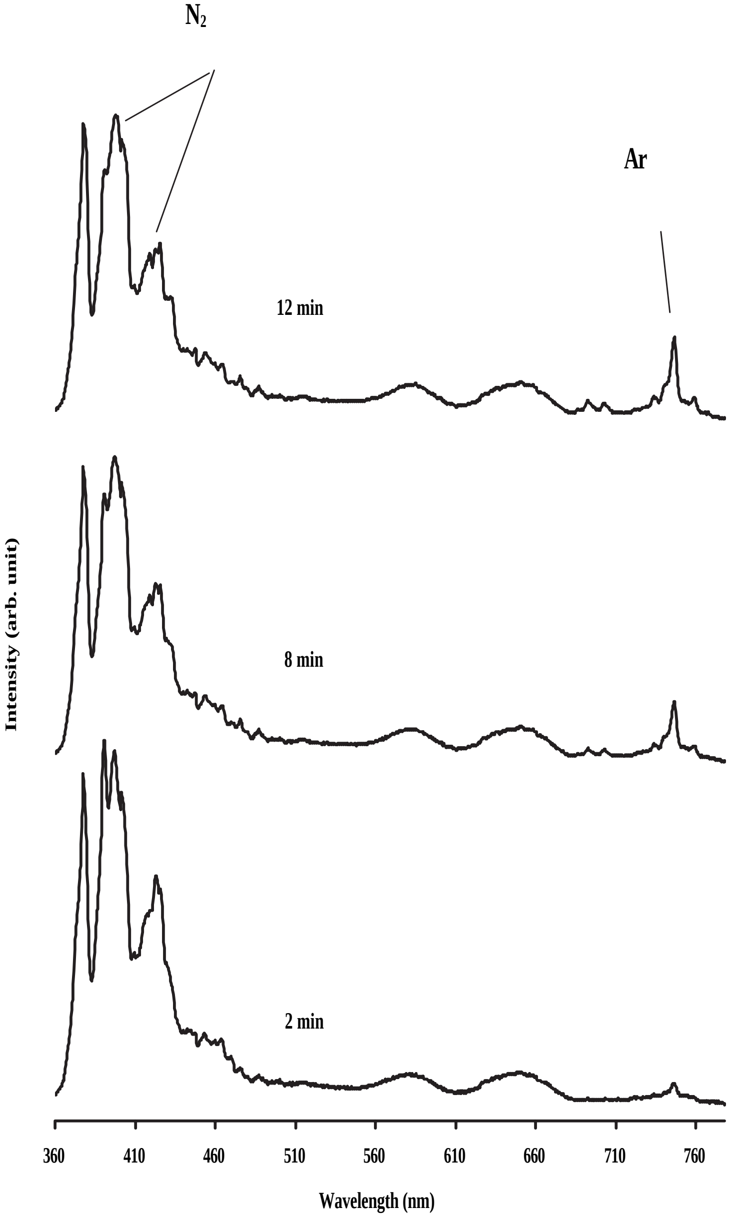

Fig. 3. Series of emission spectra obtained at different air/Ar ratios. The relative amount of Ar in the gas mixture decreases from the top to the bottom of the figure. The time indicated in the figure is measured from the moment Ar started to flow into the window. Sampling time was 2 s for each measurement.

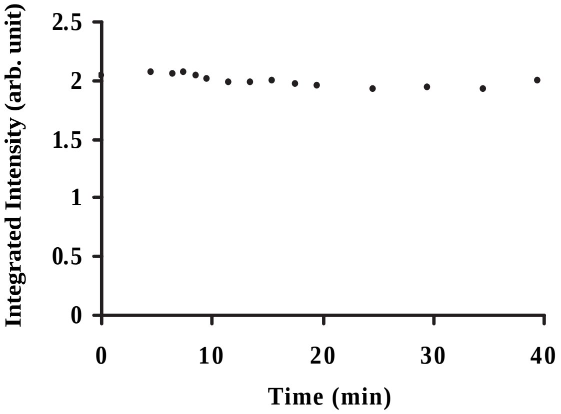

Fig. 4. Integrated emission intensities from argon line at 750 nm at fractional argon pressure P_{Ar} = 0.3 atm. Sampling time was 2 s for each measurement.

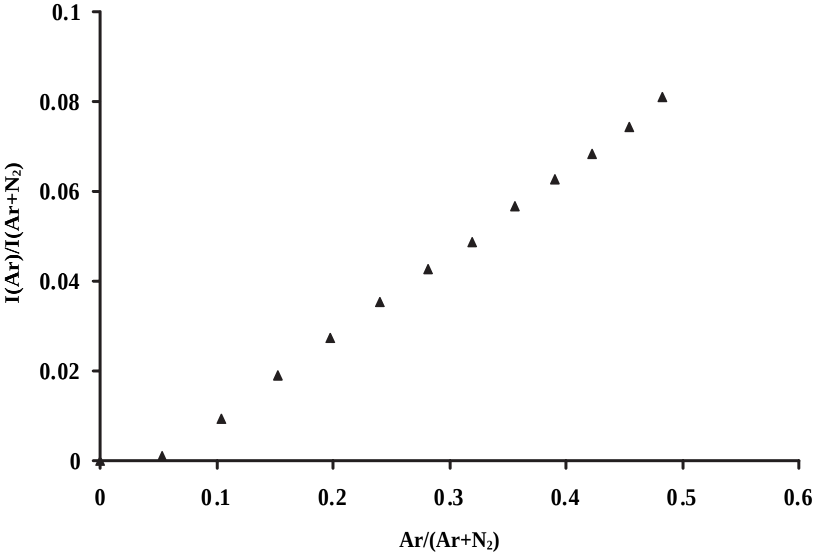

Fig. 5. Relative concentration versus relative emission intensities inferred from flow experiments. In most cases, the experimental error was smaller than the size of the markers in the graph except for two measurements at the lowest concentrations.

of nitrogen $C\,^3\prod_u(\upsilon') \rightarrow B\,^3\prod_g(\upsilon'')$, $\upsilon''-\upsilon' = 2$ (for $\upsilon' = 0, 1, 2, 3, 4$) 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:

$$\Gamma = \frac{P_{\mathrm{Ar}}}{P_{\mathrm{Ar}} + P_{\mathrm{N}_2}}, \tag{2}$$

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 Γ is attributed to the difficulties in measuring weak emissions from argon. Large errors at the lowest argon concentrations are due to difficulties in accurately subtracting background radiation in the vicinity of the weak argon line.

In summary, we have demonstrated that one can accurately determine the fractional ground state population in argon/air mixtures from observed emission intensities in their excited state created in DC electrical discharge at atmospheric pressure. Our experiment is similar to the optical actinometry approach often used in plasma processing and manufacturing (see for example ref. 9).

5. Conclusion

Our analysis indicates that the relative concentration of argon-to-nitrogen can be inferred with an accuracy of 5%. An inexpensive field-deployable instrument can use two broadband interference filters centered at 380 and 750 nm and a pair of simple photodetectors in place of a spectrograph to lower the cost and complexity.

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