

THE INFRARED ISOTOPE ANALYZER II

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Synopsis

The investigation of the new method for determining isotope ratios by infrared gas analysis has been continued.

The amount of carbon dioxide required for a $^{13}\text{C}/^{12}\text{C}$ analysis has been reduced. The sensitivity is now 0.005 at. % excess ^{13}C in 20 mg CO_2 and 0.008 at. % excess ^{13}C in 8 mg CO_2 .

The method has been extended to the determination of the $^{15}\text{N}/^{14}\text{N}$ ratio in nitrous oxide (*NNO) and the sensitivity reached is 0.015 at. % excess ^{15}N in 6 mg N_2O .

§ 1. *Introduction.* The feasibility of using an infrared gas analyzer for the determination of isotopic abundances has been demonstrated for the $^{13}\text{C}/^{12}\text{C}$ analysis in carbon dioxide. The non-dispersive double-beam gas analyzer developed to this purpose has been described previously¹⁾ and a more detailed account of that investigation may be found in the thesis of one of us²⁾. The continuation of these studies has led to a considerable reduction of the quantity of gas needed for an analysis (§ 2) and to the applicability of the method to the $^{15}\text{N}/^{14}\text{N}$ analysis in nitrous oxide (§ 4).

With respect to the infrared absorption, the determination of the $^{13}\text{C}/^{12}\text{C}$ ratio in CO_2 was the most attractive object as the shift in the ν_3 bands of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ is substantial. However, the use of ^{13}C in tracer research is rather limited by the existence of a suitable radioactive isotope ^{14}C . In the case of nitrogen, only shortlived radioactive isotopes exist, and therefore a simple method for $^{15}\text{N}/^{14}\text{N}$ analysis is the more valuable.

Nitrous oxide appears to be the obvious gaseous compound of nitrogen to be used, as the infrared absorption bands are strong and the isotope shift of $^{15}\text{N}^{14}\text{NO}$ and $^{14}\text{N}^{15}\text{NO}$ with regard to $^{14}\text{N}^{14}\text{NO}$ is respectively 22.5 and 46.5 cm^{-1} in the ν_3 band at 2223.5 cm^{-1} ³⁾ 4). Moreover, N_2O may be prepared from NH_4NO_3 (§ 3) and by the Kjeldahl method organic nitrogen may be readily converted into the ammonia group of NH_4NO_3 .

§ 2. *Improvements of the analyzer.* The gas analyzer used in this investigation was an improved version of the one described in Reference 1. By reducing

the diameters of the analysis and reference cell from 30 mm to 12 mm the amount of gas needed for an analysis was reduced. To retain the sensitivity the same amount of radiation had now to pass through the narrower cell and to this end more concentrated sources were developed.

At the same time it appeared possible to reduce the fluctuations due to the microphone membrane to the same level as the amplifier noise by a better mounting of the detector. This makes possible a lower intensity of the infrared beams. The only requirement on the intensity is to be so large that the fluctuations in the intensity (which are proportional to the intensity) are larger than the fluctuations of the detector and the amplifier noise.

The sources are now made by painting a nichrome ribbon 1 mm broad and 0.1 mm thick with red-lead, heating the ribbon, and afterwards winding it in a spiral of 17 mm diameter, loosely in the centre and more compactly towards the boundary. The spirals are mounted on plaster and protected against air currents by mica windows. The heating current is 1.0 to 1.2 A, the power consumption about 9 Watt.

The sensitivity of the modified analyzer in the neighbourhood of the natural abundance is 0.005 at. % ^{13}C at a pressure in the analysis cell (p_A) of 500 mm Hg and 0.008 at. % ^{13}C at $p_A = 200$ mm Hg. As the volume of the connections between analysis cell, manometers and manifold was not reduced, the quantity of gas needed was not reduced in the proportion of 42 cm³ to 7 cm³ (volume of the analysis cell), but only by a factor of about 4.

Throughout this investigation a pen recorder has been used as indication instrument in stead of the alternating current galvanometer. To preserve the small bandwidth and ensuing favourable signal to noise ratio, the amplified signal was rectified by a high-speed telegraph relay (Carpenter 3G1) driven by a 50 c/s current in phase with the signal.

§ 3. *The preparation of N₂O from NH₄NO₃.* Friedman and Bigelsen⁵⁾ have proved that pyrolysis of NH₄NO₃ yields N₂O with the ammonia-N in the end position and the nitrate-N in the centre position of the linear molecule NNO.

As this decomposition will also have to be applied, when the isotope analyzer is used for tracer experiments, a short report of our experiences in this respect will be given here.

The occurrence of sublimation besides the wanted decomposition is troublesome. As only small samples (about 0.1 g) are used, the loss by sublimation may be considerable. The well known explosion danger is greatly reduced at the same time by the small amounts used. The sublimation is diminished by heating in air in stead of in vacuo. When air free from carbon dioxide is used the N₂O may be separated from the air by freezing in liquid air. Commonly only $\frac{1}{2}$ atm. air was used to preclude pressures higher than 1 atm. in the

manifold. The optimal temperature is 240—250°C; at higher temperatures also NO and NO₂ may be produced. By putting the NH₄NO₃ in an 1 cm wide vertical tube and immersing this tube gradually in an oil bath of 240—250°C, loss by sublimation was reduced to a minimum and 70—80% of the NH₄NO₃ was decomposed into N₂O and water in 4 hours. The nitrous oxide is then dried by passing it through dry-ice traps. This drying has to be repeated several times. In this way samples containing 64.5% respectively 8.3% ¹⁵NNO were prepared from enriched ¹⁵NH₄NO₃ obtained from the Eastman Kodak Company.

It may be remarked, that in the same way N₂O may be prepared by thermal decomposition of (NH₄)₂SO₄ mixed with KNO₃.

The tendency of nitrous oxide to be adsorbed on many organic substances may be very inconvenient. Luckily there is no substantial adsorption on glass. To avoid adsorption the plastic tubes leading from the manifold to the analysis and reference cell had to be replaced by glass ones with plastic joints, and no glue could be used for fixing the reflecting aluminum paper to the walls of the cells.

§ 4. *Determination of the ¹⁵N/¹⁴N ratio in N₂O.* The importance of choosing suitable values for the lengths of the detection cell and analysis cell (d_D and d_A) and the pressures in these cells (p_D and p_A) has been pointed out in § 3 of Reference 1. Calculations lead to an optimal value of $d_D = 3$ mm in the case of N₂O as in the case of CO₂. Moreover, it appeared that the value of d_A had little influence on the sensitivity of the isotope analyzer, provided that p_A was adapted to the chosen value. For this reason $d_A = 60$ mm was also used in this investigation.

The optimal values of p_D and p_A were determined by experiment. The detector was filled with N₂O containing 64.5% ¹⁵NNO successively to $p_D = 401$, 315, 190 and 98 mm Hg. At each of these pressures absorption curves (% transmission versus p_A) were measured, using only a single beam, both for natural N₂O (0.37% ¹⁵N) and for N₂O enriched to 8.3% ¹⁵NNO. The curves for $p_D = 190$ mm Hg are shown in fig. 1. The difference in absorption of the isotopic gases varied from about 2 to 7% transmission when p_D and p_A were varied. The sensitivity of the analyzer depends on the size of the isotope effect divided by the unavoidable fluctuations, which limit the measuring accuracy. The optimal condition is reached for $p_D = 190$ mm and $p_A = 150$ mm. These values are not very critical, in this sense, that for other values of p_D , values of p_A may be found, which give a sensitivity only 10 to 20% less than for this combination. The fact, that these pressures are both lower than for the ¹³C/¹²C analysis in CO₂ may be explained by the stronger absorption of N₂O.

For measuring ¹⁵N/¹⁴N ratios the analyzer is used as a double beam instrument with natural N₂O in the reference cell. Typical calibration curves with

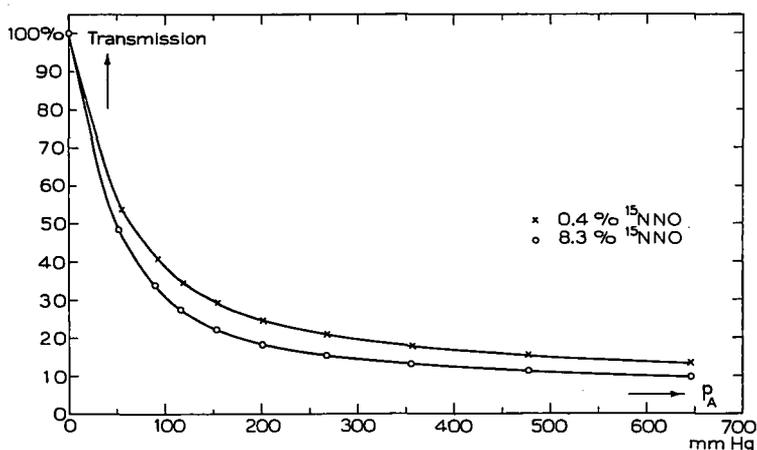


Fig. 1. Absorption curves of N_2O containing 0.4% and 8.3% ^{15}NNO ;
 $p_D = 190$ mm Hg, $d_D = 3$ mm, $d_A = 60$ mm.

$p_D = 190$ mm and $p_A = 190$ mm Hg are shown in Fig. 2. The accuracy in the neighbourhood of 0.37% ^{15}N amounts to 0.015% ^{15}N , which corresponds to a 0.05% change in the transmission.

In these measurements alternative records are made of the zero (standard N_2O in the analysis cell) and of the deflection (the sample in the analysis cell). Taking three zeros and two deflections each for 2 minutes, the fluctuations are partially averaged out.

To the uncertainty of the readings contribute the amplifier noise and the vibrations of the unexposed detector, (0.13% of the unattenuated signal), the fluctuations in the intensities of the beams (0.16%), but mostly an irregular drift of the zero with an average of about 0.5% caused by slow variations in the beam intensities. Errors in the pressure adjustment are too small to be of any influence.

§ 5. *Conclusions.* The results obtained are summed up in Table I. It should be underlined that the sensitivities mentioned are no absolute limits. These limits might be lowered by improving the construction of the sources (and the stabilization of the current through them). However, in that case one runs risk of sacrificing the great simplicity of the present isotope analyzer, which is one of its prominent assets.

TABLE I

Isotope ratio	$^{13}C/^{12}C$		$^{15}N/^{14}N$
Natural abundance	1.1% ^{13}C		0.37% ^{15}N
Gaseous compound	* CO_2		* NNO
Main absorption band	4.3 μ		4.5 μ
Size of the sample	20 mg	8 mg	6 mg
Sensitivity	0.005 at.% ^{13}C	0.008 at.% ^{13}C	0.015 at.% ^{15}N

The sensitivity is given in at.% excess near the natural abundance and decreases for higher percentages as indicated by the curved calibration curves. As the shift in the absorption bands of $^{14}\text{N}^{15}\text{NO}$ and $^{14}\text{N}^{14}\text{NO}$ is larger

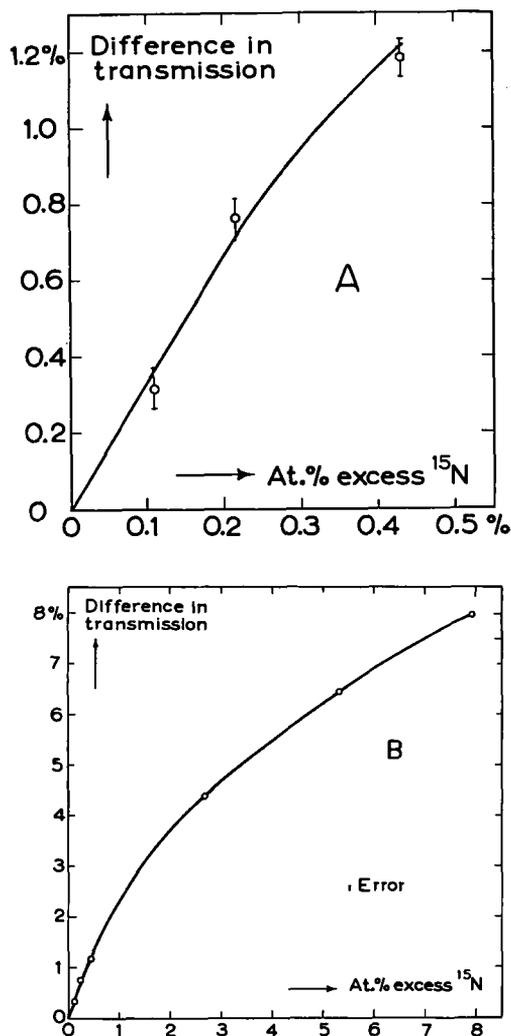


Fig. 2. Calibration curve for ^{15}N -analysis. The difference in transmission between enriched ^{15}NNO and natural N_2O is given as a function of the atom-percentages excess ^{15}N .
 $p_A = 190 \text{ mm Hg}$, $p_D = 190 \text{ mm Hg}$, $d_D = 3 \text{ mm}$, $d_A = 60 \text{ mm}$.
 Fig. 2A is a part of Fig. 2B enlarged.

than for $^{15}\text{N}^{14}\text{NO}$, the method may certainly be extended to the $^{14}\text{N}^{15}\text{NO}$ analysis in N_2O . For practical purposes, however, $^{15}\text{N}^{14}\text{NO}$ analysis will be more attractive, as it is easier to convert organic nitrogen into $^{15}\text{N}^{14}\text{NO}$

than into $^{14}\text{N}^{15}\text{NO}$. Moreover, unfortunately, no concentrated $^{14}\text{N}^{15}\text{NO}$ or $^{14}\text{NH}_4^{15}\text{NO}_3$ was at our disposal.

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