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Optosensing of Carbon Monoxide Through Paper Impregnated with Palladium(II) Chloride

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Descreve-se a determinação de monóxido de carbono, usando-se cela de fluxo com fibras ópticas. O método baseou-se nas alterações da refectância difusa, que ocorrem devido à redução do paládio(II), pelo monóxido de carbono. Os resultados foram representados pela teoria de Kubelka-Munk, a qual forneceu curvas analíticas com coeficientes de correlação entre 0,999 e 0,98. A determinação do teor de monóxido de carbono no ar foi feita na faixa de concentração de 0,05 a 100% (v/v) com desvio padrão relativo de 10%.

The determination of carbon monoxide using a optical-fiber flow cell is described. The method was based on the changes of diffuse reflectance due to reduction of palladium(II) by carbon monoxide. The results could be represented by the Kubelka-Munk theory, which yielded analytical curves with correlation coefficients in the range 0.999-0.98. Determination of carbon monoxide in the air was performed in the concentration range of 0.05-100% (v/v) with a relative standard deviation of 10%.

Keywords: *optical-fiber chemical sensor, carbon monoxide*

Introduction

Carbon monoxide[1] is one of the most poisonous chemical pollutants of the atmosphere, and there is great interest in the determination of its concentration. Due to the large variety of sources of emission and of concentration levels there are many methods[2] available for the determination of carbon monoxide. For environmental analysis, the most used procedure is nondispersive infrared spectroscopy.

The concentration of carbon monoxide varies from one location to another as well as with the atmospheric conditions under which the measurements are taken. For these reasons, continuous and *in situ* monitoring is desirable. Fiber-optic chemical sensors (FOCS)[3] have the capability of performing these kind of measurements and have other attractive characteristics[4], as compared to other sensors.

A FOCS for carbon monoxide was recently described[5]. It is based on addition of palladium(II) chloride to the monomer solution before polymerization of the fiber. The device presents all favorable characteristics of FOCS, but because of slow diffusion of carbon monoxide into the fiber, detection cannot be extended to low concentrations (response limited to 1-100%).

The present work describes the development of an optosensing method for carbon monoxide. The procedure was based on the decrease of diffuse reflectance owing to the reduction of palladium(II) by carbon monoxide in a flow cell. The reaction was:

$$PdCl_2 + CO + H_2O \rightarrow Pd^o + CO_2 + 2HCl \qquad (1)$$

Experimental Details

Instrumentation

A DMS-100 spectrophotometer (Intralab), adapted[6] to function with fiber optics, was used to record the diffuse reflectance spectra. For the analytical measurements, a simple instrumentation was used: a tungsten halogen lamp (12 V, 50 W), whose light passed through a filter (FUNBEC, maximum transmission at 600 nm) and was focused onto a single-core optical fiber (Toray) which brought the light to the optosensing cell. Another optical fiber collected the light reflected from the cell and guided it to a silicon detector photometer (Ealing Electro-Optics) connected to a recorder (ECB).

The configuration of the optosensing cell is shown in Fig. 1. The cell (4.0 x 3.0 x 2.0 cm) consists of two Perspex blocks which were held together by two pairs of screws. The reagent paper was positioned in front of the end of two optical fiber (1.0 mm diameter; 2.2 mm with jacket) at a distance of about 0.5 mm. A polyethylene tube (1.0 mm

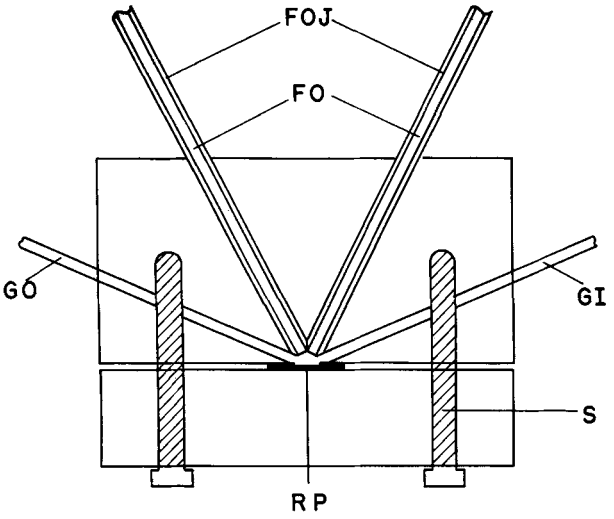

Figure 1. Optosensing cell. FOJ: optical fibers jacket; FO: optical fibers; GI: gas inlet; GO: gas outlet; S: screws; RP: reagent paper.

diameter) guided the flow of gas over the surface of the reagent paper.

Reagents and solutions

All of the chemicals were of analytical reagent grade.

Standard solutions of carbon monoxide were prepared by measuring, with syringes, calculated volumes of pure carbon monoxide (White Martins) at atmospheric pressure, and diluting them with known volumes of nitrogen. Carbon monoxide solutions were stored in gas sampling Tedlar bags.

The reagent paper was prepared by immersing one strip (1.0 x 1.0 cm) of Whatman 1 paper, for one minute, in a 0.4% palladium(II) chloride solution (in 50% water and 50% gelatin). The excess of solution on the reagent paper was removed by briefly touching the edges of the strip on a clean absorbing paper.

Procedure

The reagent paper was installed in the optosensing cell and the base line was recorded. The gas sample flow was started and the diffuse reflectance was measured at a given time, or after passing a fixed volume of gas, depending on the concentration range of the samples. For carbon monoxide concentrations 4-100% (v/v) measurements at 6 and 20 min were performed (flow rate 0.8 ml/min). For lower concentrations were done after a flow of larger volumes. The optosensing cell was covered with a black cloth during measurements, to avoid interference from ambient light.

Diffuse reflectance (R) measurements were performed after calibration with barium sulfate as standard (R=1.00). This was done by using a layer of barium sulphate in place of the reagent paper, in the optosensing cell.

Results and Discussion

Optical-fibers arrangement

Optosensing cells[7] based on reflectance have usually been built using bifurcated optical fibers. While this arrangement ensures coincidence of the acceptance cones of incident and reflected radiation, it also causes a loss of 50% of the intensity of reflectance, solely due to bifurcation. In order to avoid this loss of intensity, two fibers were used in the optosensing cell, as shown in Fig. 1. In this case, coincidence of the acceptance cones over the surface of the reagent paper was accomplished by adjusting the angle between the two fibers and the distance from the paper. For the optical fibers used in this work, for which the numerical aperture is 0.46, an angle of 55° was found to be appropriate for a distance from the paper of about 0.5 mm.

Analytical signal

Figure 2 gives the reflectance spectra of the reagent paper, and shows that reduction of palladium(II) by carbon monoxide produces a large decrease in the intensity of reflected radiation. This is due to the distinct change in color of the reagent paper, from light yellow to dark brown. It is possible to see from Fig. 2 that the largest divergence between the two spectra occurs at about 600 nm. This wavelength was used for the analytical measurements.

The typical behavior of the analytical signals as a function of time is shown in Fig. 3. It was observed that curves for all concentrations reached a constant value of reflectance after some time. Beyond this time, flowing of carbon

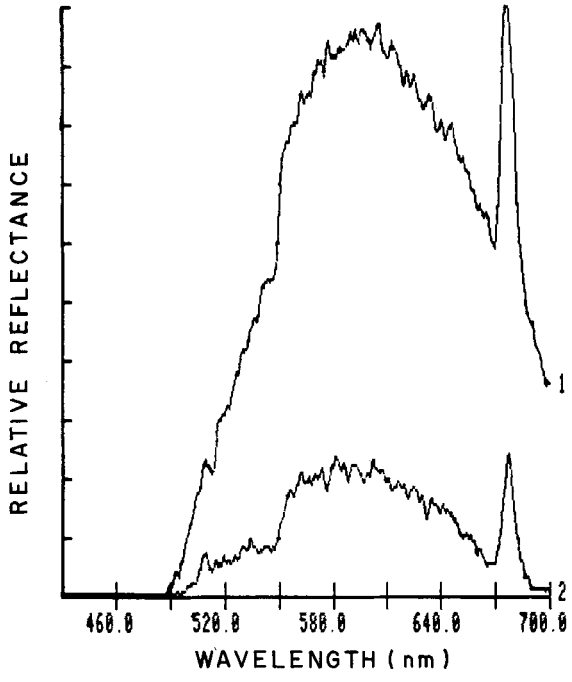

Figure 2. Reflectance spectra of reagent paper (1) before and (2) after reaction with carbon monoxide.

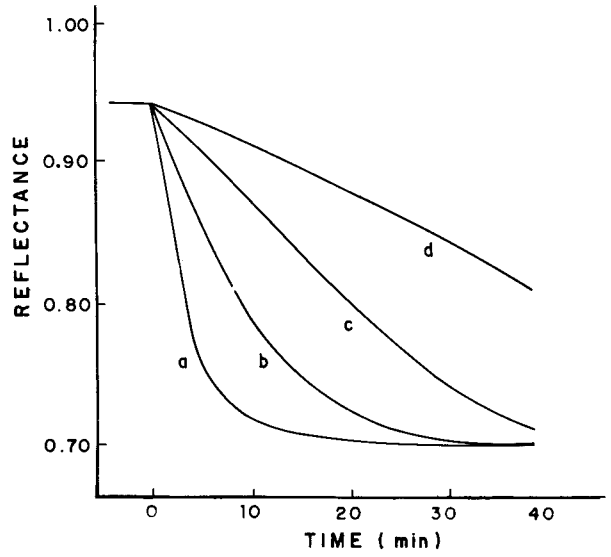

Figure 3. Profile of analytical signals. Carbon monoxide concentrations (%, v/v) equal to 100 (a), 40 (b), 11 (c) and 6 (d).

monoxide causes no further change in reflectance. However, longer times were required for lower concentrations to reach the constant value. Under these circumstances, analytical determinations can be accomplished[8] by measuring the signal, either at a fixed time (keeping constant the flow rate), or after flowing a fixed volume of the sample. The times and volumes were chosen to encompass the desired concentration range. For carbon monoxide concentrations 4-100%, measurements at two times (6 and 20 min) were found to be suitable. Table 1 gives the results, which were the averages of 2-3 determinations.

Analytical curves

The most used model for diffuse reflectance is that of Kubelka-Munk theory[9]. This model can relate the reflectance values, R, to the concentration of carbon monoxide, C, by the equation:

$$F(R) = (1-R)^2 / 2R = kC \quad (2)$$

where F(R) is the Kubelka-Munk function and k is a constant combining the absorption and scattering constants. Figure 4 shows the variation of F(R) for the results of Table 1. For measurements at 6 min, an excellent linear relationship exists for concentrations from 20-100% (correlation coefficient equals 0.999). For the set of results obtained at 20 min, the linear portion of the curve is from 4 to 20% (correlation coefficient equals 0.997). In this case, departure from linearity for concentrations above 20% is because at this time (20 min) the reaction is going to completion, with all Pd^{2+} available in the reagent paper being used up. In fact, the results for concentrations of 75 and 100% indicate that, at 20 min, the constant value of reflectance has already been reached.

The precision of reflectance measurements was evaluated by determining the concentration of 6 samples containing 20% carbon monoxide. The estimate of the relative standard deviation was 10%.

Lower concentrations

Determination of carbon monoxide in samples of concentrations below 4% were carried out by measuring the analytical signal after flowing a fixed volume of the sample through the optosensing cell. In this case, some modifications in the procedure were necessary, such as the expansion of the reflectance scale and a great increase in the flow rate. Analytical curves similar to those shown in Fig. 4 were also obtained. The volume of the sample taken depended on the concentration range, larger volumes being used for

Table 1. Results of analytical curves.

Concentration	Reflectance	
(%, V/V)	6 min	20 min
4.0	0.92	0.89
6.0	0.92	0.87
8.0	0.90	0.84
11	0.90	0.82
20	0.88	0.77
40	0.84	0.72
50	0.82	0.71
75	0.78	0.70
100	0.75	0.70

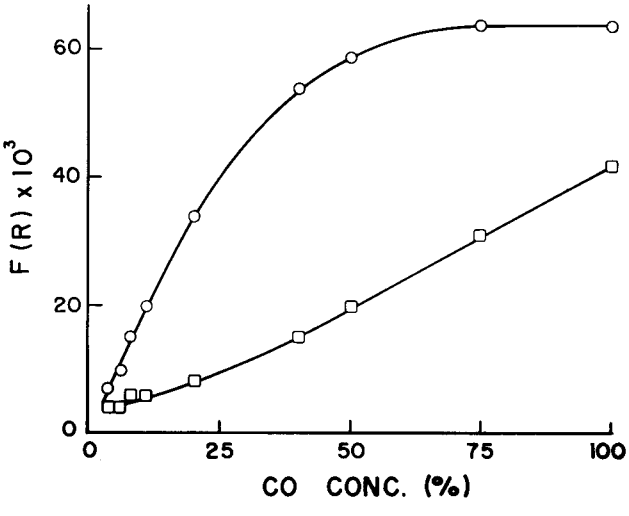

Figure 4. Analytical curves for measurements at 6 (□) and 20 (O) min.

lower concentrations. Using 20 L of samples, a linear calibration curve (7 points), represented by the equation:

$$F(R) = -0.13 + 5.5\ C \quad (3)$$

with a correlation coefficient equaling 0.98, was obtained for the concentration range of 0.25 to 0.05% (v/v).

The precision of reflectance measurements diminished at lower concentrations. This was probably due to the removal of water from the reagent paper, caused by the large flow rate needed with a large volume of the sample. In fact, it was observed that no reaction occurred when the paper became dry. This was understandable from the observation of equation (1). The decrease in reproducibility at lower concentrations limited the lowest concentration attainable to about 0.05% (v/v).

Interferences

Christian and co-workers[10] theorized that the presence of oxygen in the gas sample might cause significant interference, when using the palladium(II) reduction method. Indeed, comparison of the values[11] of standard potentials indicates that oxidation of palladium(0) by oxygen can, in theory, take place. In order to experimentally investigate this possibility, pure oxygen (White Martins) was flowed through the optosensing cell, after the reaction of carbon monoxide with the reagent paper was completed. No change in reflectance was observed, nor was any modification in the dark-brown color of the reagent paper seen. Also, samples of carbon monoxide diluted with air gave the same results as those using nitrogen as the solvent. It was concluded that the presence of oxygen in the gas sample causes no interference in the procedure developed in this work. A similar conclusion has been found[12] for a spectrophotometric method using the same reaction [eq. (1)] for the determination of carbon monoxide.

Reducing gases such as sulphur dioxide and nitrogen dioxide can cause interference in methods for determination of carbon monoxide using reduction of palladium(II). However, this interference can be eliminated by using a pre-trap[13] in the flow of the sample.

Conclusions

Experimental characterization of a new optosensor for carbon monoxide was accomplished in this work. The sensor developed may be applicable in detecting leakage of air contamination by carbon monoxide. In this case, especially in an industrial setting, optical-fiber sensors offer an unique advantage over electrical based detectors, since there is no risk of electrical spark ignition. The analysis can be performed *in situ* using low cost components. Also, the procedure can be adapted for continuous measurement by using a paper type cassette and a drive motor.

Comparison of our sensor with that previously reported[5] seems to indicate that both devices have similar performance and give the same results with regards to precision. However, our procedure allows higher sensitivity in detection.

Acknowledgments

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