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GAS CHROMATOGRAPHIC MEASUREMENT OF CARBON MONOXIDE IN HYDROCARBON MATRICES WITH A REDOX CHEMILUMINESCENCE DETECTOR

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SUMMARY

The rapid measurement of trace levels of carbon monoxide in ethylene by gas chromatography with redox chemiluminescence detection is described. Linear response for carbon monoxide over three decades and a detection limit in the sub-parts per million by volume (ppmv) concentration range were observed without methanation or preconcentration of the sample. Samples containing 0.2 ppmv of carbon monoxide in ethylene were readily quantitated.

INTRODUCTION

Carbon monoxide is a major atmospheric pollutant and an important industrial gas. Its accurate measurement at trace levels is of great concern in many fields. In the petrochemical industry, for instance, it is desirable to make such measurements in hydrocarbon matrices. Some industrial processes require that carbon monoxide concentrations be in a narrow working range, because higher levels of carbon monoxide may inhibit certain catalytic processes[1]. Other catalysts are poisoned altogether by even trace amounts of carbon monoxide[2]. The concentration of carbon monoxide in ambient air is an important indicator of air quality.

Carbon monoxide can be detected by many methods, such as infrared absorption, colorimetry, electrochemical methods based on selective membranes, and catalytic combustion combined with gas chromatography (GC) and thermal conductivity detection (TCD)[3]. Sub-part per million levels of carbon monoxide are easily detected when converted to methane by a methanator and measured by a flame ionization detector[4], but this method is susceptible to interference from traces of compounds containing methylene units. In this paper, we demonstrate that the newly developed redox chemiluminescence detector is particularly sensitive to carbon monoxide, and samples can be rapidly analyzed for carbon monoxide at sub-part per million by volume (ppmv) levels without any sample pretreatment, such as methanation or preconcentration. In addition, the redox chemiluminescence detector can be used to measure other species that cannot be sensitively measured with flame ionization detectors[5].

EXPERIMENTAL

Apparatus

The construction of the gas chromatographic redox chemiluminescence detector has been described previously[5,6]. Briefly, the system consists of a purified carrier gas, a gas chromatograph, a reagent gas metering device, a redox reaction zone, an ozone source and a nitric oxide/ozone chemiluminescence measuring system.

Redox reaction catalyst chamber and reagent gas metering device

The redox reaction catalyst chamber consisted of a 6 mm O.D. × 1.8 mm I.D. quartz tube (Corning Glass Works, Corning, NY, U.S.A.) packed with 0.1 g of 230/320-mesh soda-lime glass beads coated with elemental palladium. The beads were held in place by small wads of quartz wool, 4–8 μm diameter fibers (Heraeus-Amersil, Sayreville, NJ, U.S.A.); the bed was approximately 1 cm long after packing. The beads were prepared by evaporating an aqueous solution of palladium chloride (Fisher Scientific, Fair Lawn, NJ, U.S.A.) onto the beads, followed by reduction of Pd(II) to Pd(0) at 400°C under flowing hydrogen. The metal coating on the glass beads was approximately 2.5% by weight. The temperature of the catalyst was controlled within ±4°C with a temperature controller (Model E 924, Omega Engineering, Stamford, CT, U.S.A.). Heating was achieved through the use of a stainless-steel block, wrapped with 2.5 cm × 0.6 m long heating tape (Thermolyne Corporation, Dubuque, IA, U.S.A.).

The reagent gas metering device consisted of one or more gravimetrically calibrated NO_2 permeation tubes in a dilution chamber. The concentration of the nitrogen dioxide in the reagent gas stream when two permeation tubes were placed in the glass metering device was approximately 300 ppmv. The permeation tubes, consisting of 15-cm lengths of 0.635-cm O.D. × 0.11-cm wall-thickness FEP tubing (Galtek, Chaska, MN, U.S.A.), were filled while being cooled in an ice-bath, with liquid NO_2/N_2O_4 and capped with machined plugs of extruded FEP. Prior to being used to fill the permeation tubes, liquid NO_2/N_2O_4 (Matheson Gas Products, Secaucus, NJ, U.S.A.) was collected in an ice-bath cooled flask and purged with oxygen to remove nitric oxide.

Samples

Samples of carbon monoxide in ethylene were produced by static dilution[7]. A high concentration (100–1000 ppmv) mixture of carbon monoxide in ethylene was first prepared in order to make mixtures of lower concentrations by dilution. The high concentration mixture was made by evacuating an aluminum cylinder of known volume, adding a known volume of carbon monoxide, and finally pressurizing the cylinder with ethylene to a known pressure. The ethylene used for preparation of standard samples was determined by independent analysis to contain substantially less than 0.2 ppmv of impurity carbon monoxide. Standard samples containing the lower concentrations of carbon monoxide in ethylene were prepared by adding known aliquots of the high concentration mixture, by means of a gas-tight syringe (Series A-2, Precision Sampling Corporation, Baton Rouge, LA, U.S.A.), through a septum, into a 1-l gas-sampling syringe which contained a known volume of ethylene. Before the addition of the aliquot was made, the large syringe was thoroughly

purged with clean ethylene. Mixing was achieved through the use of several 2-mm glass beads contained within the barrel of the large syringe. The carbon monoxide and the ethylene used were C.P. Grade (Scientific Gas Products, Ashland, South Plainfield, NJ, U.S.A.). Sample injections were made with a 5-cm³ gas-tight syringe or with a 6-port injection valve (Valco Instruments Company, Houston, TX, U.S.A.) equipped with a 0.46-cm³ sample loop. Standards of nitric oxide in nitrogen were obtained from Scott Specialty Gases (San Bernardino, CA, U.S.A.).

Instrumentation

A Hewlett-Packard Model 5750 gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.) was used for the gas chromatographic investigations. A Hewlett-Packard 3390A integrator was used to record chromatograms. The column used was a 3 m × 1.2 mm I.D. stainless-steel tube packed with Chromosorb 102, 80/100-mesh (Manville Corp., Denver, CO, U.S.A.). Helium carrier was purified by traps containing molecular sieve 5A (Alfa/Ventron, Danvers, MA, U.S.A.) and Hopcalite (Mine Safety Appliances Company, Pittsburg, PA, U.S.A.). The chemiluminescence measuring system used was a Model 207 RCD (Sievers Research, Boulder, CO, U.S.A.) for exploratory experiments, and for the quantitations, a Model 10 chemiluminescent NO/NO_x analyzer (Thermo Electron Corporation, Waltham, MA, U.S.A.) which had been modified extensively in a manner similar to that previously reported[5].

Procedures

The selectivity of the palladium catalyst for carbon monoxide and ethylene was investigated as a function of catalyst temperature. This involved making injections of carbon monoxide and ethylene samples and comparing the relative responses for the amount injected at various catalyst temperatures. The carbon monoxide and ethylene responses were also compared to responses expected if 100% of the analyte reacted to form nitric oxide. This was done by making injections of nitric oxide standards directly into the flow stream at a point between the catalyst and the nitric oxide/ozone chemiluminescence analyzer, and comparing these peaks with responses from known concentrations of analytes that were mixed with nitrogen dioxide and passed through the heated catalyst zone.

A schematic drawing of the chromatographic system with the catalyst bypass switching valve is shown in Fig. 1. Immediately after carbon monoxide is eluted, the effluent from the column is redirected to bypass the redox chemiluminescence detector to prevent overloading of the detector from the high quantity of ethylene contained in the sample matrix. Changing the switching valve position allowed bypassing, while a matched flow of helium was passed over the catalyst, so that there was only a small perturbation of flow in the catalyst chamber. Although other techniques for keeping the helium flow constant could be used to maintain steady-state conditions within the catalyst chamber, as a matter of convenience in this instrument, which was already equipped with a thermal conductivity detector, a switching valve was connected in series to the two exhaust ports. This allowed easy flow matching by simply adjusting the analytical column and reference column flow-rates to the same value. Chromatograms were obtained at a column temperature of 50°C, with a 30 ml/min flow of helium carrier. Under these conditions, carbon monoxide was eluted at 0.8 min and ethylene at 2.1 min.
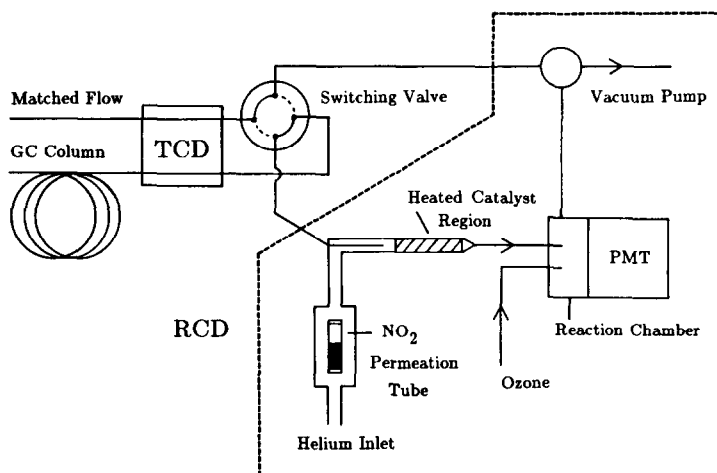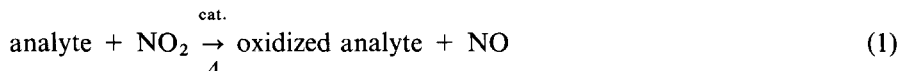
Fig. 1. Schematic drawing of the redox chemiluminescence detector for GC. A switching valve allows for bypass of the redox chemiluminescence detector by selected major constituents of samples. Abbreviations: TCD = thermal conductivity detector; RCD = redox chemiluminescence detector; PMT = photomultiplier tube.

The catalyst bypass procedure was as follows: an injection of sample was made, and 30 sec after the carbon monoxide peak had been eluted, the analytical column effluent was switched to allow ethylene to bypass the catalyst bed; then 3 min later the original flow paths were re-established by switching the valve to its original position.

RESULTS AND DISCUSSION

Redox chemiluminescence chromatographic measurement is based on a two-step reaction and detection scheme[5,8]. In the first step, an analyte such as carbon monoxide, for example, reacts rapidly with nitrogen dioxide on gold surfaces at elevated temperatures according to eqn. 1[9,10]. Carbon monoxide reacts with nitrogen dioxide more slowly on gold surfaces even at room temperature[10]. In the second step, the nitric oxide formed during the oxidation of the analyte is subsequently quantitated by its chemiluminescent reaction with ozone (eqn. 2).

$$\text{analyte} + NO_2 \xrightarrow[\Delta]{\text{cat.}} \text{oxidized analyte} + NO \qquad (1)$$

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu \qquad (2)$$

Eqn. 1 is rate-limited, and consequently, the degree of conversion can be modified through the use of different catalysts, catalyst-bed temperatures, or other operating conditions. The extent of conversion depends on how rapidly the analyte is oxidized under given reaction conditions. Under the same conditions, various analytes may react with the reagent with differing efficiencies. In order for an analyte to be detected, appreciable amounts of nitric oxide must be formed during the short residence time

of the analyte in the catalyst bed. The calculated residence time of an analyte in the catalyst bed is less than 1 s. Increasing the dimensions of the catalyst bed may have the effect of increasing the amount of conversion to nitric oxide for a given analyte, but this increase in nitric oxide production might be offset by a corresponding increase in band-broadening and peak asymmetry. This also would increase the formation of background nitric oxide from the thermal decomposition of the reagent, nitrogen dioxide, which occurs to a limited degree even in the absence of a reducing analyte. For the measurement of carbon monoxide, effective catalyst temperatures are low enough that nitrogen dioxide decomposition causes no significant problem. Rapid conversion of carbon monoxide is observed in catalyst beds containing either gold or palladium at temperatures between 300 and 400°C.

Alkanes do not yield an appreciable redox chemiluminescence response when the catalyst is gold coated on soda-lime glass-beads, except at temperatures above 400°C[5]. Therefore, carbon monoxide can be selectively measured in the presence of alkanes when a gold catalyst is used below 400°C. Other important compounds giving little or no redox chemiluminescence response under these conditions are the fully chlorinated hydrocarbons, water, nitrogen, oxygen, carbon dioxide and the noble gases. These compounds represent the major constituents of many sample matrices and are important mobile phases in GC, supercritical fluid chromatography, and liquid chromatography. None of these compounds interfere with redox chemiluminescence detection, and thus, they can be used as carriers in chromatographic systems with the RCD.

Most organic compounds containing oxygen, nitrogen, sulfur, or reactive functional groups can be detected by redox chemiluminescence. Other rapidly oxidized compounds such as olefins, aromatic hydrocarbons, ammonia, hydrogen, hydrogen sulfide, hydrogen peroxide, and sulfur dioxide produce good responses[5,6,8]. Olefins, carbon monoxide and some sulfur compounds produce chemiluminescence in the blue region of the spectrum upon reaction with ozone[11]. The emission from the nitric oxide and ozone reaction is in the red and near infrared region of the spectrum. Therefore, a red-passing filter was used to suppress the chemiluminescence signals from other reactions.

Several porous polymer packing materials are available that can quickly and adequately separate carbon monoxide from ethylene. The present work demonstrates that the selectivity of a redox chemiluminescence detector coupled with a chromatographic separation can be used to perform rapid analyses of low levels of carbon monoxide in a hydrocarbon sample matrix. Ordinarily, traces of ethylene cause no problem for the detector, but when ethylene comprises the major constituent in a sample, then overloading or saturation of the detector will decrease the rate at which sample injections can be made. In order to make analyses as rapidly as possible, separation procedures were devised to minimize the amount of ethylene delivered to the detector.

Carbon monoxide and ethylene give redox chemiluminescence responses with both palladium and gold catalysts; however, carbon monoxide gives a much higher response than ethylene, especially at low catalyst temperatures (up to 200°C). It should be noted that the concentrations of the reactants and the length and configuration of the catalyst bed in the present chromatographic study are markedly different than those used by Fahey et al.[10], in which the reduction of nitrogen dioxide

by carbon monoxide was 96% complete at 25°C. The temperature selectivity of the catalyst was investigated to address the problem of overloading the detector from the large quantity of ethylene contained in the sample matrix. In order to avoid the potential problem of overloading the detector, we also investigated a means of mechanically switching the column effluent away from the catalyst while ethylene was eluted from the column. The implementation of this approach is particularly simple, since ethylene is eluted later than, and is easily separated from, carbon monoxide. A typical chromatogram obtained by redox chemiluminescence detection for a 1-cm³ sample of 10 ppmv carbon monoxide in ethylene obtained by using the flow switching technique is shown in Fig. 2.

The responses of carbon monoxide and ethylene as a function of the temperature of the palladium catalyst are plotted in Fig. 3. At temperatures up to 400°C, the molar response of carbon monoxide is always greater than that of ethylene. The response of carbon monoxide at room temperature is almost three orders of magnitude greater than that of ethylene. However, while the response of carbon monoxide is large compared to that of ethylene, the overall fraction of carbon monoxide that is oxidized to form NO under these temperature, flow and concentration conditions is only approximately 0.1%. At higher catalyst temperatures, the fraction of carbon monoxide that reacts to form NO increases to as much as 95% at 500°C, but the discrimination favoring carbon monoxide signal over that of ethylene decreases.

In addition, at the higher temperatures there is a corresponding increase in the thermal decomposition of nitrogen dioxide to generate nitric oxide and oxygen. The nitric oxide formed in this manner appears as a background signal and contributes to the overall noise in this detection system. Thus, while the conversion of carbon monoxide is nearly quantitative at very high catalyst temperatures (> 500°C), the
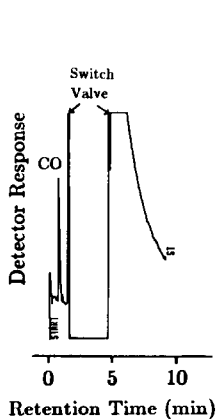

Fig. 2. A typical chromatogram obtained by redox chemiluminescence detection of a 1-cm³ injection of 10 ppmv carbon monoxide in ethylene is shown. Arrows indicate when the valve was switched during the elution of ethylene.
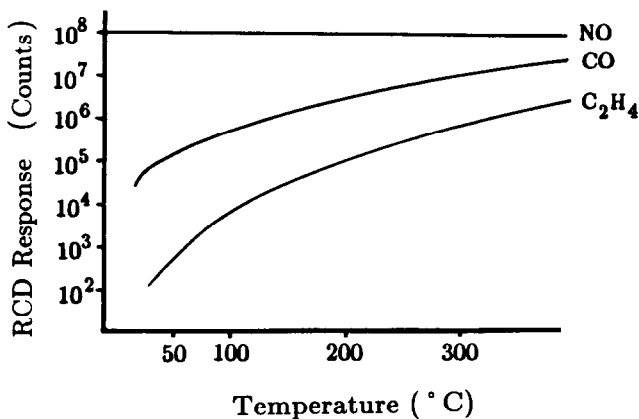
Fig. 3. Responses of carbon monoxide and ethylene as a function of catalyst temperature for a catalyst bed containing 2.5 mg of palladium (2.5% by weight) on 230/320 mesh soda-lime glass-beads. The top line indicates the theoretical response for the analytes expected if they had been quantitatively converted to nitric oxide.

practical carbon monoxide detection limit is actually poorer than at a lower catalyst temperature (*e.g.*, 350°C), at which the yield of nitric oxide is not nearly as great. This is illustrated in Fig. 4 by a plot of the signal-to-noise ratio (S/N) as a function of palladium catalyst temperature for a 10 ppmv carbon monoxide sample. Low ppmv levels of carbon monoxide were difficult to detect at catalyst temperatures from 20 to 100°C, because the fraction of carbon monoxide undergoing reaction to generate nitric oxide at these temperatures is low. Accordingly, the compromise intermediate temperature range (300–400°C) appears most suitable for quantitation of low concentration levels of carbon monoxide. Another consideration in choosing the catalyst temperature is that carbon monoxide peaks exhibit less tailing and are more symmetrical at higher catalyst temperatures. Presumably, this is because carbon monoxide is more readily adsorbed on these surfaces at lower temperatures.

Gold and palladium catalysts exhibit similar response characteristics for carbon monoxide and ethylene, although the response produced with the palladium catalyst is approximately 50% higher than for the same volume, weight, and temperature of a gold catalyst. Gold catalysts are superior to palladium catalysts in some other circumstances. Alkanes do not give a redox chemiluminescence response when a catalyst consisting of gold on soda-lime glass is used at temperatures below 400°C; thus a gold catalyst offers some selectivity that a palladium catalyst does not. Furthermore, occasional poisoning of palladium catalysts from repeated injections of some sulfur compounds has been observed. Gold catalysts do not appear to be as susceptible to poisoning by these sulfur compounds. Other metals (Ni, Rh, Pt, Cu, and Ag) have been investigated as redox catalysts in this system. Palladium and gold are superior in most cases because of higher sensitivities and lower backgrounds, although these other metals have shown different selectivities that might be useful in other applications.

The redox chemiluminescence response for carbon monoxide from 1 to 100 ppmv in ethylene is shown in Fig. 5. The figure was produced by plotting peak areas from 1-cm³ sample injections of different concentrations of carbon monoxide in ethylene. A gas-tight syringe was used to make these sample injections. Good linearity
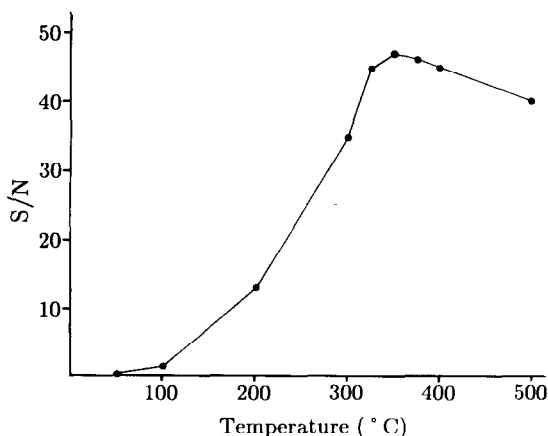

Fig. 4. Plot of the signal-to-noise ratio (S/N) for 1-cm³ sample injections of 10 ppmv carbon monoxide in helium as a function of palladium catalyst temperature (same catalyst as in Fig. 3).
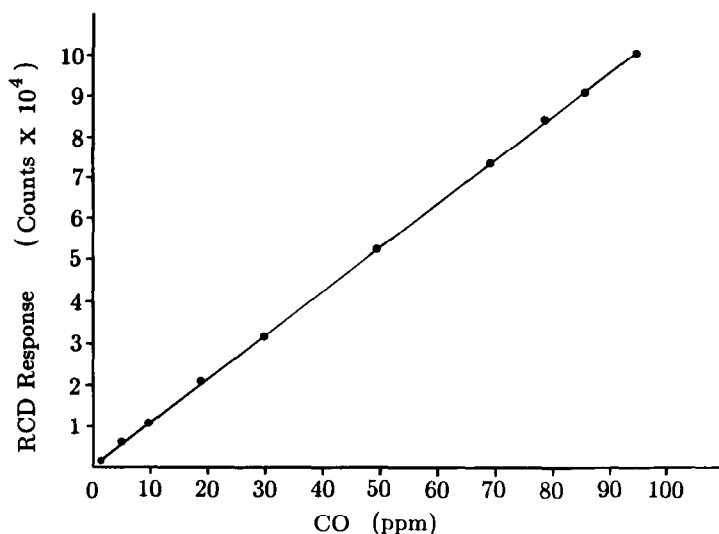
Fig. 5. Linearity of redox chemiluminescence response *vs.* concentration of carbon monoxide in ethylene with palladium catalyst (same as in Fig. 3) at 350°C.

from 0.96 to 96 ppmv is shown in Fig. 5 and has been observed over another decade. The correlation coefficient of the least squares linear fit of the data points was 0.9991. Relative standard deviations of peak areas from five repetitive injections (using an injection valve with a sample loop) of samples containing 10 and 475 ppmv were 6 and 1%, respectively. Over a period of one week, the relative standard deviations of absolute response were less than 25%. Signal (peak height) to noise ratios at 0.18 ppmv carbon monoxide concentration were between three and four times the peak-to-peak baseline noise. A useful working range for carbon monoxide concentrations from less than 1 ppmv up to 1000 ppmv was observed. At higher carbon monoxide concentrations, the carbon monoxide response was less than expected because of rate limitations resulting perhaps from too little nitrogen dioxide available for reaction or possibly stemming from photomultiplier tube saturation.

A discernible peak, but less than $S/N = 3$, arising from impurity carbon monoxide was observed from a 1-cm^3 sample injection of the ethylene that was used for preparation of the samples of carbon monoxide in ethylene. This trace impurity of carbon monoxide in the diluent ethylene probably contributed to the higher than expected signal-to-sample size ratios observed at concentrations of carbon monoxide below 1 ppmv. Offsetting this, but contributing to potential errors in the actual concentration of carbon monoxide in the standards, is possible adsorption of carbon monoxide on surfaces. To minimize absorption losses, especially for carbon monoxide at low concentrations, it is important to make measurements immediately after preparation of standards or collection of samples.

Sample injections were made every 10 min, demonstrating that this technique for the trace analysis of carbon monoxide in ethylene can be performed repetitively and possibly automated. The injection frequency could be increased by developing a method that perturbs the flow over the catalyst to a lesser extent during the catalyst bypass process. A column backflushing method could be used to shorten analysis

times to only twice the time it takes for carbon monoxide to be eluted. This method should also reduce the change of long term catalyst poisoning if the sample contained late-eluting sulfur compounds, such as mercaptans or sulfides. With the apparatus used, it is possible to simultaneously record chromatograms using redox chemiluminescence detection and TCD, since the redox chemiluminescence detector is serially coupled to the thermal conductivity detector of the gas chromatograph. In this manner, the redox chemiluminescence detector can be used to measure certain trace components, while the thermal conductivity detector would be used as a nearly universal detector to measure the major constituents. Also of note is that this serial detector configuration did not lead to appreciable peak broadening in the two resulting chromatograms.

ACKNOWLEDGEMENTS

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