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CONCENTRATION TECHNIQUE FOR DETERMINATION OF AIR POLLUTANTS AT SUB-MICRO LEVEL

A NEW TECHNIQUE FOR CONCENTRATION OF CARBON MONOXIDE

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SUMMARY

The advantages, scope and limitations of a step-wise technique for concentrating permanent gases, particularly carbon monoxide, up to 2000 times before gas chromatographic, spectrophotometric or mass spectrometric determination are described. Determination of less than 0.01 ppm of carbon monoxide has been carried out with an error of $\pm 10\%$ by using this pre-concentration technique, followed by gas chromatography, with catalytic conversion of the carbon monoxide into methane before flame ionisation detection. The system used without pre-concentration could not detect less than 1 ppm of carbon monoxide.

INTRODUCTION

Increasing awareness of the need for assessment and control of atmospheric pollutants has resulted in significant advances in the development and application of such instrumental methods as adsorption and partition chromatography, mass spectrometry, IR spectrophotometry, and polarography for determining traces of toxic elements in respirable air. Although such work has often extended the scope and possibilities of micro-analysis offered by such conventional methods as iodimetry and colorimetry, the limitations imposed by instrumental noise restricts the useful range of instruments. In order to determine gaseous pollutants in amounts much lower than is possible by the methods enumerated above, concentration of the sample to bring the toxic constituents to determinable levels may be necessary, and various techniques have been suggested for this purpose¹⁻⁹.

GENERAL TECHNIQUE OF CONCENTRATION

Concentration is normally carried out by fractionation at sub-ambient temperature or at ambient temperature without use of any sorbent, or by selective adsorption-desorption of the desired constituents on a suitable solvent-coated sor-

bent. The retained constituents are subsequently desorbed or evaporated at a conveniently elevated temperature for detection and determination by any suitable method. As the initial volume of sample is often large, high efficiency in stripping the sample of its desired constituents is rarely achieved in ordinary fractionation unless very long cooling coils are used. Adsorption (adsorption and solution) methods, on the other hand, have high mass-transfer efficiency because of the large interacting surfaces of sorbents, and a tube filled with conveniently selected materials can be used to concentrate the desired constituents; sometimes, the chromatographic column itself can be used for this purpose¹⁰.

The maximum sample volume that can be drawn through a concentration tube for quantitative retention of any constituent may be calculated from the results of a frontal-analysis experiment in which the effluent from the adsorption tube is monitored by a suitable detector¹¹. Glueckauf's treatment¹², involving graphical integration of the breakthrough curve, also provides a useful method for determining the maximum volume that may be retained. Cropper and Kaminsky³ arrived at similar figures for a small absorption tube designed to concentrate a sample containing various industrial pollutants by assuming an approximately Gaussian distribution towards the outlet of the tube.

Zocchi¹³ determined hydrocarbons at the sub-micro level by using Carbowax 20M on alumina (40–60 mesh) as gas-liquid partition packings at liquid-oxygen temperature (-183°). Lower hydrocarbons present as pollutants have also been efficiently concentrated by using dimethylsulfolan on C-22 fire-brick maintained at ice-water temperature¹, by various traps of the adsorbent and gas-liquid partition types², by a column of active carbon⁵ and by PTFE powder coated with Apiezon L⁶. In all these methods, separation and estimation were effected by gas chromatography (GC), with various types of ionisation detectors. Cropper and Kaminsky's exhaustive treatment of the concentration technique³ related to both the adsorption and gas-liquid partition type of trap gives details on the theory and practice involved in the technique.

LaHue *et al.*⁹ estimated 300 ppb of atmospheric nitrous oxide by a concentration technique with a molecular sieve 5A trap and a thermal-conductivity detector.

The literature on the concentration of permanent gases in nature is small, although traces of nitrogen in cylinder argon have been determined by concentration of a 2-litre sample on the molecular sieve 5A column of a GC unit, followed by subsequent elution with argon and measurement by thermal-conductivity detection¹⁴. The method, however, is hardly suitable for other than binary mixtures, is applicable only in certain ranges, and is likely to exhibit tailing problems when large volumes of sample are used. Pre-concentration of, *e.g.*, carbon monoxide, argon, nitrogen, methane or oxygen is difficult because of the high retention volume of the normal permanent-gas constituents of the air from which they are to be concentrated.

By using an ordinary concentration technique with molecular sieve 5A as trap material, even with mercury suction only 40% of the total pollutant could be recovered when the adsorption temperature was kept at $-18 \pm 2^\circ$ and subsequent desorption was at 80° . Elution of the gas with carrier gas resulted in such an increase in the volume of the concentrated gas that more than 20-fold concentration could not be achieved.

EXPERIMENTAL

A single permanent gas, carbon monoxide, of considerable importance in view of its high toxicity was selected for studying desorption characteristics of the sorbed gas at various desorption temperatures.

Single-stage concentration

Accurately prepared carbon monoxide samples were first dried by passage through two traps containing calcium chloride and phosphorus pentoxide and then freed from carbon dioxide by passage through a Carbosorb tube; it was then passed to a U-tube containing 5 g of molecular sieve 5A (-60 to $+72$ B.S.S.) and placed in a Dewar flask containing ice and salt (temperature -19°); the traps were evacuated before introduction of the gas to permit assessment of the exact volume passed through the tube for concentration. The adsorbed gas was subsequently desorbed at 100° and eluted by the carrier gas (argon). The samples were periodically analysed with a Panchromatograph (Pye Unicam, Cambridge, Great Britain) with a 1.5-m molecular sieve 5A column and a flame ionisation detector preceded by a hydrogenation catalyst.

Figs. 1-3 show how the carbon monoxide was distributed in the volume eluted; although the recovery was 100%, the single-stage method used achieved a concentration factor of only about 20.

Two-stage concentration

The assembly used for two-stage concentration is shown in Fig. 4. A sample containing less than 1 ppm of carbon monoxide was prepared and led through the flow-meter to traps for the removal of moisture and carbon dioxide. The moisture-free gas was then passed at 120 ml/min through a U-tube (the first stage) containing

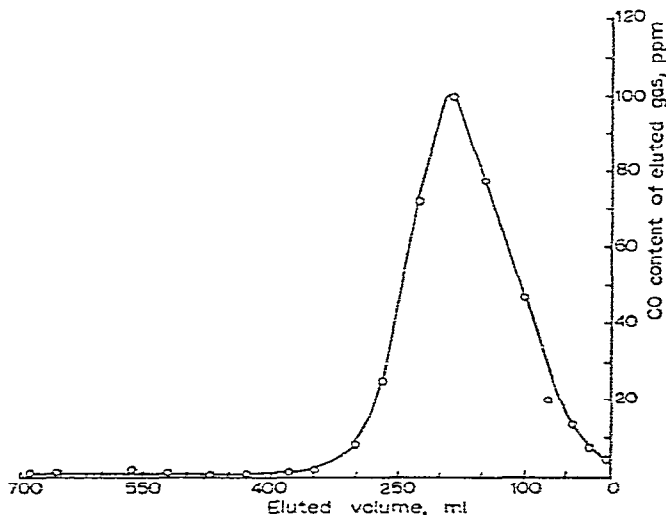


Fig. 1. Distribution of carbon monoxide in the eluted gas for a concentration in the main sample of 10 ppm; desorption temperature 50° .

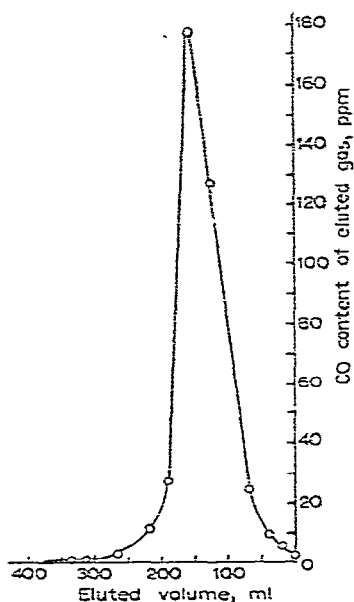


Fig. 2. Distribution of carbon monoxide in the eluted gas for a concentration in the main sample of 9.3 ppm; desorption temperature 80°.

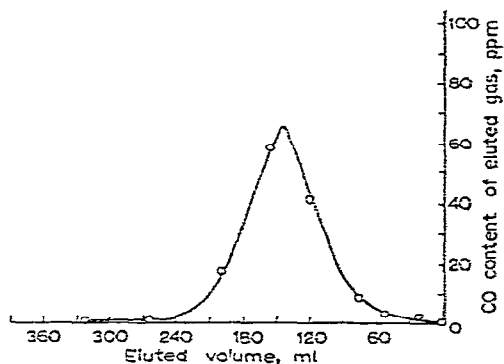


Fig. 3. Distribution of carbon monoxide in the eluted gas for a concentration in the main sample of 3.3 ppm; desorption temperature 80°.

5 g of molecular sieve 5A that had been activated at 250° and was kept at $-18 \pm 2^\circ$ in an ice-salt mixture, the exit gas being passed to the atmosphere. The Dewar flask was then replaced by a boiling-water bath, and the desorbed carbon monoxide (and air) was led through another U-tube (the second stage) containing 0.20 g of molecular sieve 5A that had been activated and was kept at $-18 \pm 2^\circ$ as before. Cylinder nitrogen gas (50 ml; free from carbon monoxide) was then flushed through the first-stage U-tube via stopcock 4 (Fig. 4) to purge this tube. By turning stopcocks 6 and

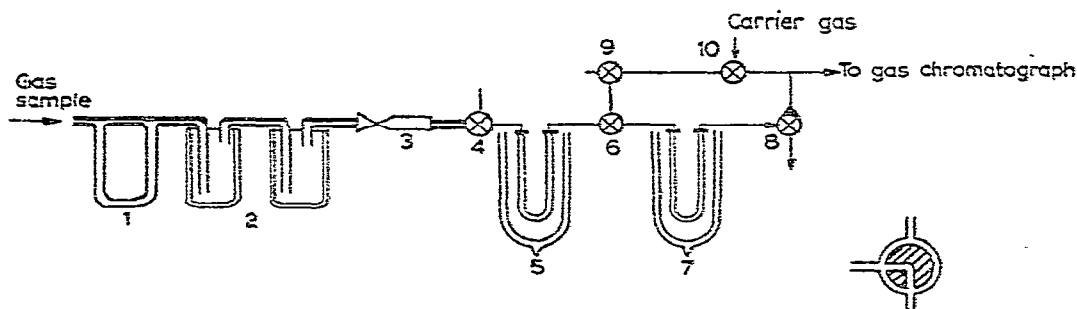


Fig. 4. System for two-stage concentration of carbon monoxide. 1 = flow-meter; 2 = calcium chloride trap; 3 = Carbosorb trap; 4, 6 and 9 = three-way stopcocks (T-type); 5 = first-stage trap (5 g of molecular sieve 5A); 7 = second-stage trap (0.2 g of molecular sieve); 8 and 10 = stopcocks of type shown in the insert.

8, after the freezing mixture has been replaced by a boiling-water bath, the carrier gas was allowed to elute the desorbed and concentrated carbon monoxide to the GC column containing molecular sieve. After separation, the carbon monoxide was catalytically hydrogenated to methane by a nickel catalyst between the column and the detector. For the determination, the GC column was operated at 50°, the carrier gas (argon) flow-rate was 60 ml/min, the detector current was 10⁻⁹ A, and a Honeywell 1-mV strip-chart recorder was used.

RESULTS AND DISCUSSION

The results of analysing seven samples of air containing different concentrations of carbon monoxide are given in Table I; cylinder nitrogen was tested by the method and found to contain no carbon monoxide. Atmospheric air around the laboratory building was found to contain 0.049 ppm of carbon monoxide.

The retention of carbon monoxide on molecular sieve is appreciably affected by the presence of moisture, and it is therefore imperative thoroughly to dry the sample before introducing it into the trap. Although it is not shown in Fig. 4, a short column filled with phosphorus pentoxide should be included between the calcium chloride and Carbosorb traps.

In our early experiments, the total volume of gas retained was about 10 ml

TABLE I
ANALYSIS OF AIR SAMPLES FOR CARBON MONOXIDE

Total volume of sample passed (ml)	Total volume of eluted gas after final collection (ml)	Concentration (ppm) of CO in			Remarks
		Concentrated sample (GC value)	Prepared sample (calculated)	Prepared sample (detected)	
3500	16.75	33.1	0.120	0.15	Sample diluted with air from outside the laboratory
4900	12.60	10.43	0.050	0.040	Sample was diluted with air drawn through Hopcalite, fused CaCl ₂ and P ₂ O ₅
5950	18.79	15.66	—	0.050	Sample of air collected at CMRS and not analysed otherwise
5050	18.89	11.27	0.043	0.042	Sample diluted with cylinder nitrogen
4000	18.49	7.32	0.030	0.035	Sample diluted with Hopcalite-cleansed air
8000	18.12	2.91	0.018	0.018	Sample diluted with cylinder nitrogen
8000	18.00	0.0	—	0.0	Sample of cylinder nitrogen
5000	—*	—**	—	0.033	

* The concentrated sample was fed directly to the GC column.

** The sample (30 ml, containing 12 ppm of CO) was diluted to 10 litres; calculated CO concentration, 0.04 ppm.

(eluted in a volume of 16–18 ml) and small sample volumes were applied to the GC column; by suitable choice of the amounts of adsorbent in the two stages, it was possible to limit the volume to 1.5–2 ml, so that, with 1 litre of air sample, a concentration factor of 500 can be attained. In such an instance, the sample can be directly eluted to the GC column with carrier gas.

The first-stage trap, with its accessories, can be conveniently accommodated in a compact box, and samples up to 1 litre in volume can be collected and brought to the laboratory before transferring the adsorbed gas to the second-stage trap and finally to the chromatograph. With a conventional GC unit, using catalytic hydrogenation and flame ionisation detection, the lower limit of determination is 0.5 ppm; with two-stage concentration, this limit can be extended to 0.001 ppm.

Detection limit and accuracy

The GC unit, with a hydrogen flame ionisation detector and the available amplification system, had a detecting limit of 0.25 ppm at the highest amplification. This was ascertained from a number of readings for which the average observed deviation was ± 1 division; the carbon monoxide content of the sample fed to the GC unit averaged 2.9 ppm for the lowest reported concentration. With ± 1 division of ± 0.25 ppm deviation, the accuracy for very low concentration has been found to be ± 0.002 ppm. By taking a larger original sample and using three-stage concentration, the detection limit may be extended to still lower concentrations.

CONCLUSION

As well as being useful for the reliable monitoring of permanent pollutants in the atmosphere, the step-wise concentration technique described offers possibilities for the early detection of spontaneous combustion, for studying the distribution of carbon monoxide in the upper atmosphere, and for pollutant-cycle studies over oceans.

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