Isotopic measurement of atmospheric nitrogen compounds

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ABSTRACT

A short review of nitrogen isotope studies as related to atmospheric compounds is presented. Methods utilized for the collection and conversion of various nitrogen containing compounds found in the atmosphere to N_2 suitable for mass spectrometric measurement are described. Preliminary results obtained on the concentration of and $^{15}N/^{14}N$ ratio in N_2 from NH_4^+, NO_3^-, N_2O and NO_2 in air and other samples are given and the results with respect to NH_4^+ and NO_3^- in precipitation are discussed briefly.

Introduction

Isotope ratio determinations provide a useful tool for assessing the importance of various sources and sinks as well as physical and chemical reactions of trace constituents in the atmosphere. The isotopic content of a particular chemical compound is related to its origin and is modified by various physical and chemical reactions involving the compound and the conditions under which these reactions occur. Isotopic fractionation can occur under equilibrium conditions or for irreversible reactions. These may be illustrated with reactions of ammonia by:

$$^{15}NH_{3(g)} + {}^{14}NH_{3(l)} \rightleftharpoons {}^{15}NH_{3(l)} + {}^{14}NH_{3(g)} \qquad (1)$$

$$\alpha = (^{15}N/^{14}N)_l/(^{15}N/^{14}N)_g$$

and

$$^{14}NH_4^+ \xrightarrow{K_1} {}^{15}NO_3^- \qquad (2\,a)$$

$$^{15}NH_4^+ \xrightarrow{K_2} {}^{15}NO_3^- \qquad (2\,b)$$

$$\beta = K_1/K_2$$

where K_1 and K_2 refer to the reaction rate constants in the rate determining step and the ratios α and β are the equilibrium and kinetic isotope fractionation factors. Application of isotope ratio determinations to geochemical problems involves a review of the various chemical compounds and their possible sources, consideration of possible relationships among them, and investigation of these relationships by determination of isotope fractionation factors for possible reactions in laboratory studies and field experiments. Nitrogen compounds appear to be of great importance in urban pollution problems and in relation to the stratospheric ozone budget. However, few isotopic studies of nitrogen in atmospheric compounds have been undertaken. Hoering (1957) determined the $^{15}N/^{14}N$ ratio in NH_4^+ and NO_3^- ions separated from several precipitation samples. The $^{15}N/^{14}N$ ratios for various nitrogen compounds and N_2 found in soil have been reported (Cheng et al., 1964; Delwiche & Steyn, 1970) as have alterations in the $^{15}N/^{14}N$ ratio due to biological microorganisms (Wellman et al., 1968; Hoering & Ford, 1959). These latter studies relate to the sources of the atmospheric nitrogen containing compounds. The lack of isotopic studies on nitrogen compounds in the atmosphere may be due to (1) their low concentration in the atmosphere, (2) their being somewhat labile, and (3) the relatively large amount of N_2 (0.08 mg) necessary for isotopic analysis.

It is the purpose of this paper to present preliminary results on $^{15}N/^{14}N$ ratios in a variety of atmospheric nitrogen compounds. Techniques are described to isolate various nitrogen compounds and convert them to N_2 for isotopic determination. Nitrogen isotope ratios are determined using a 15 cm Nuclide Associates double beam isotope ratio mass spectrometer. Nitrogen isotope results are reported in units of per mil deviations from that of atmos-

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pheric molecular N_2 as:

$$\delta^{15}N = \frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard}}{(^{15}N/^{14}N)_{standard}} 1\,000 \quad (3)$$

Experimental methods

In order to obtain N_2 suitable for isotopic measurement, collection and chemical conversion procedures must be quantitative or must involve a known degree of fractionation. Collection procedures must not allow conversion to or exchange with other compounds during or following collection. Methods for collection and conversion to N_2 have been developed for N_2O, NO_2, particulate NH_4^+ and NO_3^-, and NH_4^+ and NO_3^- in precipitation. Procedures used presently are as follows:

Nitrous oxide: N_2O is collected by passing air through a cold trap cooled to between -185°C and -195°C with liquid N_2. Condensation of a large amount of O_2 is prevented by reducing the pressure of air passing through the collector or by pressurizing the liquid N_2 in order to raise the temperature. The noncondensables are pumped away and the sample is transferred to a cold trap cooled to -80°C. This removes H_2O and the remaining CO_2–N_2O mixture is transferred to a calibrated section of the vacuum system for volume measurement. A small portion of this CO_2–N_2O sample is reserved for mass spectrometric determination of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios and the N_2O content. The latter procedure is described below. The remaining N_2O–CO_2 mixture is then passed over Cu at 700°C. This converts N_2O to N_2. The CO_2 is frozen out at -195°C and the N_2 is measured manometrically and finally transferred to an ampoule cooled to -195°C and containing a single grain of carefully outgassed cocoanut charcoal. The ampoule is then sealed and saved for $^{15}N/^{14}N$ ratio determination. One sample of stratospheric N_2O was collected by passing air through molecular sieve. The sieve material is then heated to release the trapped gases and the sample is processed as described above. This sampling system is described by Ashenfelter et al. (1972).

Mass spectrometric analysis of N_2O in CO_2: As a cross calibration on the manometric determination of N_2O and to determine N_2O on small samples of air, a method which makes use of the dual inlet mass spectrometer has been developed. Since N_2O and CO_2 each have the same mass number, 44, a mass spectrometer with a 15 cm radius of curvature cannot resolve these molecules. Therefore, the method developed makes use of the difference in cracking patterns between N_2O and CO_2 and the absence of molecules with interfering peaks at mass 30. The cracking ratio from mass 44 to 30 for CO_2 is approximatively 6,000 while that for N_2O is approximately 16. This results in a relative increase in sensitivity at mass 30 of about 350 for N_2O. If a CO_2 standard and a CO_2–N_2O sample mixture are matched to the same signal height at mass 44 and then are scanned at mass 30, the increment at mass 30 is directly proportional to the N_2O content of the sample. Because it is difficult to adjust to the same absolute signal each time, but rather simple to adjust sample and standard to the same peak height, a known N_2O–CO_2 mixture also is determined and the peak heights corrected to that of the standard. The ppm chart reading is then taken and the result applied to the unknown sample N_2O concentration. In practice the sensitivity is usually about 0.02 ppm per chart division. Estimation to 0.2 chart divisions results in an error of ± 0.005 ppm. The sensitivity can be improved by passing the sample over ascarite to remove a portion of the CO_2. Approximately 0.5 cm^3 of CO_2–N_2O mixture is necessary for analysis. If a larger amount of CO_2–N_2O mixture is available, it can be enriched in N_2O to increase the sensitivity. The probability of interfering peaks at mass 30 is reduced by freezing out condensables at -80°C and, in turn, freezing out the CO_2 and N_2O at -195°C and pumping away residual gases as described above. It should be noted that this method depends on an analysis of the CO_2 or knowledge of its concentration in air. When the CO_2 is not directly determined, the concentration assumed is 320 ppm. A comparison of results for three fractions of a single sample of air are shown in Table 1. Fraction A was measured as described above and also manometrically by conversion of the N_2O to N_2. Fractions B and C were measured as above, enriched over ascarite, measured again and then measured manometrically. The accuracy of this method depends upon the various manometric measurements involved in preparing the sample and standard and are estimated to be approximately ± 3%.

Table 1. *Comparison of N_2O analysis methods N_2O content (ppm)*

Fraction	Mass spectrometric		Mano-	$\delta^{15}N$
	Original	Enriched	metric	per mil
A	0.250	—	0.252	6.6
B	0.228	0.230	0.246	5.1
C	0.242	0.241	0.243	5.3
Mean ± S.D. (all determinations)			0.242 ± 0.09	5.7 ± 0.8

Ammonium and nitrate ions: Particulate matter containing ammonium ion and nitrate ion is collected by passing air through efficient polystyrene filters (Microsorban 99/98). The filter system used has been descri bedelsewhere (Poet et al., 1972). The filters are placed in a modified Kjeldahl distillation apparatus and concentrated NaOH solution is added. The NH_3 is distilled into standard HCl and titrated with NaOH to pH 7 with a pH meter. The solution is then made slightly acid, evaporated to a small volume and reacted with NaOBr (Hoering, 1955). This converts NH_4^+ quantitatively to N_2. The N_2 is cycled over hot Cu and its volume measured. It is then transferred to an ampoule in the manner described above. (See also Brenner, 1968 for general methods.)

To convert NO_3^- to NH_4^+, Zn coated with Cu is added to the distillation flask and the distillation described above is repeated.

Ammonium and nitrate ions in seawater and rainwater are separated by means of ion exchange resins in a manner similar to that described by Hoering (1967). After removal of the ions from the exchange resins, the samples are distilled and converted to N_2 as before.

The collection and determination of nitrate ion in stratospheric samples is described by Lazrus et al. (1968, 1972). These samples are converted to NH_4^+ and to N_2 as described above. These samples probably consist of HNO_3 vapor (Lazrus et al., 1972).

Nitrogen dioxide: NO_2 is collected by passing air through a polystyrenefilter to remove particulates and then through a Whatman 541 filter impregnated with KOH-triethanolamine (TEA) solution. This technique has been shown to be quite efficient for SO_2 collection (Forrest & Newman, 1973). It also has been shown that reaction with TEA does not convert NO_2 to NO and that TEA does not react with NO (Levaggi et al., 1972). Under the conditions used the collection efficiency for a single filter is ~85% and for two filters in series, approximately 98%. There is only a slight degree of isotope fractionation between the first and second filter. The impregnated filters are treated as described above. Impregnated filters suitable for NH_3 collection are being developed.

Preparation of standard nitrogen: N_2 used for isotopic comparison is prepared by passing an air sample repeatedly over hot Cu and through a trap cooled to −195°C. This removes H_2O, CO_2, O_2 and most other impurities except Ar. The latter has no effect on the isotopic comparisons. N_2 prepared in this manner was compared to a National Bureau of Standards N_2 standard some years ago (Hoering & Moore, 1958) and was found to be identical.

Experimental results and discussion

Isotopic results are shown in Table 2 and Fig. 1. The precision for individual sample measurements is estimated to be ±0.2 per mil. Errors due to instability of the mass spectrometer are smaller. However, conversion of the various compounds to N_2 introduces an additional small error. The errors cited in column

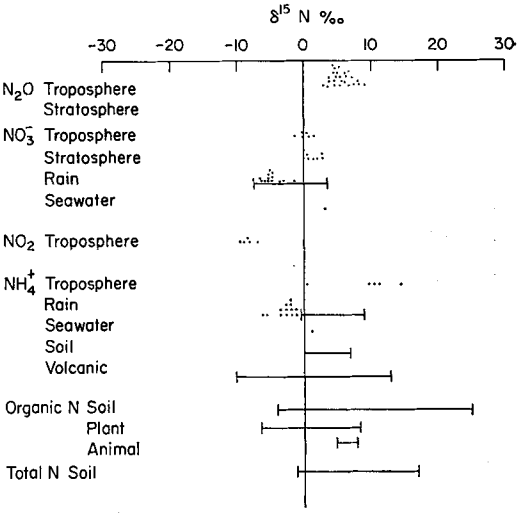

Fig. 1. Variation in $^{15}N/^{14}N$ ratios for various samples. The dots indicate values determined in the present study. The bars represent ranges of values found by other authors.

Table 2. *$^{15}N/^{14}N$ in various nitrogen containing compounds*

Sample		No. of samples	Ratio range (‰)	Mean (‰ ± S.D.)
N_2O	Tropospheric	26	0.0 to 9.3	5.2 ± 2.0
	Stratospheric	1	19.2	—
NO_2	Tropospheric	5	−7.0 to −9.1	−8.4 ± 0.9
NO_3^-	Tropospheric	6	−1.5 to 1.5	0.0 ± 1.0
	Stratospheric	7	0.8 to 2.8	1.9 ± 0.9
	Rain	14	−1.5 to −8.9	−5.2 ± 1.9
	Seawater	1	1.1	—
NH_4^+	Tropospheric	6	9.8 to 14.4	11.4 ± 2.0
	Rain	14	0.1 to −6.0	−2.5 ± 1.7
	Seawater	1	3.1	—

4, Table 2, are one standard deviation from the mean for samples listed in column 2. Included in Fig. 1 are published results of other authors (Hoering, 1958; Delwiche & Steyn, 1970; Cheng et al., 1964; Volynets et al., 1967). The N_2O results include samples collected on the roof of the NCAR laboratory and at altitudes up to 13.1 km using NCAR aircraft. Vertical profiles of N_2O will be published elsewhere. The mean concentration for these samples is 0.24 ± 0.02 ppm and is relatively constant with altitude. The per mil value for stratospheric N_2O is that for a single sample collected by balloon on molecular sieve at 20.8 km over Mildura, Australia. The per mil value shown for this sample may not be representative of stratospheric N_2O because molecular sieve appears to decompose some of the N_2O under the conditions used. This problem is under investigation. The stratospheric NO_3^- was collected at altitudes from 21.3 to 27.4 km over Australia and over Alaska. The seawater sample is surface water from Port Aransas, Texas. The other samples were collected on the rooftop of the NCAR laboratory in Boulder, Colorado. The concentration of NH_4^+, NO_3^- and NO_2 in atmospheric samples is shown in Table 3.

Except for NH_4^+ and NO_3^- in precipitation, most of the results are preliminary. Hoering (1958) measured the $^{15}N/^{14}N$ for NH_4^+ and NO_3^-

Table 3. *Concentration of particulate NH_4^+, NO_3^- and NO_2 in atmospheric samples*

Date (1972)	Concentration ($\mu g/m^3$) NH_4^+	NO_3^-	NO_2	NH_4^+–N/NO_3^-–N
March 21–23	0.62	0.53	—	4.1
June 2–6	0.37	0.47	0.12	2.7
July 19–21	0.26	0.25	0.41	3.7
July 21–24	0.06	0.22	0.33	1.0
July 24–28	0.18	0.19	0.55	3.3
July 28–31	0.28	0.25	0.55	3.9

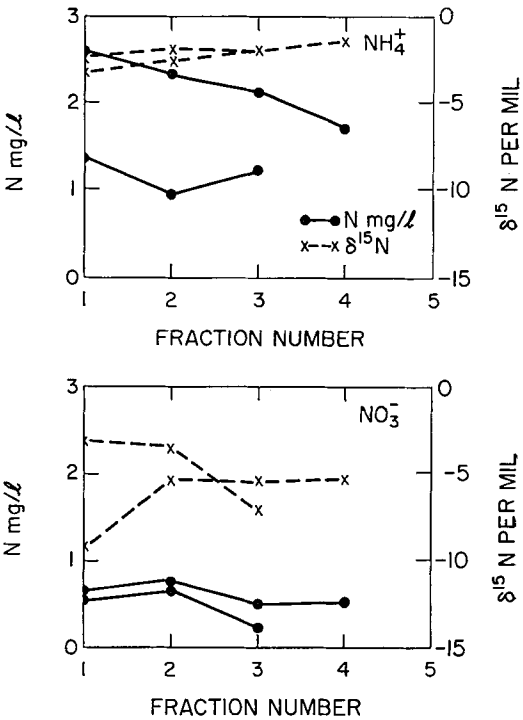

Fig. 2. Concentration of NH_4^+ and NO_3^- and $^{15}N/^{14}N$ ratios determined for a sequence of samples from rainfall.

in precipitation and concluded that the NO_3^- was due to oxidation of NH_3 as indicated by equations (2a) and (2b) and calculated a value of $\beta = 1.004_3 \pm 0.001_4$ from his measurements. Eriksson (1958) suggested an alternate reaction mechanism which involves no oxidation step, but rather involves equilibrium exchange between the gas and liquid phases for NH_3 and NO or NO_2, as indicated by equation (1). In order to test this possibility, Eriksson suggested measurement of these compounds in atmospheric samples. Hoering (1958) suggested a further test consisting of the analysis of a sequence of samples from the same rainfall. The $^{15}N/^{14}N$ ratio presumably would increase as the rainfall progresses if an equilibrium process is operative and should remain constant if the oxidation mechanism is correct. Another check would be to calculate β for a larger number of precipitation samples. Results of analyses of such samples are shown in Figs. 1 and 2.

The $^{15}N/^{14}N$ ratios for NH_4^+ and NO_3^- in precipitation have a much narrower range of values and for NH_4^+ are lower than ratios reported by Hoering. The mean value for β calculated for these samples is $1.002_4 \pm 0.001_5$. This value would tend to support Hoering's hypothesis. However a comparison of the $^{15}N/^{14}N$ ratio in NH_4^+ in particulate matter collected on filters, and in soil suggests that most of the particulate NH_4^+ in air is due to entrained soil particles and that the NH_4^+ in rain must come from another source, presumably NH_3 in the atmosphere. Unfortunately, no isotopic results have yet been obtained for atmospheric NH_3.

Cheng et al. (1964) indicate that the $^{15}N/^{14}N$ ratio for NO_3^- in soil (N-mineralized) varies between 1 and 6 per mil. A comparison of the $^{15}N/^{14}N$ ratio for NO_3^- in rain, in aerosols, and in soil again suggests that the NO_3^- in aerosols must be airborne soil and that the NO_3^- in rain must originate from NO or NO_2 in the atmosphere. The few results for the $^{15}N/^{14}N$ ratio in NO_2 (Fig. 2) would tend to confirm this finding. The equilibrium fractionation factor, α, for equation 1 is 1.005 (Kirshenbaum et al., 1947). No fractionation factor has been reported for the reaction involving NO_2, but if it is of the same magnitude, the $^{15}N/^{14}N$ ratio for NO_3^- in rain would be slightly higher than that of NO_2 in the atmosphere. Such appears to be the case. Calculation for α for the isotopic distribution of ^{15}N and ^{14}N in NO_2 between gas and liquid phases using the average value (Table 2) yields $1.003_2 \pm 0.002_1$.

The data in Table 3 also indicate that particulate NH_4^+ and NO_3^- in the atmosphere is due to the entrainment of soil particles. The ratio of NH_4^+–N to NO_3^-–N varies from 1 to 4.1. While this ratio might be expected to vary widely due to recent agricultural practices, these values do compare favorably with ratios of 2.2 to 4.9 found by Richardson (1938) in grassland soils in England.

The data in Fig. 2 suggests that the $^{15}N/^{14}N$ ratio for nitrogen in NH_4^+ increases as the rain progresses, but that the $^{15}N/^{14}N$ for NO_3^- does not vary in a regular manner. Also the $^{15}N/^{14}N$ ratio in NH_4^+ appears to increase as the concentration of NH_4^+ decreases, while the opposite applies for NO_3^-. A better understanding must await the analysis of a greater number of samples. However, it appears that the NH_4^+ and NO_3^- in rain result from the incorporation of NH_3 and NO_2 after the formation of water droplets. It is not yet clear whether or not oxidation of NH_3 accounts for an appreciable fraction of the NO_2 in the atmosphere, but the origin of NH_4^+ and NO_3^- in precipitation does not appear to be as simple a situation as that proposed by Hoering.

Future experimental studies must include analysis of a larger number of samples of greater variety. Also laboratory studies to determine the equilibrium and kinetic isotope fractionation factors are needed for comparison with possible fractionation processes which may occur in the atmosphere.

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ИЗОТОПНЫЕ ИЗМЕРЕНИЯ АТМОСФЕРНЫХ АЗОТНЫХ СОСТАВЛЯЮЩИХ

Представлен краткий обзор изотопных исследований азота, связанных с атмосферными составляющими. Описываются методы, используемые для сбора и превращений различных составляющих, содержащих азот, с целью проведения масс-спектрометрических измерений. Представлены предварительные результаты измерений концентраций и отношения $^{15}N/^{14}N$ в N_2, полученном из NH_4^+, NO_3^-, N_2O и NO_2, находящихся в атмосферных и других пробах. Обсуждаются кратко также результаты исмерений в отношении к NH^+ и NO_3^- из осадков.