Note

Direct determination of ambient carbon dioxide and nitrous oxide with a high-temperature 63Ni electron-capture detector

P. G. SIMMONDS

International Science Consultants, The Pines, The Chase, Hurn Road, Ringwood, Hants. (Great Britain)

(Received July 25th, 1978)

Current interest in the atmospheric concentrations of carbon dioxide, (CO_2) and nitrous oxide, (N_2O) arises not only from their role as principal constituents of two of the major biogeochemical cycles; but also from their potential long-term effect upon the global environment. Systematic observations of the concentration of carbon dioxide since about 1958 indicates an annual increase of about 0.2%, this had lead to concern over the so-called, "greenhouse effect", due to the special role of carbon dioxide in the heat balance of the earth-atmosphere system.[1] Interest in monitoring atmospheric nitrous oxide has been stimulated from the recent awareness of its importance in ozone chemistry through its stratospheric reaction with excited oxygen $O(^1D)$ atoms to form nitric oxide, (NO), which in turn leads to the natural destruction of photochemically produced ozone. The increasing world-wide use of nitrogenous fertilizers releases additional nitrous oxide into the atmosphere through the action of denitrifying soil bacteria, with the potential consequence of a significant decrease in the level of stratospheric ozone[2].

Infrared spectrometry has become the established analytical method for the measurement of atmospheric carbon dioxide[3], and to a lesser extent for nitrous oxide[4]. Gas chromatography has also been used to determine nitrous oxide using pre-concentration techniques[5,6]; although the use of a high-temperature (>300°) electron-capture detector provides a method for the direct determination of ambient levels of nitrous oxide by gas chromatography[7–9]. This report describes the simple modification of the electron-capture gas chromatography method whereby the normally used high-purity nitrogen carrier gas is deliberately doped with about 100 ppm of oxygen. The addition of oxygen to the carrier gas produces a signal for carbon dioxide, possibly through a charge transfer mechanism, while still preserving the usual response to nitrous oxide. Thus both gases can be determined by direct analysis of a single sample of ambient air.

EXPERIMENTAL

The gas chromatograph used in these experiments was a Pye 104 (Pye Instruments, Cambridge, Great Britain) equipped with a 63Ni electron-capture detector with a maximum operating temperature of 380°. The electron-capture detector was

operated in the constant pulse mode, although the interval between pulses could be altered to different fixed values. The optimum pulse conditions derived by experiment were amplitude 50 V, pulse width 1 μsec and pulse period 700 μsec. The chromatographic column was made from 5 ft. $\times$ $^1/_4$ in. O.D. aluminium tubing packed with 80–100 mesh Poropak QS (Waters Assoc., Milford, Mass., U.S.A.). The column was maintained isothermally at a temperature of 40°. The carrier gas was high-purity nitrogen containing 100 ppm of oxygen (Air Products, Crewe, Great Britain). Oxygen-free nitrogen was also used in some experiments and in this case high-purity nitrogen (oxygen content <10 ppm) was further purified by passage through an oxysorb trap (Alltech Assoc., Arlington Heights, Ill., U.S.A.) Calibration of the detector was performed using certified gas mixtures of 45 ppm of nitrous oxide in nitrogen and 500 ppm of carbon dioxide in nitrogen (Air Products). Dilutions of these standard mixtures in stainless-steel cylinders with nitrogen provided concentrations of each gas over the range of interest. All gas samples were injected using a gas sampling valve with a 3-ml loop (Carle, Fullerton, Calif., U.S.A.).

RESULTS AND DISCUSSION

Fig. 1A illustrates the response of the electron-capture detector operating at a temperature of 270° and with oxygen-doped nitrogen as carrier gas to a 3-ml sample of ambient air. The first peak eluted from the column after oxygen is carbon dioxide followed by nitrous oxide. The response of the detector to these two gases is in contrast to Fig. 1B where oxygen-free nitrogen was used as the carrier gas, and there is no response to carbon dioxide. The unusual response of the electron-capture detector to both carbon dioxide and nitrous oxide is strongly dependant on detector temperature. This is clearly seen in Fig. 2, where the detector response is plotted *versus* detector temperature. Whereas the response to nitrous oxide increases with increasing
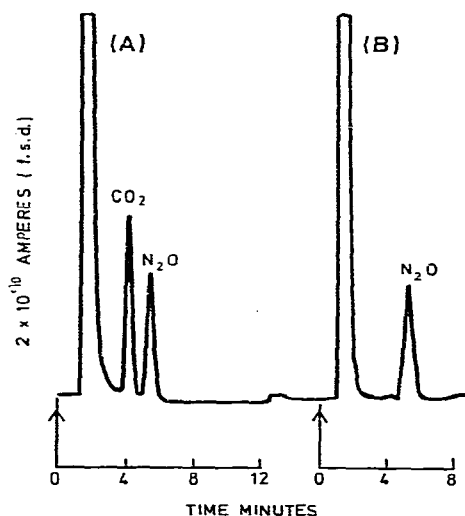

Fig. 1. Response of electron-capture detector to 3 ml of ambient air. (A) Nitrogen carrier gas doped with 100 ppm of oxygen; (B) nitrogen carrier gas. Detector temperature, 270°.
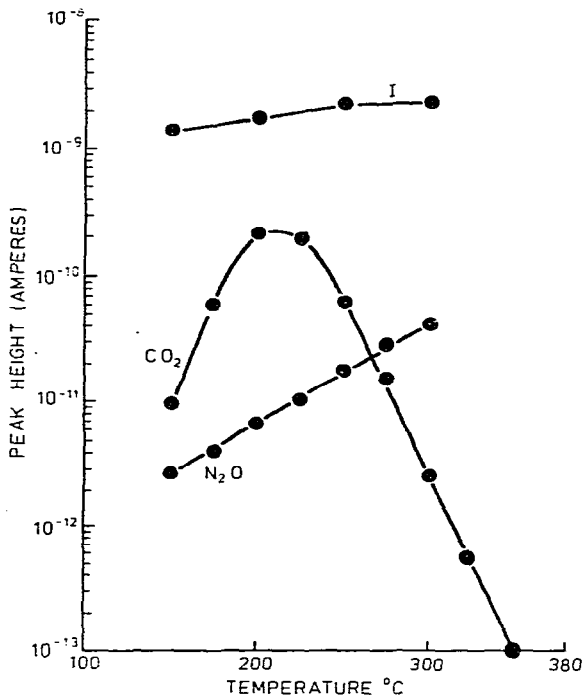
Fig. 2. Detector response to carbon dioxide and nitrous oxide *versus* detector temperature. Curve I, detector standing current. Carrier gas nitrogen and 100 ppm oxygen.

detector temperature, as noted by Wentworth and Freeman[7]; carbon dioxide first increases to a maximum at about 220° and then sharply declines to the point where no signal is observed for carbon dioxide at temperatures in excess of 350°. The detector standing current *versus* temperature is also plotted on Fig. 2 and increases slightly with increasing detector temperature; the opposite result to that ordinarily observed with pure nitrogen as carrier gas. It should also be noted that as the concentrationof oxygen in the carrier gas is increased, not only does the magnitude of the response to carbon dioxide increase but the maximum observed in Fig. 2 shifts towards higher detector temperatures. However, the oxygen cannot be increased much beyond about 1 % without significant loss of standing current and eventual loss of signal particularly for nitrous oxide.

In this study a compromise was reached by fixing the oxygen concentration at a nominal level of 100 ppm which caused only a 10 % loss in the standing current compared with pure nitrogen. The response of the electron-capture detector to nitrous oxide was found to be linea rover the range 50–800 ppb* as shown in Fig. 3. In contrast, the carbon dioxide response (Fig. 4) *versus* concentration becomes non-linear as the concentration starts to exceed about 500 ppm by volume. It is almost certain that the extent of linear response to carbon dioxide is very much dependent on the actual concentration of oxygen in the carrier gas, particularly if the O_2^- ion participates in reaction as will shortly be discussed.

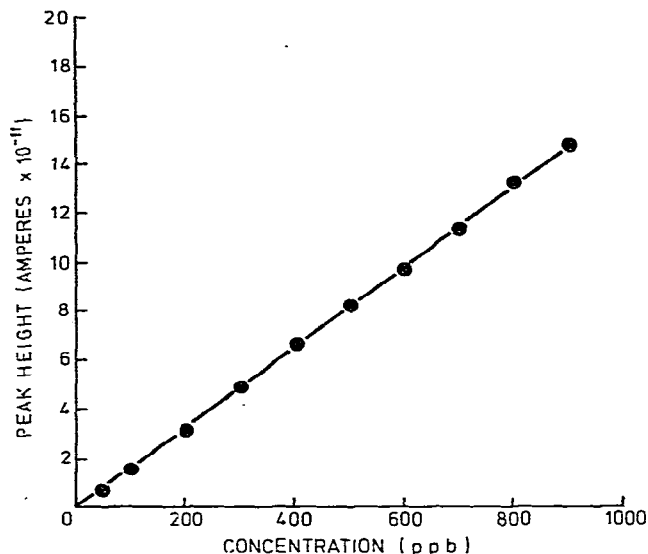* The American billion (10^9) is meant.

Fig. 3. Plot of detector response *versus* concentration of nitrous oxide. Carrier gas nitrogen and 100 ppm oxygen.
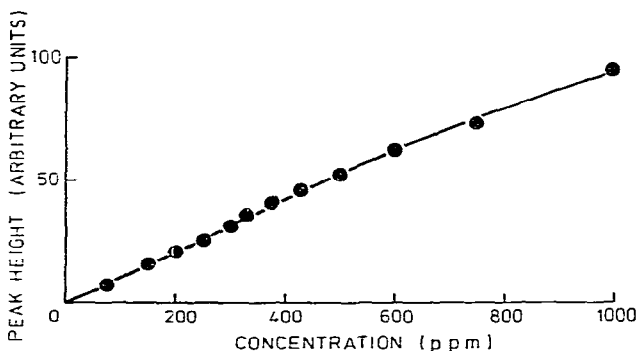

Fig. 4. Plot of detector response *versus* concentration of carbon dioxide. Carrier gas nitrogen and 100 ppm oxygen.

The novel response of a conventional electron-capture detector to carbon dioxide when the carrier gas is doped with small concentrations of oxygen compared with the absence of any signal in oxygen-free nitrogen suggests that a mechanism other than direct electron attachment is involved. A possible clue to the mechanism comes from the study of reactant ions in negative ion plasma chromatography[10,11] which in many aspects parallels the operation of an electron-capture detector. In the presence of oxygen the principal reactant ion found in the plasma chromatograph is the O_2^- ion[12,13]. In the presence of ubiquitous water vapour cluster ions of the type $(H_2O)_nO_2^-$ are also readily formed, with $(H_2O)O_2^-$ predominating[14]. With O_2^- ions, electrons and carbon dioxide present in an electron-capture detector the most likely reactions are

those of charge transfer and three body electron attachment processes. The inter-change of O_2^- with CO_2 as in reaction[1] is not believed to be significant.

$$O_2^- + CO_2 \rightarrow CO_2^- + O_2 \tag{1}$$

This is because the bent configuration of the CO_2^- ion is unstable and favours electron detachment to the linear ground state of carbon dioxide[15]. Alternative interchange reactions are:

$$O_2^- + CO_2 \rightarrow CO_3^- + O \tag{2}$$

$$(H_2O)O_2^- + CO_2 \rightarrow CO_4^- + H_2O \tag{3}$$

Reaction 2 has not been studied extensively, although the formation of the CO_3^- ion is well documented in drift tube and ion mobility experiments[16,17]. The formation of the CO_4^- ion depicted in reaction 3 is inferred from electron mobility data[16], and is also suggested by Claydon et al.[18] to be the ion formed in reaction 2. However, Spangler and Collins[10] have calculated that the level of CO_2 available in the ambient atmosphere is insufficient for the formation of the CO_4^- ion in ion-mobility spectra. The three body electron attachment reaction

$$e^- + O_2 + CO_2 \rightarrow CO_4^- \tag{4}$$

as proposed by Parkes[17] is also a plausible explanation for the mode of action of the electron capture observed in this work. Furthermore, it is significant that the rate constant for attachment to oxygen in the following reaction:

$$e^- + O_2 + M \rightarrow O_2^- + M \tag{5}$$

is about 30 times greater when carbon dioxide rather than nitrogen can act as the third body[19].

It is also of interest that the response of the detector to nitrous oxide is slightly enhanced in the presence of oxygen compared with the response in pure nitrogen. Negative ion–molecule reactions may compete with electron attachment to a limited extent and the series of reactions studied by Parkes[20] may be of some importance in this context.

It seems reasonable to expect that the electron-capture detector may also give an enhanced response to other compounds with oxygen-doped carrier gas. The addition of impurities other than oxygen to the carrier gas may provide a general technique for increasing the response to weak electron adsorbers.

REFERENCES

1 *Man's Impact on the Global Environment*, MIT Press, Cambridge, Mass., 1970.
2 M. B. McElroy, J. W. Elkins, S. C. Wolfsy and Y. L. Yung, *Geophys. Space Phys.*, 14 (1976) 143.
3 C. W. Brown and C. D. Keeling, *J. Geophys. Res.*, 70 (1965) 6077.
4 R. M. Goody, *Planet Space Sci.*, 17 (1969) 1319.
5 K. Schutz, C. Junge, R. Beck and B. Albrecht, *J. Geophys. Res.*, 75 (1970) 2230.
6 M. D. LaHue, H. D. Axelrod and J. P. Lodge, *Anal. Chem.*, 43 (1971) 1113.
7 W. E. Wentworth and R. R. Freeman, *J. Chromatogr.*, 79 (1973) 322.
8 R. A. Rasmussen, J. Krasnec and D. Pierotti, *Geophys. Res. Lett.*, 3 (1976) 615.
9 K. A. Brice, A. E. J. Eggleton and S. A. Penkett, *Nature (London)*, 268 (1977) 127.
10 G. E. Spangler and C. I. Collins, *Anal. Chem.*, 47 (1975) 393.
11 F. W. Karasek, *Anal. Chem.*, 43 (1971) 1982.
12 M. W. Siegel and M. C. McKeown, *J. Chromatogr.*, 122 (1976) 397.
13 J. L. Moruzzi and A. V. Phelps, *J. Chem. Phys.*, 45 (1966) 4617.
14 M. Arshadi and P. Kebarle, *J. Phys. Chem.*, 74 (1970) 1483.
15 J. F. Paulson, in J. L. Franklin (Editor), *Ion-Molecule Reactions*, Vol. 1, Plenum Press, New York, 1972, Ch. 4.
16 F. W. Karasek, M. J. Cohen and D. I. Carroll, *J. Chromatogr. Sci.*, 9 (1971) 390.
17 D. A. Parkes, *J. Chem. Soc., Farad. Trans. I*, 68 (1972) 627.
18 C. R. Claydon, G. A. Segal and H. S. Taylor, *J. Chem. Phys.*, 52 (1970) 3387.
19 J. L. Pack and A. V. Phelps, *J. Chem. Phys.*, 45 (1966) 4316.
20 D. A. Parkes, *J. Chem. Soc., Farad. Trans.*, 68 (1972) 2103.