

CHROM. 6609

Note

Measurement of atmospheric nitrous oxide using an electron capture detector in conjunction with gas chromatography

Atmospheric nitrous oxide, N_2O , is currently measured using either gas chromatography or infrared spectrometry¹. However, both of these techniques have certain inherent disadvantages. The infrared measurements are unreliable due to the presence of secondary sample components such as carbon dioxide and water. The use of gas chromatography, and more specifically the thermal conductivity detector, requires that the nitrous oxide be concentrated on some adsorbant such as molecular sieve or silica gel prior to injection. Consequently, elaborate trapping techniques, which often require the use of cold traps, a series of adsorption tubes, or even vacuum pumps are necessary²⁻⁶. All of this additional experimental paraphernalia is external to the gas chromatograph and detector, which not only complicates the analysis, but also serves as a potential source of error.

Recently, thermal electron attachment to nitrous oxide was investigated⁷ using the electron capture detector (ECD) in the pulse sampling mode⁸. The results of this investigation indicate that at high temperatures (*ca.* 350°), this technique could be used to quantitatively measure the concentration of nitrous oxide in the parts per billion (p.p.b.)* range, if indeed the temperature dependence of the capture coefficient remains linear at high temperatures. Use of the ECD would eliminate the need for a concentration technique, for a portion of the air sample could be injected directly on the column, thereby reducing not only the time of analysis, but also the need for excessive sample manipulation. Also the procedure is straightforward and should be suitable for use in the field.

The experimental apparatus is quite similar to that reported in ref. 7 with the following two exceptions: (1) a 30 mCi ⁶³Ni foil was used as a source of ionizing radiation which permitted the electron attachment to nitrous oxide to be investigated over the temperature range 187-400° and (2) the response of the detector was linearized prior to display. Linearization of the signal greatly enhances the linear dynamic range of the ECD⁹.

The temperature dependence of the capture coefficient for N_2O is shown in Fig. 1. Data of this nature are routinely illustrated by plotting $\ln KT^{3/2}$ versus $1/T$. The quantity, K , is defined as the electron capture coefficient, and is related to the potentiometric response of the detector in the following manner:

$$(b - [e^-]) / [e^-] = Ka$$

where $[e^-]$ and b are the concentration of electrons with and without a capturing species present, and a is the concentration of capturing species. From Table I it is observed that the dependent variables from this work and those variables reported in

* Throughout this article the American p.p.b. (10^{-9}) is meant.

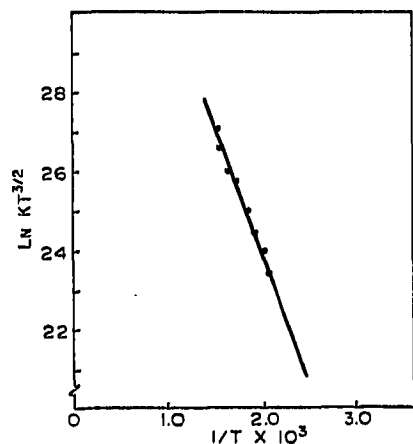


Fig. 1. The temperature dependence of the capture coefficient for nitrous oxide.

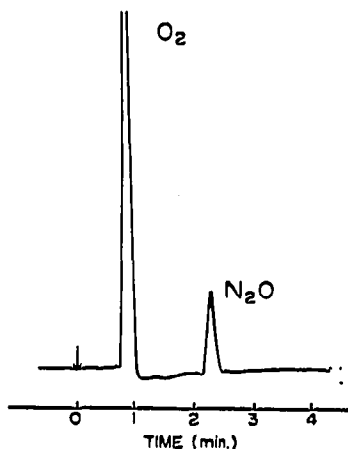


Fig. 2. Linearized electron capture chromatogram of nitrous oxide. Column, 10 ft. \times 1/8 in. stainless steel; packing, Porapak Q, 80-100 mesh; carrier gas, zero nitrogen (32 ml/min); sample size, $7.97 \cdot 10^{-12}$ moles N_2O ; attenuation, 16.

TABLE I

A COMPARISON OF THE DEPENDENT VARIABLES FROM THIS WORK AND THE VARIABLES REPORTED IN REF. 7

Reference	Slope	Intercept
This work	-6.09 ± 0.15	36.26 ± 0.67
Ref. 7	-5.26 ± 0.19	34.39 ± 0.46

ref. 7 are comparable, thereby indicating that the attachment processes in both instances are the same.

From Fig. 1, it is observed that the temperature dependence of the capture coefficient is linear for temperatures greater than 50° ; consequently, it should be possible to measure nitrous oxide at the p.p.b. level using elevated detector temperatures. In order to verify this hypothesis, a $3.98 \cdot 10^{-7} M$ solution of nitrous oxide in purified oxygen was made. On a weight basis this represents 12.2 p.p.m. N_2O in O_2 . 20 μ l of this solution, representing $7.97 \cdot 10^{-12}$ moles of N_2O , were injected directly on the Porapak column. The detector temperature was 395° . The response of the ECD to this amount of N_2O appears in Fig. 2. A detector response similar to that in Fig. 2 is realized if one "injects" 0.90 ml of a $8.92 \cdot 10^{-9} M$ solution of N_2O (275 p.p.b.), for this too represents $7.97 \cdot 10^{-12}$ moles of N_2O . The calculations indicate that the measurement of nitrous oxide at the p.p.b. level using electron capture detection is possible.

It is interesting to note that the sensitivity of the ECD to nitrous oxide is 1,000 times less at 20° than at 400° . Although this is but one measurement, it illustrates how the ECD can be used to detect N_2O in the atmosphere and can greatly simplify a complex analytical problem. It also emphasizes how an expanded temperature range greatly enhances the versatility of the ECD.

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