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THE DETERMINATION OF CARBON MONOXIDE IN AIR IN THE PARTS PER BILLION* RANGE BY MEANS OF A HELIUM DETECTOR

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SUMMARY

The separation and quantitation of traces of carbon monoxide from air have been performed using molecular sieve columns and helium ionization detectors. Calibration curves obtained by the exponential dilution method are linear down to about 50 parts per billion. A comparison of the curves obtained using helium or air as diluting gases is made.

INTRODUCTION

During the past few years, various instrumental methods have been developed for the analysis of carbon monoxide in air. Of these methods, the most widely used and commercially available are non-dispersive infrared analysis, infrared spectro-photometric analysis and gas chromatography.

Such methods are well established, and are reliable when analyses of urban atmospheres have to be carried out, and good, simple and reasonably priced instruments are available for this purpose. However, these instruments are unsatisfactory when the p.p.b. level of concentration has to be examined.

The first two methods have the disadvantage that water and carbon dioxide interfere, so that special techniques have to be used in order to eliminate these compounds from the air before it enters the cell. The minimum detectable amount of carbon monoxide has been estimated to be about 0.5 p.p.m.

The gas chromatographic method, which is based on the flame ionization detection of CO after its catalytic conversion into methane[1], has the advantage of a very low detection limit. More recently, a similar apparatus has been developed for the detection of both carbon monoxide and methane[2]. However, the need for a pre-column, backflushing and catalytic reactor are serious limitations both for semi-continuous operation and for the reliability of measurements at low concentrations.

On the other hand, since the background levels of CO in the atmosphere have been estimated to average between 0.01 and 0.2 p.p.m.[3], the measurement of this pollutant at the p.p.b. level is important and a simple, reliable and semi-continu-

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

ously working apparatus is desirable. This paper reports the first results obtained in this direction.

The helium ionization detector, first described by HARTMAN AND DIMICK[4], has a detection limit in the low p.p.b. range for CO, and provided that the correct experimental conditions are used, it appears to be a suitable tool for the aim of the present work.

EXPERIMENTAL

Gas chromatograph

A Carlo Erba Model GH gas chromatograph was used. This chromatograph, which is equipped with a helium flame ionization detector, is made for this particular application. The gas lines were arranged so as to avoid every possible contamination by the atmosphere, so that the detector could be operated under the optimum conditions. Details of the apparatus have been described elsewhere[5]. The gas chromatograph was modified so as to permit syringe injection with a double-membrane, gas-purged device, similar to that described by DODD[6]. The syringe injection device was inserted in the sampling loop line of the chromatograph and no significant increase in the background or decrease in the sensitivity was observed.

The syringe sampling system permits the analysis of small amounts of sample, which is impossible by using the standard system that requires the sample to flow continuously into the loop for at least 15 sec so as to ensure that the injections are reliable.

With this device, we were able to determine 4 p.p.m. of CO contained in a sample the total amount of which was 1.5 ml (S.T.P.) of gas. Such an analysis would never be possible without the syringe inlet system.

Column

A 2-m stainless-steel column (5 mm I.D., 6 mm O.D.) filled with 40–80 mesh molecular sieve 13X was used. The length of this column, which is excessive for ordinary analyses, is necessary when very small amounts of CO have to be detected in air.

The column was activated in the gas chromatograph at 270° for 24 h under a stream of highly pure hydrogen. The oven was then cooled to 80° under a stream of highly pure helium and the detector was connected. The background decreased slowly and after 1 day the apparatus was ready for use. The best signal to noise ratio was observed when the excitation potential was maintained at 500 V.

The gas chromatograph can be operated for 10 days before the column requires re-activating. The column temperature during the analysis of CO was maintained at 80°, which gave the best compromise between a reasonable retention time and the need to separate a large amount of nitrogen from CO.

Calibration

The exponential dilution method described by LOVELOCK[7] was used for calibration. A glass exponential dilution flask (E.D.F.) manufactured by Carlo Erba, with a total volume of 235 ml, was inserted in the gas line before the sampling loop. The E.D.F. was fed with helium of the same purity as that used as carrier gas (highly

pure helium N56 from SIO, Milan) in order to obtain the calibration curve in the absence of air.

When the calibration curve to be used in the monitoring of CO in air was to be obtained, the E.D.F. was fed with synthetic air (an 80:20 mixture of highly pure nitrogen and oxygen). The synthetic air was first tested to check for the absence of carbon monoxide. When this gas was injected into the column, no CO peak was observed on the tail of the nitrogen peak, even at the maximum possible sensitivity, so that the concentration of this compound, if present, was below the detection limit.

The operating conditions of the helium detector are strongly affected by the impurities of the gas stream that flows into it. The reason for using air as the diluent gas during the calibration is to carry out the calibration and measurements under the same conditions, because carbon monoxide appears in the tail of the nitrogen peak.

The calibration curve was obtained by injecting 0.5 ml of CO into the E.D.F. at a flow-rate of the diluting gas of 28 ml/min. An automatic injection device was used. Injections were made every 12 min and the injection time was checked with a chronometer so as to avoid possible errors in the injection mechanism.

RESULTS AND DISCUSSION

In Fig. 1, the calibration curves obtained when using helium or air as the diluting gas are shown; a noticeable discrepancy can be observed between the two curves. Although a suitable explanation of this discrepancy is not easy to find,
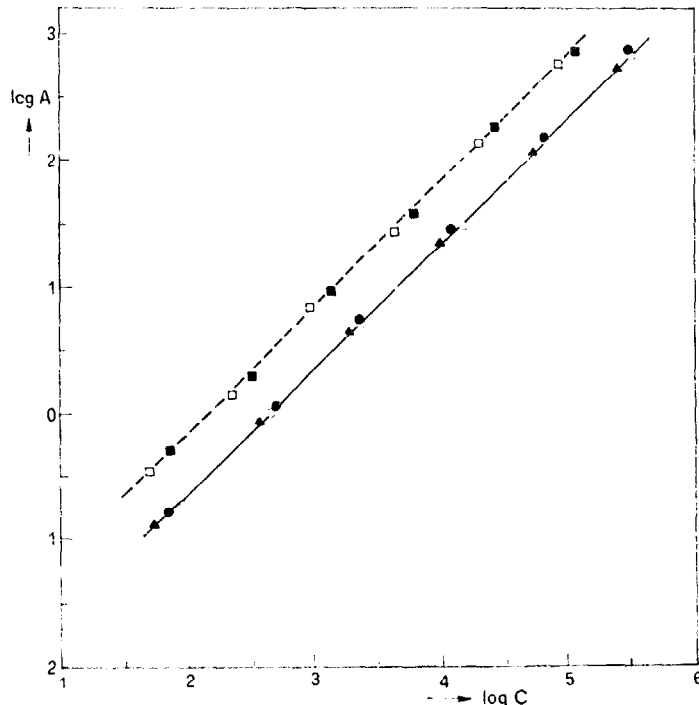

Fig. 1. Calibration curves for carbon monoxide. Diluting gases: air (dotted line), helium (full line). A = Arbitrary units for peak area; C = concentration (p.p.b.).

it can be tentatively postulated that the detector response to carbon monoxide is affected by the presence of trace amounts of nitrogen.

Peak areas were calculated by weighing the recorder chart. The lower limit of the area corresponding to the CO peak was determined by considering the area above the tail of the nitrogen peak, as shown by the dotted lines in Fig. 2. Fig. 2 shows the final part of the chromatogram yielding the calibration curve when using air as the diluting gas.
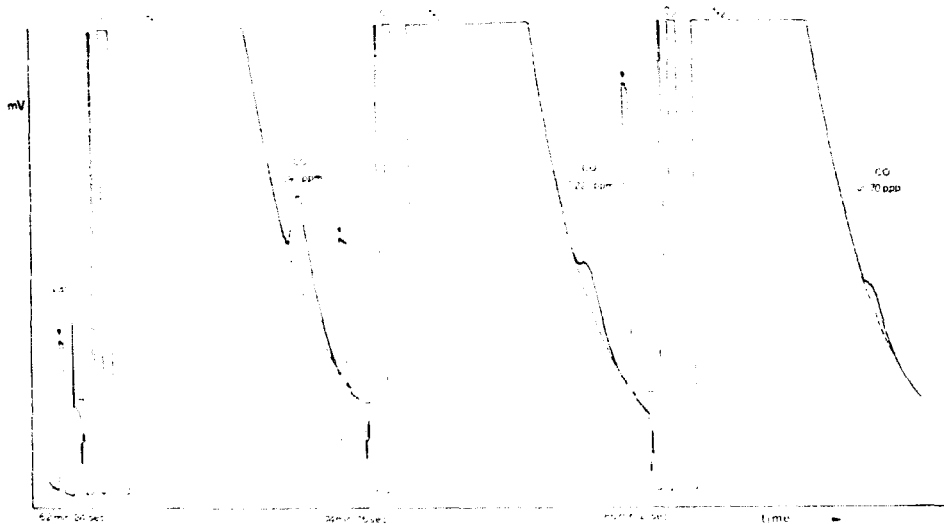

Fig. 2. Final part of the calibration chromatogram when using air as the diluting gas. Column: 2 m × 0.5 cm I.D., molecular sieve 13X. Temperature, 78°; inlet pressure, 0.8 kg/cm²; flow-rate, 50 ml/min; air flow-rate, 25 ml/min.

The reproducibility of the different calibration curves, shown by the different symbols in Fig. 1, is very good, all curves being coincident within experimental error. The linearity of the calibration graphs extends from the detection limit to more than 500 p.p.m.

These limits are about the same when either helium or air is used as the diluting gas, being about 70 p.p.b.

The chromatogram in Fig. 3 shows the analysis of a calibration mixture used for the infrared analyser with a controlled carbon monoxide content. The carbon monoxide content guaranteed by the manufacturer was 75 p.p.b. Our analysis gave a result of 70 p.p.b., which is in good agreement with the manufacturer's value.

These results show that the helium detector can be used for the detection of very small amounts of carbon monoxide. A previous paper reported a minimum amount detected of 0.2 p.p.m.[5], while 0.5 p.p.m. was the minimum amount of this gas detected in air[4], although the ultimate detection limit should be about 10 or 20 p.p.b. The chromatogram in Fig. 3 shows this possibility if nitrogen or other retained gases are not present in very large amounts.

Regarding the improvement of CO measurements in air, the main problem to be solved seems to be that of the column, which should be able to elute nitrogen

without tailing. Moisture and carbon dioxide should also be removed from the column if this has to be continuously operated for more than 3 days.
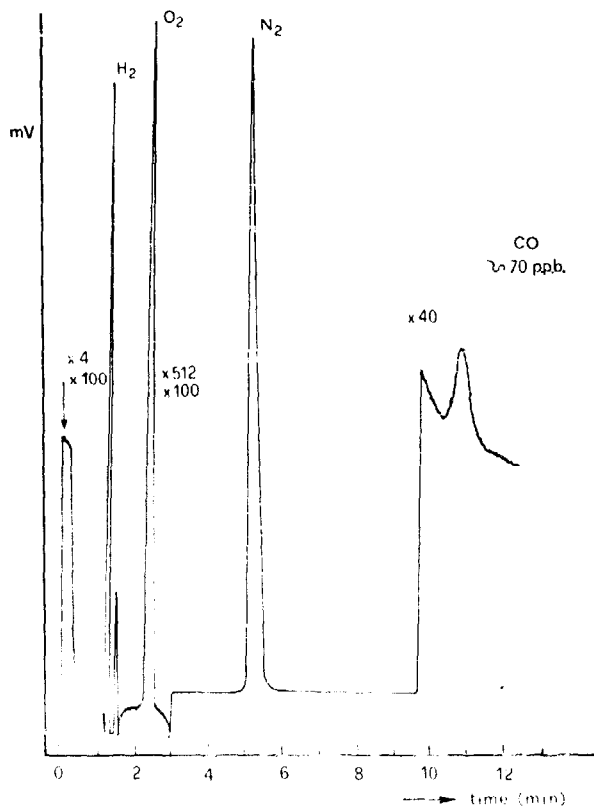

Fig. 3. Analysis of the CO content in a helium cylinder. Sampling loop: 3 ml. Other experimental conditions as in Fig. 2.

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