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DETERMINATION OF CARBON MONOXIDE CONCENTRATIONS IN AIR BY GAS CHROMATOGRAPHY USING AN ARGON IONIZATION DETECTOR

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SUMMARY

A simple gas chromatographic method using an argon detector and a simple enrichment technique permits the determination of carbon monoxide concentrations in air within the range 0.3–300 ppm. Results from measurements at a Leipzig street crossing over a period of about 28 h are given.

INTRODUCTION

Automobile exhaust gases are among the most important sources of atmospheric pollution in towns. Of the toxic compounds emitted by automobiles, carbon monoxide and hydrocarbons are particularly important owing to their high concentrations.

Whereas the gas chromatographic analysis of hydrocarbons in air is relatively simple because of the high sensitivity of the flame-ionization detector[1], the detection of inorganic gases, especially carbon monoxide, is more difficult. Although the helium detector is extremely sensitive to carbon monoxide[2], its application is limited because of its insufficient reliability.

This paper describes a simple gas chromatographic method using an argon detector and a simple enrichment technique for the determination of carbon monoxide concentrations in air.

EXPERIMENTAL

A Chromatron GCHF 18.3 gas chromatograph equipped with an argon detector, developed at the Central Institute for Isotope and Radiation Research, Leipzig[3], was used for the measurements.

The air samples were collected using glass sampling bulbs. Gas samples were injected with gas-tight syringes. The lower detection limit of the argon detector for carbon monoxide was 3 ppm when the size of the air sample was 25 ml.

In order to determine smaller carbon monoxide concentrations, the air samples from the glass bulbs were led into a pre-column by means of a stream of

neon, cooled at liquid nitrogen temperature and filled with molecular sieve 5A. The pre-column (stainless steel, 12 cm × 4 mm I.D.) was fixed on the gas sampling valve of the gas chromatograph instead of the sample loop.

At the desired time, the pre-column was heated and at the same time the sample was led into the carrier gas by means of the gas sampling valve. The neon flow-rate and the time, in which the neon streams through the column, were chosen so that the air was flushed out of the cooled loop, but the retention time of carbon monoxide was so long that at the time of the injection it had not reached the end of the pre-column. The chromatographic column consisted of a glass tubing (1 m × 3 mm I.D.) filled with molecular sieve 5A. With this procedure, it was possible to enrich carbon monoxide concentrations from air samples up to 250 ml.

RESULTS AND DISCUSSION

Air samples were collected at a Leipzig street crossing and carbon monoxide concentrations were determined in samples taken over a period of about 28 h. During the busy periods, the carbon monoxide concentrations reached levels of over 20 ppm

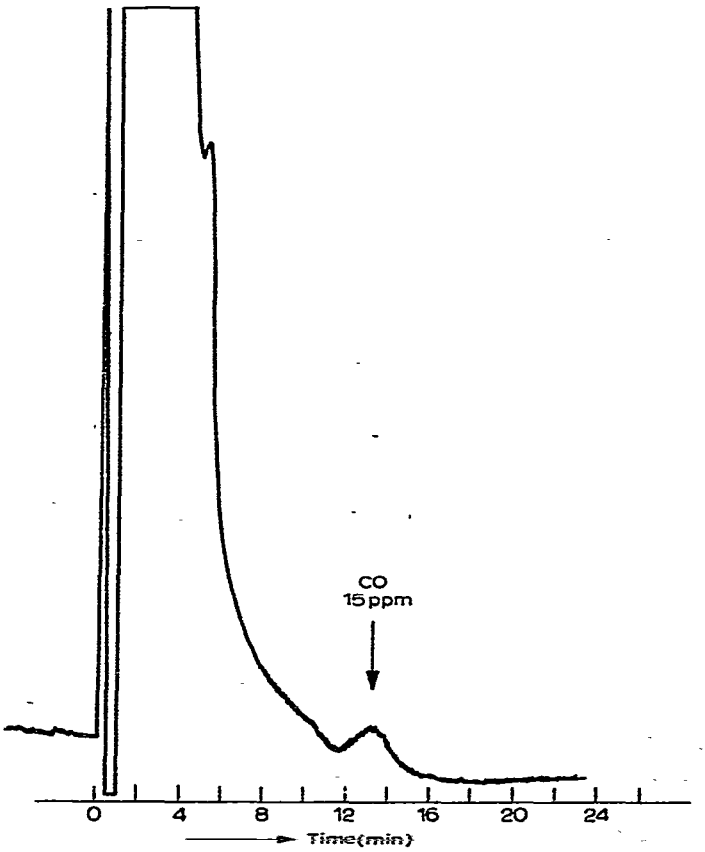

Fig. 1. Analysis of air at a street crossing: temperature, 28°; argon flow-rate, 30 ml/min; air sample size, 25 ml.

and it was possible to determine the concentrations by means of injections with gas-tight syringes. A chromatogram of an injection of 25 ml of air containing 15 ppm of carbon monoxide is shown in Fig. 1.

During the night the carbon monoxide concentrations decreased to a minimum of 0.5 ppm. Because the lower detection limit of the argon detector was 3 ppm (with a 25-ml air sample injected), the carbon monoxide concentration was determined by using the enrichment procedure described above. The volume of the air sample carried with the neon stream into the pre-column was calculated by using the equation for exponential dilution:

$$C = C_0 e^{-Qt/V}$$

where C = concentration of air at time t, C_0 = initial concentration, Q = dilution neon flow-rate and V = volume of the glass bulb. It was possible to determine carbon monoxide concentrations down to 0.3 ppm (enriched from a 250-ml air sample) by this means. A chromatogram obtained in such a way is shown in Fig. 2. The air

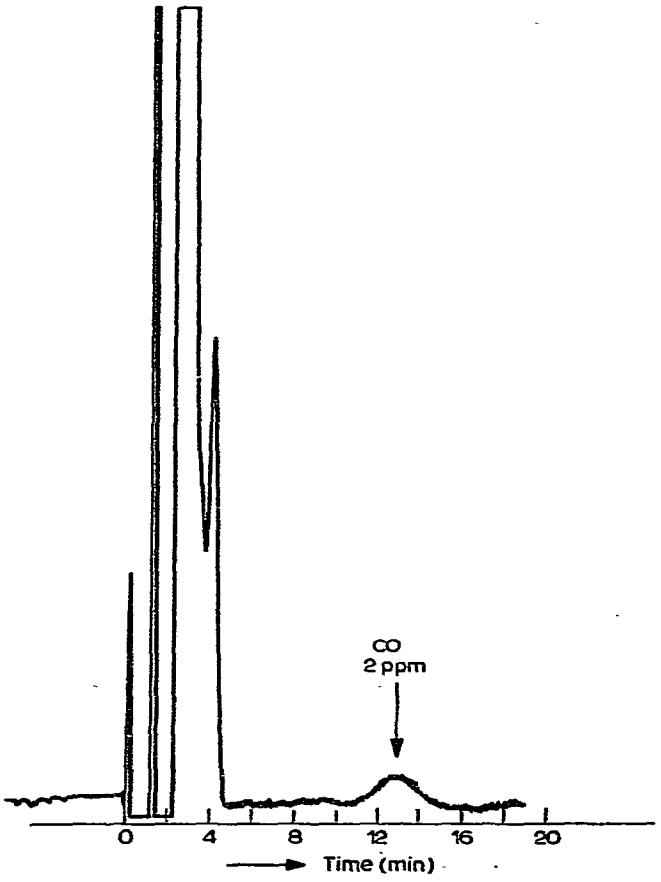

Fig. 2. Analysis of air at a street crossing: temperature, 28°; argon flow-rate, 30 ml/min; sample size, 1.5 ml of neon and air containing carbon monoxide from 200 ml of air.

volume, calculated according to the exponential law, was 200 ml. The carbon monoxide peak corresponded to a concentration of 2 ppm.

The change in carbon monoxide concentration over a period of about 28 h, depending on the density of traffic, is shown in Fig. 3. The carbon monoxide concentration and the density of traffic increase and decrease in parallel, but shifted with respect to time, both minimal and maximal carbon monoxide concentrations being reached 2–3 h later than the corresponding minimal and maximal densities of traffic. Maximal concentrations up to 21 ppm of carbon monoxide were obtained with 2000 cars/h and minimal concentrations down to 0.5 ppm with 50–100 cars/h.

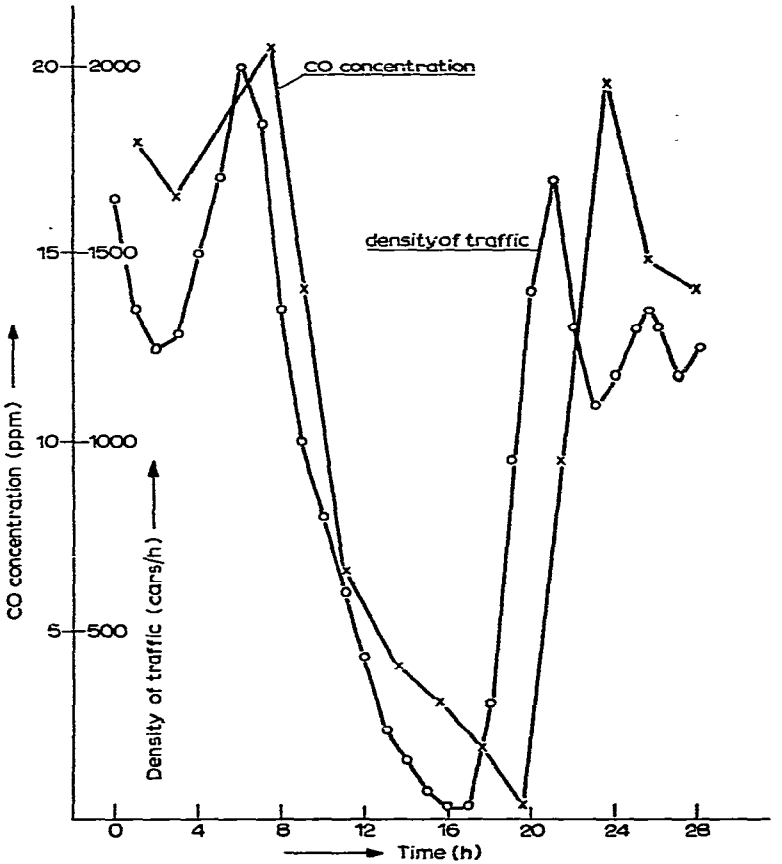

Fig. 3. Carbon monoxide concentration at a street crossing depending on the density of traffic.

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