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DETECTION OF CARBON MONOXIDE AT AMBIENT LEVELS WITH AN N₂O-SENSITIZED ELECTRON-CAPTURE DETECTOR

PAUL D. GOLDAN* and FRED C. FEHSENFELD*

Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303 (U.S.A.)

and

MICHAEL P. PHILLIPS**

Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303, and Department of Chemistry, University of Colorado and Cooperative Institute for Research in the Environmental Sciences, University of Colorado/NOAA, Boulder, CO 80309 (U.S.A.)

SUMMARY

It is observed that the response of the electron-capture detector (ECD) for carbon monoxide can be dramatically increased by the addition of N_2O to the nitrogen carrier gas. In this way a detection limit for carbon monoxide in air of $3.4 \cdot 10^{11}$ molecules (16 pg) has been achieved. This detection limit compares favorably with that obtained using other state-of-the-art CO detectors. A mechanism to explain the observed enhancement of the N_2O-doped ECD is proposed. The implication of the present results for the N_2O-doping technique and the application of this method to detection of CO in the atmosphere are discussed.

INTRODUCTION

Carbon monoxide is produced in the earth's atmosphere as a byproduct of the oxidation of hydrocarbons from both natural and anthropogenic sources. In turn, CO is an active participant in the chemistry of atmospheric minor constituents. The oxidation of CO by OH is an important reaction in the atmospheric odd-hydrogen chemistry[1] and initiates a sequence of reactions, which in the presence of NO provides a mechanism for ozone production in "clean" air[2]. Since the concentration of carbon monoxide in the atmosphere reflects the reaction sequences which produce and destroy it, considerable effort has been expended to measure CO as a function of time, latitude and altitude[3–6].

The instruments developed for measurement of CO in air may be generally classified as colorimetric, mass spectrometric (MS), infrared (IR) absorption and gas chromatographic (GC) techniques. The colorimetric techniques which have been described[7,8] are suitable only for CO mole fractions of several ppm or greater and are thus inapplicable to background atmospheric sampling without sample enrichment. The use of MS for the detection of CO in whole air samples is severely hampered by

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* Fellow of the Cooperative Institute for Research in the Environmental Sciences (CIRES), University of Colorado/NOAA, Boulder, CO 80309, U.S.A.

** Present address: Rocky Mountain Analytical Laboratory, Arvada, CO, U.S.A.

the extremely small mass difference between CO and N_2 (0.01123 a.m.u.). Ions of these two species can be distinguished only by high-resolution MS.

Because of these difficulties, most of the measurements to date have been made using optical absorption and GC techniques. Typical commercially available instruments for the measurement of CO in air, relying on either dispersive IR absorption or non-dispersive IR photometry, have sensitivities yielding detection limits of approximately 10 ppm (v/v) and 0.5 ppm (v/v), respectively. Both of these methods suffer from interference from H_2O and CO_2. Long path IR absorption spectrometry using laser sources and an absorption path length of some 25 m has significantly lowered these detection limits and demonstrated a capability of measuring CO at ambient background concentrations (0.05–0.5 ppm, v/v) under favorable conditions[9]. This method still suffers from interference from H_2O, CO_2 and O_3 limiting its usefulness. Efforts to reduce the effects of such interferences have led to the development of a non-dispersive IR gas filter correlation instrument[10]. The noise equivalent CO mixing ratio for this instrument is approximately 20 ppb (v/v)*. This reasonably low detection limit, wide dynamic range (up to 100 ppm, v/v) and rapid response make it suitable for microscale studies where rapid variations are important, but its relative complexity makes it unattractive as a general monitoring instrument.

A completely different spectroscopic technique for the measurement of CO takes advantage of the chemical reaction between CO and HgO to produce CO_2 and Hg in the gas phase. The resulting mercury vapor is measured by absorption of resonance radiation at 2537 Å provided by a mercury lamp[11–13]. Although providing very low detection limits for CO (some 2–3 ppb, v/v), this technique is also sensitive to other reducing gases such as H_2, SO_2 and olefins and aldehydes that also reduce hot HgO and can cause erroneously high CO readings if not removed prior to analysis.

Since GC columns are readily available which separate CO from other potentially interfering species in atmospheric samples, attention has been drawn to the development of sensitive detectors to be used in conjunction with these columns. Currently the most widely used gas chromatographic CO detector is the flame ionization detector (FID), which measures the CH_4 produced by the catalytic conversion of CO[14–18]. Using a molecular sieve column to separate the CO in an air sample and under ideal laboratory conditions, the amount of CO required to produce a signal-to-noise ratio of 2 in the FID is some $4 \cdot 10^{11}$ molecules (18 pg), corresponding to a mole fraction of 15 ppb for a 1 standard cm^3 air sample. Helium ionization detectors that utilize the energetic, long-lived excited states of atomic and molecular helium to produce detectable secondary ionization in analyte gases of lower ionization potential[19] have been successfully used for the detection of atmospheric CO (ref. 3). Unfortunately this detector is also sensitive to N_2, and the CO appears as a small shoulder on a large tailing N_2 peak, making quantitation difficult at ambient CO levels in air[20].

We previously reported that the sensitivity of an electron–capture detector (ECD) to non-electron attaching compounds and to compounds, such as vinyl chloride, that attach electrons only weakly can be enhanced by the addition of N_2O to the carrier gas stream of a gas chromatograph[21–23]. In the present study we find that the detection limit for carbon monoxide in air is $3.4 \cdot 10^{11}$ molecules (16 pg) using this

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* Throughout this article, the American billion (10^9) is meant.

enhancement technique. This detection limit corresponds to a CO mole fraction of 13 ppb for a 1 standard cm^3 air sample and is achieved with no sample enrichment. This detection limit is comparable to, or better than, that achieved under optimal conditions using the detection methods mentioned above. The combination of sensitivity, simplicity and freedom from interfering species using the GC technique makes it an attractive option for the measurement of carbon monoxide in clean air.

EXPERIMENTAL

The gas chromatograph used in this study was designed and built in collaboration with Valco Instruments (Houston, TX, U.S.A.). Entirely contained in a 60 × 40 × 20 cm aluminum "suitcase", it is equipped with a cylindrical ECD with a 10-mCi ^{63}Ni foil lining the 0.63-cm^3 detector volume. Sample inlet and current collector are axially symmetric within the detector, which is operated at 350°C in a fixed frequency variable current mode. The entire system plumbing: multiport gas injection valve, columns, oven and detector, are housed in a sealed chamber which is flushed with the nitrogen carrier gas so that gas composition, temperature and pressure surrounding these elements can be controlled[24].

Two columns, both packed in 1/8-in. stainless-steel tubing, are used with a nitrogen carrier flow of approximately 40 cm^3/min. The first, a precut column, is 2.4 m long, packed with Porapak Q (100–120 mesh), and operated at the ambient box temperature of approximately 55°C. The second, analytical, column is 2.8 m long, packed with molecular sieve 5A (100–120 mesh), and operated at 80°C. A schematic diagram of the plumbing arrangement is shown in Fig. 1. When the valve is in the load position, sample is introduced into the sample loop by a flush and fill technique. When the valve is rotated to the inject position, as shown in Fig. 1, the sample passes first through the Porapak Q column where relatively heavy chlorinated species to which the ECD is extremely sensitive such as CF_2Cl_2, $CFCl_3$, C_2HCl_3 and CCl_4 are retarded while the H_2, O_2, CH_4 and CO contained in the sample pass quickly into the molecular sieve column. As soon as these latter species have passed into the molecular sieve column (approximately 2 min after injection), the valve is returned to the sample
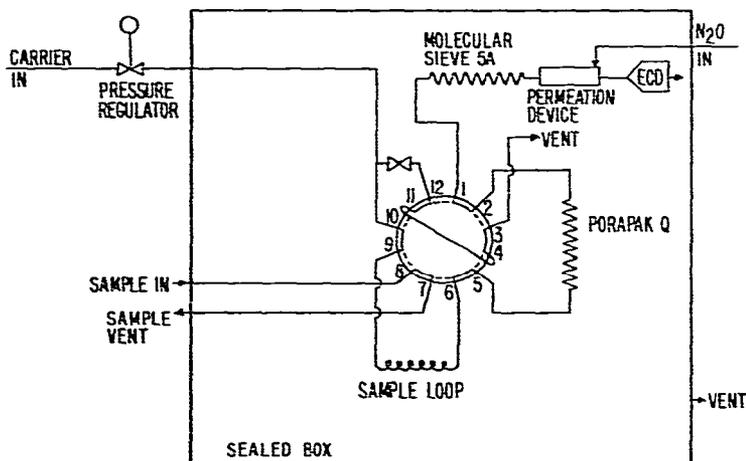
Fig. 1. Schematic diagram of gas chromatograph gas handling system.

load position allowing the H_2, O_2, CH_4 and CO to be separated on the analytical column while the remaining air sample components are dumped from the precut column. A restrictor supplants the precut column when the valve is in the load position so that the carrier gas flow through the detector is independent of the valve position, thus avoiding switching transients. Dumping the unwanted species from the precut column allows repetitive sampling on a 15-min basis.

Nitrous oxide at a mole fraction of approximately 30 ppm (v/v) is introduced into the carrier gas stream between the analytical column and detector by means of a permeation device which has been previously described[23]. The N_2O source used is a 250-cm^3 stainless-steel cannister which was evacuated and filled with "electronic grade" N_2O to a pressure of approximately 400 kPa. The N_2O consumption is quite small, being typically 300 standard cm^3 per year for continuous operation.

In order to remove CO and other impurities from the commercial grade N_2 used as carrier gas before it enters the chromatograph, it is passed through a Hopcalite (Mine Safety Appliances Company, Pittsburgh, PA, U.S.A.) trap followed by a molecular sieve 13X trap, both of which are used at room temperature. The Hopcalite serves to oxidize CO to CO_2 which is subsequently removed along with H_2O, hydrocarbons and other impurities by the molecular sieve. Both traps are activated by heating for 10–12 h; the Hopcalite to 150–200°C and the molecular sieve to 300–350°C, with a nitrogen flow of 40–60 standard cm^3/min.

Carbon monoxide standards were prepared by static dilution with "zero air"* of a previously calibrated mixture containing a CO mole fraction of 1.6 ppm (v/v) in "zero air". The diluted standards at a CO mole fraction of approximately 270 ppb (v/v) were then checked against the 1.6 ppm (v/v) standard using the flame ionization technique described earlier. All sensitivities and detection limits quoted are with respect to these diluted secondary standards.

RESULTS

A chromatogram of a whole air sample obtained using the sealed chromatograph with N_2O doping in the carrier gas is shown in Fig. 2. Because of the precut column configuration described in the Experimental section, the chromatogram consists of only four peaks, *i.e.*, those due to H_2, O_2, CH_4 and CO. The sample size is 2.2 standard cm^3 and the concentration of the components are 20% (v/v) O_2, 0.6 ppm (v/v) H_2, 1.67 ppm (v/v) CH_4 and 390 ppb (v/v) CO. All of these compounds are easily detected at these levels using this technique. However, with no N_2O in the carrier gas, only the O_2 is detectable in this system and the CO detection limit increases to greater than 10^2 μg per sample.

The signal-to-noise ratio of the N_2O doped ECD for CO is essentially independent of the N_2O mole fraction between the doping levels of 16 and 70 ppm (v/v), so that the N_2O concentration need only be set at some convenient level in this range. Slow reduction of the N_2O level due to decreasing pressure in the N_2O cannister at a rate of approximately 3 kPa per month has little effect upon the system performance. The detector response to CO as a function of detector temperature is similar to that

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* "Zero air" refers to a synthetic mixture of 80% N_2, 20% O_2 and no detectable levels of any other gas of consequence in the present study.
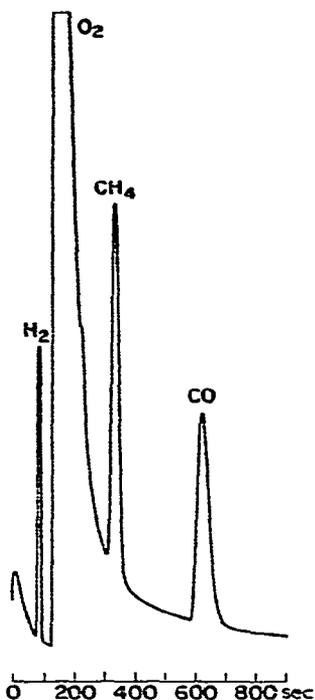
Fig. 2. Chromatogram of a 2.2 standard cm^3 air sample with pre-cut obtained with the N$_2$O-sensitized ECD.

reported for several other gases[21-23]. That is, the response is greatest at the maximum operating temperature of the detector, 350°C, and decreases by approximately a factor of 10 as the detector temperature is lowered to 200°C.

The response of the N$_2$O-doped ECD to CO has been found to be linear within the 2% precision of the measurement from the CO detection limit of $3.4 \cdot 10^{11}$ molecules (16 pg) per sample up to $1.7 \cdot 10^{13}$ molecules (790 pg) per sample. Departures from linearity do not exceed 10% up to $5.3 \cdot 10^{13}$ molecules per sample, corresponding to a mole fraction of 2 ppm for a 1 standard cm^3 sample. Quantitation outside this range can be accomplished by the use of appropriate calibration data.

DISCUSSION

The sensitivity of the N$_2$O-enhanced ECD to CO can be explained in the following way. In the ECD, free electrons are in an N$_2$O-induced reactive steady state with O$^-$ through the reactions

$$e + N_2O \xrightarrow{k_1} O^- + N_2 \tag{1}$$

$$O^- + N_2O \xrightarrow{k_2} NO^- + NO \tag{2}$$

$$NO^- + M \xrightarrow{k_3} NO + M + e \tag{3}$$

where M is any collision partner and k_1, k_2 and k_3 are the reaction rate constants for the corresponding reactions. This mechanism is discussed in detail in our previous publications[21-23]. Any compound that reacts with O^- to form a stable negative ion will interrupt this reaction cycle causing a reduction in the electron density and thus a detector response.

According to this scheme, however, the N_2O-sensitized ECD should have no intrinsic sensitivity to CO since CO does not directly react with O^- to form a stable negative ion. Rather, it seems that the observed response results from the oxidation of CO to CO_2 within the ECD with subsequent reaction of CO_2 with $O^{-\,21}$. Although there are several possible mechanisms for the oxidation of CO to CO_2 in or near the ECD, it seems most likely that this oxidation takes place on the hot detector walls. Strong support for this speculation is provided by recent findings that an N_2O-oxidized polycrystalline platinum surface at about 350°C rapidly converts CO to CO_2.[25] It seems most likely that the gold, nickel and stainless steel surfaces within the ECD at 350°C in the presence of N_2O will effectively oxidize CO, *i.e.*

$$CO + N_2O/_{wall} \xrightarrow{\tau_w} CO_2 + N_2/_{wall} \tag{4}$$

with τ_w being the associated time constant. Further support for this contention is gained from the observations that although the CO sensitivity of an N_2O-doped ECD may decrease after long use or after injection of "dirty" samples, it can be restored by passing H_2 for several hours through the detector while it is kept at 350°C. Presumably the hydrogen strips impurities which inhibit reaction 4 from the internal surfaces of the detector. Following reaction 4, the CO_2 reacts with O^- causing the ECD response:

$$O^- + CO_2 + M \xrightarrow{k_5} CO_3^- + M \tag{5}$$
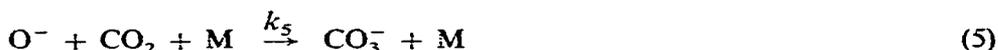
The rate equations which describe eqns. 1–5 are

$$\partial[e]/\partial t = S - k_1 [e] [N_2O] + k_3 [NO^-] [N_2] - L [e] \tag{6}$$

$$\partial[O^-]/\partial t = k_1 [e] [N_2O] - k_2 [O^-] [N_2O] - k_5 [O^-] [CO_2] [N_2] \tag{7}$$

$$\partial[NO^-]/\partial t = k_2 [O^-] [N_2O] - k_3 [NO^-] [N_2] \tag{8}$$

$$\partial[CO_2]/\partial t = [CO]/\tau_w - (k_5 [O^-] [N_2] + 1/\tau_R) [CO_2] \tag{9}$$

$$\partial[CO]/\partial t = Q_{CO} (t)/V_D - (\tau_R^{-1} + \tau_w^{-1}) [CO] \tag{10}$$

where S is the ionization source rate associated with the radioactive source lining the detector walls (electron–ion pairs per $cm^3 \cdot sec$), L is the net electron loss due to diffusion, recombination with positive ions, attachment to impurities in the carrier gas, ventilation, etc. which are not explicitly stated in eqn. 6, and $[N_2]$ as the most likely collision partner has been substituted for $[M]$. $Q_{CO}(t)$ is the time dependent

influx rate of CO molecules (molecules per sec), V_D is the detector volume, τ_R is the mean residence time of the sample within the detector and τ_w has been defined in eqn. 4.

For the column and operating conditions specified in the Experimental section, and listed for convenience in Table I, the CO peak is roughly Gaussian in shape with a width at half maximum of approximately 30 sec, a time long compared to $\tau_R \approx 0.7$ sec. Thus, during the passage of the CO peak through the detector, the chemistry approaches a steady state and the remainder of the discussion deals with the steady state solutions to eqns. 6–10 with the pertinent reaction rate constants listed in Table II.

TABLE I

ELECTRON-CAPTURE DETECTOR PARAMETERS AND SYMBOLS USED IN THE TEXT

Detector internal volume, V_D	0.65 cm^3
Carrier gas flow, Q_{N_2}	≈ 40 standard cm^3/min
Pressure in the detector (ambient pressure at 1600 m), P	≈ 0.8 atm
Gas residence time in the detector, $\tau_R = V_D P/Q_{N_2}$	≈ 0.7 sec
^{63}Ni foil activity (67 keV β-rays), R	10 mCi $= 3.7 \cdot 10^8$ sec^{-1}
Foil area, A_f	2.55 cm^2
Ionizing flux from foil, $j = R/4\pi A_f$	$1.2 \cdot 10^7$ cm^{-2} sec^{-1} steradian^{-1}
Effective ionizing flux density, $J = 3\pi j^*$	$1 \cdot 10^8$ cm^{-2} sec^{-1}
Ionization rate per unit path length (67 keV β-rays in 625 Torr N$_2$), γ_β	$5 \cdot 10^2$ electron–ion pairs per cm^{26}
Volume ionization rate, $S = J r_\beta$	$5 \cdot 10^{10}$ electron–ion pairs per cm$^3 \cdot$ sec
Detector temperature, T_D	350°C
Detector pulse repetition rate, f	10^3 Hz
In the absence of analyte in the detector (see text)	
Detector current, I_0	$1 \cdot 10^{-9}$ A
Electron density, $[e]_0 = I_0 (q f V_D)^{-1}$	$\approx 10^7$ cm^{-3}
Electron loss rate, $L = S([e]_0)^{-1}$	$\approx 5 \cdot 10^3$ sec^{-1}
Atomic oxygen negative ion density, $[O^-]_0$	$\approx 1.5 \cdot 10^6$ cm^{-3}

* Because of the short cylinder geometry, a typical point inside the detector is exposed to the ionizing radiation over only 3π steradians.

TABLE II

REACTION RATE CONSTANTS AT 350°C

Reaction	Rate constant	Ref.
1	$k_1 = 3.3 \cdot 10^{-11}$ cm^3/sec	27, 28
2	$k_2 = 2.2 \cdot 10^{-10}$ cm^3/sec	29, 30
3	$k_3 \approx 10^{-11}$ cm^3/sec*	
5	$k_5 = 3 \cdot 10^{-28}$ cm^6/sec	32

* Estimated from results in ref. 31.

In the absence of CO,

$$[e] = [e]_0 = S/L \tag{11}$$

and

$$[O^-]_0 = k_1 [e]_0 / k_2 \tag{12}$$

At 350°C $k_1/k_2 \approx 0.15^{21}$. For the pulsed ECD, assuming all the electrons within the detector are collected during each pulse, the detector standing current is

$$I_0 = qf \int [e]_0 dV \approx qf [e]_0 V_D \tag{13}$$

where q is the charge on the electron and f is the pulse frequency of the detector. The approximate values calculated for $[e]_0$, $[O^-]_0$, S and L in the absence of CO for typical operating conditions are listed in Table I.

In the N_2O-enhanced ECD, we observe a sensitivity for CO approximately equal to that observed for CO_2. To be consistent with our understanding of the enhancement process this implies that a majority of the CO is converted to CO_2 in or before the CO reaches the detector. Undoubtedly this conversion proceeds most rapidly at the highest temperatures[25] which in the present system is in the electron capture detector. The efficiency required for this conversion process is limited by the residence time $\tau_R \approx 0.7$ sec. This time must suffice for most of the CO to contact the hot walls and for the chemical conversion to be accomplished.

Transport of CO to the detector walls does not represent a limitation as this will occur in a time short compared to τ_R. In cylindrical geometry, the diffusion time constant, τ_D, in the fundamental mode is

$$\tau_D \approx R^2/D_{CO} (2.4)^2 \approx 0.036 \text{ sec} \tag{14}$$

where D_{CO} is the diffusion constant for CO in N_2 at atmospheric pressure, R is the cylinder radius and 2.4 is the first zero of $J_0(x)$, the zeroth order Bessel function of the first kind. This represents an upper limit to the actual diffusion time constant since end effects, diffusion to the central electron collector electrode and turbulent mixing in the detector will all contribute to reducing τ_D.

The remaining uncertainty involves the efficiency with which CO is converted to CO_2 on the detector walls. If diffusional transport to the walls is much more rapid than the wall oxidation process, then the CO density will be approximately uniform inside the detector and, according to simple kinetic theory, the loss rate of CO will be given by

$$\frac{\partial [CO]}{\partial t} = \frac{1}{4} \bar{v} [CO] \gamma A_D/V_D = [CO]/\tau_w^* \tag{15}$$

where $\bar{v}$ is the mean thermal speed of CO, A_D is the surface area involved and γ is the fraction of wall collisions leading to CO oxidation. The time constant, τ_w^*, for the present detector geometry and temperature is:

$$\tau_w^* \approx 10^{-5}/\gamma \tag{16}$$

If $\gamma > 2 \times 10^{-5}$, $\tau_R > \tau_w^* \gg \tau_D$, diffusion is not a significant limitation as stated above and a sizable fraction of the CO introduced into the detector will be converted to CO_2. For comparison, Adlhoch *et al.*[25] found that for a polycrystalline platinum surface at about 350°C, $\gamma \approx 4 \times 10^{-3}$. It is certainly possible that clean metal surfaces within the detector will have oxidation efficiencies at least 1% of that ob-

served for platinum. It should be noted that as γ increases the rate of oxidation at the wall is finally limited by the rate of transport, τ_D, so that the actual wall oxidation time constant τ_w is always greater than or equal to τ_D.

The steady state solution to eqns. 6–10, neglecting τ_w/τ_R and $\tau_R k_5 [O^-][N_2] \leqslant 0.004$ with respect to 1, and with CO present yield:

$$[CO] = Q_{CO}(t) \tau_w/V_D \tag{17}$$

$$[CO_2] = \tau_R [CO]/\tau_w \tag{18}$$

$$[e] = [e]_0 \left\{ 1 + \frac{k_1 k_5 [N_2] Q_{CO}(t)\tau_R}{V_D k_2 L \left(1 + \dfrac{k_5 [N_2] Q_{CO}(t)\tau_R}{V_D k_2 [N_2O]} \right)} \right\}^{-1} \tag{19}$$

In the limit as $Q_{CO}(t) \to 0$

$$[e] = [e]_0 \left\{ 1 - \frac{k_1 k_5 [N_2] Q_{CO}(t)\tau_R}{V_D k_2 L} \right\} \tag{20}$$

and the electron density and therefore the detector current become linearly dependent on $Q_{CO}(t)$, the CO influx rate.

Furthermore, from eqn. 19 and 20 we may calculate the fractional change in current expected from the injection, into the gas chromatograph, of a sample containing a given number of CO molecules. For a Gaussian peak with width parameter σ, the total number of CO molecules passing through the detector is

$$N_{CO} = Q_{CO}(t_0) \int_{-\infty}^{\infty} \exp - [(t - t_0)^2/\sigma^2] \, dt = \sqrt{\pi} \, \sigma \, Q_{CO}(t_0) \tag{21}$$

where t_0 is the arrival time of the peak maximum. Substituting this result in eqn. 20 yields at peak maximum:

$$1 - \frac{[e]}{[e]_0} = \frac{k_1 k_5 [N_2] \tau_R N_{CO}}{V_D k_2 L \sqrt{\pi} \, \sigma} \tag{22}$$

Numerical values from Table I substituted into eqn. 22 predict that the peak fractional change in electron density, and therefore the fractional change in detector current, should be approximately $3 \times 10^{-15} N_{CO}$ for values of N_{CO} sufficiently small so that eqn. 20 is valid. For $N_{CO} = 1.45 \cdot 10^{13}$ molecules (2 standard cm^3 sample with a CO mole fraction of 270 ppb), eqn. 22 predicts a fractional change in current of 4 %. This is to be compared with the experimentally observed value of 4.0 %. Although the agreement is obviously fortuitous considering the uncertainties in the ECD parameters, the gas phase reaction rate constants and the approximations used to formulate and solve eqns. 6–10, this agreement supports the correctness of the arguments presented above.

Application and comparison

As may be seen from the chromatogram of the whole air sample shown in Fig. 2, H_2, CH_4 and CO are readily quantitated at clean air levels. It should be mentioned that the simultaneous measurement of atmospheric concentrations of CO, CH_4 and H_2 cannot be achieved with the other detectors currently used for *in situ* atmospheric CO measurement.

Atmospheric mixing ratios of CO are currently being monitored at an atmospheric sampling site west of Boulder that is jointly maintained by the National Oceanic and Atmospheric Administration and the University of Colorado. Located on Niwot Ridge at an altitude of 3050 m (longitude 105° 32′, latitude 40° 30′), the site is usually swept by the prevailing winds which blow from west to east. Under these conditions the concentrations of minor atmospheric constituents represent clean, continental, rural air. Occasionally, "upslope" conditions exist during which winds from the east transport pollution from the Denver metropolitan area to the Niwot Ridge site.

Carbon monoxide mixing ratios found during the onset of such an episode on September 22, 1980 are shown in Fig. 3. The morning was overcast, foggy and calm. At about 1:00 p.m. MST the cloud cover broke and a slight breeze from the southeast developed. By 2:00 p.m. the wind was from the east at 5–10 mph and a strong "upslope" easterly wind condition existed. Fig. 3 clearly shows the increase in CO mole fraction from about 250 ppb (v/v) to more than 400 ppb (v/v) during this period. Concurrent measurements showed that the ozone concentration doubled, increasing from 31 ppb (v/v) to 59 ppb (v/v), during the same period.

Carbon monoxide mixing ratios have been monitored intermittently at this site with the N_2O-sensitized ECD technique since August 2, 1980. From August 2 to September 22 the concentration ranged from 160 to 473 ppb (v/v), with mixing ratios in excess of 300 ppb (v/v) being observed only during the strong "upslope" on September 22. Analysis of these data showed a CH_4 mole fraction of 1.7 ppm (v/v) and an average H_2 mole fraction of 0.6 ppm (v/v).
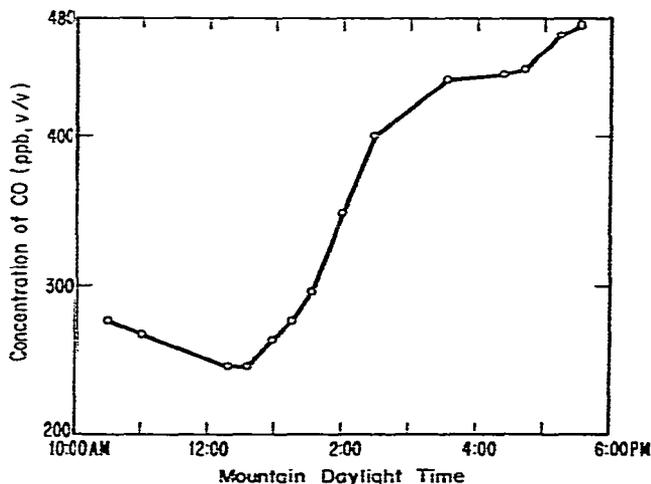
Fig. 3. CO mixing ratio over a 7-h period at Niwot Ridge, Colorado.

During this period the results obtained with the N_2O-sensitized ECD technique were compared with similar measurements made using an FID with catalytic conversion of CO to CH_4 (Baseline Industries, Model 1030A) and an HgO-reduction, resonance-absorption instrument (Trace Analytical Company, Model RDG-1). The N_2O-sensitized ECD achieved approximately equal sensitivity to the HgO-reduction technique and considerably better than the FID. In terms of quantifying atmospheric concentrations of CO (relatively high CO levels in a multicomponent gas mixture), the N_2O-sensitized ECD was as free of interferences, as dependable and somewhat more linear than the other instruments.

The detection limits for CO using FID with catalytic converter, HgO reduction, and helium ionization detection were reported[3] in connection with a measurement program intended to determine vertical profiles of CO, as well as several other trace gases, in the mid-latitude atmosphere. This intercomparison indicated detection limits for helium ionization detectors of 15 ppb (v/v), nickel catalysis-FID of 5 ppb (v/v) and HgO reduction detection of 1 ppb (v/v). Since the sample size used in these measurements was not specified, the quoted detection limits are somewhat nebulous. However, using a 20-cm³ sample at atmospheric pressure, the N_2O-sensitized ECD configured as it is in the present GC has a detection limit comparable to the HgO reduction detector quoted above.

CONCLUSIONS

The N_2O-sensitized ECD exhibits remarkable sensitivity for carbon monoxide. This sensitivity is explained by the catalytic conversion of CO to CO_2 in the presence of N_2O on the hot detector walls. The effect is stable and reproducible. Although the data reported here were obtained using a specially designed nitrogen purged instrument, comparable results have been obtained using a standard Perkin-Elmer instrument equipped with an ECD. Detectors which have been subjected to "dirty" samples, and occasionally new detectors which have been improperly cleaned, do not exhibit the reported sensitivity to CO, but these may be restored to adequate sensitivity by purging with H_2 at 350°C for several hours.

To our knowledge this is the first quantitative observation of catalytic gas conversion in these detectors, although such processes have often been suspected, and it is certainly the first use of such a process in a practical instrument. The N_2O-sensitized ECD coupled with a gas chromatograph is currently our method of choice for the *in situ* measurement of CO in the atmosphere. For such use, however, care must be taken to remove trace CO impurities contained in the carrier gas. This is of considerable consequence since CO is a very common impurity in gases pressurized in steel cylinders.

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