# Silver-Gelatin Method for the Determination of Trace Amounts of Carbon Monoxide in Air

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The use of silver-gelatin complex was found suitable for the determination of trace amounts of carbon monoxide in air. Silver-gelatin complex is reduced by carbon monoxide to give intensely colored sol. Measurement of the color intensity of the stable silver sol enables the determination of carbon monoxide successful under various environmental conditions. The detection limit is 2—100 ppm. The relative standard deviation for the determination of 10 ppm carbon monoxide is 2.6%.

Carbon monoxide is a man-made pollutant widely distributed in the atmosphere. As the gas is neutral in its character, it is difficult to impinge. It can react with various metals and hence stabilize many low valent metals. Recently with the increased concern about the effects of atmospheric pollution, several methods have been developed for the determination of carbon monoxide in air.

There are many instrumental methods which are often useless for the field evaluation. Though the nondispersive infrared (NDIR) spectroscopy and Robbins[1)] photometric methods are suitable for carbon monoxide determination, these methods are of little importance for the routine and continuous determination of carbon monoxide under the environmental conditions. Similarly, gas chromatographic techniques[2,3)] are rather sophisticated though the detection limit is about 0.1—1000 ppm. Colorimetric methods for the determination of carbon monoxide date back to more than 50 years but are still gaining ground.[4—8)]

The well-known carbon monoxide and iodine pentaoxide reaction can be used for the determination of carbon monoxide by estimating the liberated iodine by various means.[9,10)] Gravimetric method[11)] converting carbon monoxide into carbon dioxide, color reaction of impregnated silica gel,[12,13)] etc. are inexpensive and easy, but the accuracy is not satisfactory. Lambert[14,15)] and his coworkers have developed certain reagents for the colorimetric estimation of carbon monoxide, but the sensitivity and instability make the reagents unsuitable for the routine continuous analysis. The use of the less stable silver sol method[16,17)] is suitable for the colorimetric estimation of carbon monoxide. The method by Simonescu et al.[16)] can be employed in a concentration range of 5—500 ppm and the determination error is less than 3% for carbon monoxide. The last two methods stand on the basis of formation of metallic silver sol from the complex of silver ions with sulfamoyl groups in alkaline medium. Considering the obvious difficulty of impingement of carbon monoxide, West et al.[17)] extended the method by Simonescu for the field evaluation just by using a permeation technique.

It was observed that some weak metal-amino acid complexes in alkaline medium were easily reduced by trace amounts of carbon monoxide to form colored metallic sol.[13)] But silver sol easily breaks into black precipitates rendering difficulty in color intensity measurements. The present paper describes a simple method for the determination of trace amounts of carbon monoxide using silver-gelatin complex in alkaline medium. The method can be reliably applied to field evaluation without the use of toxic chemicals. Even, no tedious preparation like the recently reported octaethylporphyrinatoruthenium(II)[18)] is needed. Moreover, the sol is better stabilized in solution by gelation than by any other previously reported method.

## Experimental

**Apparatus.** A Cary-17D (Varian) spectrophotometer was used to measure all absorbance values.

**Impinger.** Simple impingers of length 21 cm and internal diameter 2.2 cm were used for gas absorption. The outer wall was covered with black paint to protect the reagent from direct sunlight.

**Silver-Gelatin Reagent Solution.** The reagent solution was prepared by dissolving 0.5 g gelatin powder (E. Merck) in 100 ml of boiled and warm distilled water with constant stirring. Sixty ml of $10^{-3}$ M (M=mol dm$^{-3}$) silver nitrate solution was added. If any turbidity appeared, it was removed by adding a few drops of 2 M sodium hydroxide solution. The solution was heated at 50—60 °C for five minutes. The solution was diluted with 0.5 M sodium hydroxide solution to 250 ml. The reagent solution was stored in an amber-colored bottle and kept in the dark. The solution remained stable for more than 10 weeks.

**Reagents.** All reagents used were of analytical grade without any further purification.

## Results and Discussion

**Calibration Curve.** Ten ml of silver-gelatin reagent solution was placed in the impinger and exposed to a known concentration of carbon monoxide for a specified period of time, typically 50 ppm for 6 h. Preparation of carbon monoxide-air mixtures was accomplished by successive dilution of a pure carbon monoxide stream with streams of purified air, nitrogen or inert gases; rotameters were used to measure flow rates. Upon completion of the exposure using a flow-rate of 500 ml min$^{-1}$ the solution was kept for 1h and the absorbance was measured at 415 nm against a reagent blank. The concentration of carbon monoxide

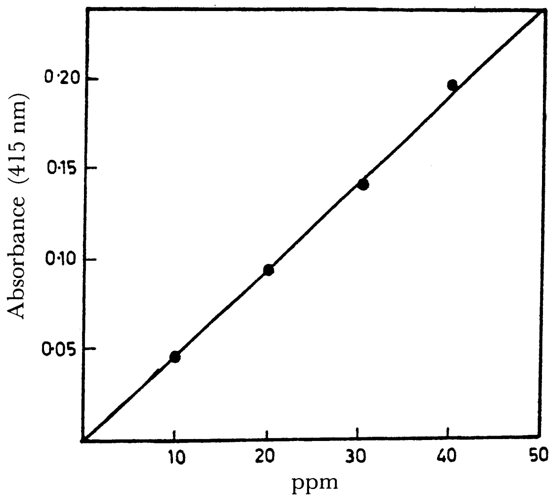

Fig. 1. Calibration curve for CO determination.

was calculated from the equation $A=kCt$; where $k$ is a constant determined experimentally, $C$ is the concentration of carbon monoxide, $t$ is the time of exposure, and $A$, the absorbance at 415 nm (Fig. 1).

**Interferences.** The interferents were injected into the carbon monoxide-air stream by using a motor-driven syringe.[19] The accuracy of this syringe technique was checked by controlling the plunger speed by standard methods. Gaseous acetylene, aqueous solutions of formaldehyde (30%), aqueous ammonia (50%), and standard chlorine water were introduced. The results of the interference studies are shown in Table 1.

Data reported for sulfur dioxide, nitrogen dioxide, carbon dioxide, and hydrogen sulfide are based on 24 h exposures to 10 ppm carbon monoxide and interferent species at the level indicated. It was observed that several reducing agents like $SO_2$ and $NO_2$ gave unexpected lower absorbance values. This may possibly due to quicker reduction of the silver-gelatin complex and hence aggregation of sol lowers the absorbance values. For maintaining interferent levels of chlorine, ammonia, acetylene, and formaldehyde studies were conducted with 6 h exposures to 40 ppm carbon monoxide and interferent species at four times the level indicated.

The silver-gelatin method has two serious drawbacks. First, the reducing gases like $H_2S$, $SO_2$ must be removed by classical means. Secondly, a less serious disadvantage is that the exposed solution is to be taken for the measurement at least after 1 h time.

Numerous techniques for eliminating or reducing interferences were tried without success. It has been reported[19] that potential interferences from hydrogen sulfide for this reagent can be eliminated by passing the air sample through the silver-gelatin complex absorbed on silica gel. The advantage of this method over the conventional methods[16,17] is the stability of the exposed silver sol solution in gelatin.

In conducting the investigations, the concentration levels of possible interferent species were chosen in relation to appropriate Indian standards; the concentration of carbon monoxide chosen was 20 ppm, which corresponds to the typical background level of carbon monoxide found in the laboratory during the study.

**Field Evaluation.** In order to confirm the usefulness of the proposed method, it was applied to the determination of carbon monoxide in both the laboratory as well as the rural environment. The air sample was sucked after removing the acidic gases like $SO_2$, $CO_2$, $H_2S$ using aqueous sodium hydroxide and lead acetate traps. The results are summarized in Table 2, together with the results obtained by the permeation method[17] carried out for comparison.

**Precision and Accuracy.** The relative standard

Table 2. Determination of Carbon Monoxide in Air Samples

| Date | Laboratory air (ppm) | | Urban air (ppm) | |
|---|---|---|---|---|
| | A | B | A | B |
| 3/1/86 | 40 | 42 | 20 | 20 |
| 4/1/86 | 22 | 22 | 18 | 17 |
| 5/1/86 | 16 | 15 | 20 | 19 |
| 6/1/86 | 42 | 41 | 19 | 19 |
| 7/1/86 | 45 | 45 | 25 | 23 |
| 8/1/86 | 40 | 39 | 22 | 22 |

A; Present method: B; Permeation method.[17]

Table 1. Determination of Carbon Monoxide (10 ppm) in Synthetic Air Samples Containing Potentially Interfering Gases
Flow rate of the gas 500 ml min$^{-1}$; time of standing after exposure 1 h

| Interferent | Concentration/ppb | Net absorbance (415 nm) | Change/% |
|---|---|---|---|
| None | — | 0.074 | — |
| $NO_2$[a] | 200 | 0.070 | −5.4 |
| $SO_2$[a] | 130 | 0.064 | −13.5 |
| $H_2S$[a] | 50 | 0.088 | +18.9 |
| $C_2H_2$[b] | 200 | 0.076 | +2.7 |
| $NH_3$[b] | 50 | 0.078 | +5.4 |
| $Cl_2$[b] | 20 ppm | 0.073 | −1.3 |
| $CH_2O$[b] | 50 | 0.080 | +8.1 |
| $CO_2$[b] | 200 | 0.074 | Nil |

a) Exposure time 24 h. b) Exposure time 6 h and data were obtained using gas concentrations of 4 times the levels indicated.

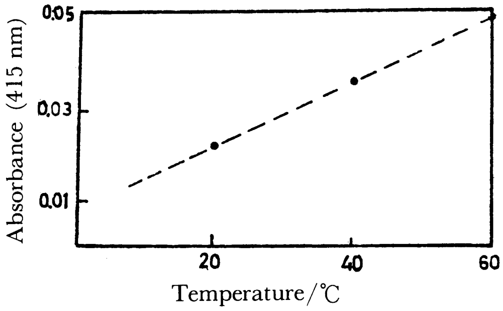

Fig. 2. Temperature effect, flow rate of sample gas 500 ml min$^{-1}$, standing time after exposure 1 h. CO concentration 8 ppm.

deviation and confidence limits for the determination of carbon monoxide with silver-gelatin complex were calculated and found to be 2.6% and 7.6±0.04 respectively, while the carbon monoxide concentration was 10 ppm and the flow rate of the gas was kept at 500 ml min$^{-1}$.

**Temperature Effect.** The reduction of silver-gelatin complex by carbon monoxide is temperature dependent. The effect of temperature was studied by keeping all other factors constant. The same amount of silver-gelatin complex was taken in a different impinger and reduced with the same amount of carbon monoxide at different temperatures. The results are given in Fig. 2, where each point represents an average of six determinations. The data indicate that there may be an error in the determination of carbon monoxide by this method of about 2.3% per degree centigrade, for each degree of temperature difference between the temperature at which a measurement is made and the temperature at which the device was calibrated.

**Response of Measurement System.** The response of the system as measured by the product $Ct$ ($C$, Concentration of carbon monoxide; $t$, time of exposure) must be uniform throughout the useful range of the method. The absorbance value obtained on exposure to 30 ppm for 5 h should be same as that obtained on exposure to 15 ppm for 10 h, for example. It was observed that the absorbance ($A$) value varies with time ($t$), and for a sample with a given concentration ($C$) of carbon monoxide the absorbance is expressed by the equation $A=f(C, S, D, T, t)$, where $S$ stands for gas reagent interface, $D$ for diffusion coefficient, and $T$ for temperature. This observation was made within 1 h time after the disconnection of the gas flow (500 ml min$^{-1}$) through the absorbing solution (10 ml).

**Effect of Light.** The diffused sunlight or indoor lighting in the laboratory produces no deterioration in either exposed or unexposed reagent for periods of one week. It was found during the present investigation that placement of exposed and unexposed reagent in direct sunlight results in complete loss of color in about 5 h. As a result of this observed deterioration in the presence of direct sunlight, it was necessary to shield the impinger from light in the shelter used in field evaluations. As a precaution the reagent also was stored in amber-colored bottles and kept in dark place in the Laboratory.

**Stability of the Reagent.** The present method was developed to determine average concentrations of carbon monoxide over periods of several hours. It was essential, therefore, that the response of the reagent is essentially uniform during the entire exposure period. Any silver sol formed early in the exposure period must be stable during the remainder of the exposure period, and the response of any unexposed reagent must be the same during the last portion of the exposure period as during the early portion.

To determine the stability of both exposed and unexposed reagent, carbon monoxide (400 ppm) was bubbled for 3 h through 50 ml of reagent at a flow rate 500 ml min$^{-1}$, and the gas flow was then discontinued and sample of exposed and unexposed reagents were placed in constant-temperature baths. The absorbance of each sample was measured at periodic intervals. The results are shown in Table 3. Each absorbance value represents an average of at least three determinations.

The data indicate that the intensity of the color produced by the silver sol is found to decrease with time; the net decrease average is about 1.0% in 6 h and 3.1% in 24 h at 25 °C and the instability increased with temperature.

The blank value at higher temperatures tended to stabilize at an absorbance value of 0.042—0.055 after 48 h. The present method offered the advantage of stabilizing the silver sol over a wide range of concentration of silver and hence silver sol is not precipitated unlike the methods as referenced in literature.

The method developed here is simple, inexpensive and reliable for the determination of average concentrations of carbon monoxide in the ambient atmosphere. The technique requires no electrical or mechanical connections to complex equipment, and

Table 3. Stability of Exposed and Unexposed Silver-Gelatin Reagents

| Time/h | Temp 25 °C | | Temp 30 °C | | Temp 40 °C | |
|---|---|---|---|---|---|---|
| | Blank[a] | Rgt.[b] | Blank | Rgt. | Blank | Rgt. |
| 0 | 0.033 | 0.193 | 0.033 | 0.195 | 0.033 | 0.192 |
| 6 | 0.033 | 0.191 | 0.035 | 0.192 | 0.037 | 0.189 |
| 24 | 0.034 | 0.187 | 0.038 | 0.189 | 0.039 | 0.178 |

a) Unexposed reagent. b) Reagent exposed to 400 ppm CO.

no tedious sampling technique is required. The method has some limitations, however.

The method is not suitable where high interferent concentrations may be present, nor is it suitable for process stream analysis where very rapid measurement is required and the temperature variation also affect the results.

The reagent is stable at ordinary room temperature up to 10 weeks, and the absorbance value of the blank at 30 °C is less than 0.005; this value varies by less than 0.001.

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