ISC-882

Contribution No._____. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

The Absolute Abundance of the Nitrogen Isotopes in the Atmosphere and Compressed Gas from Various Sources

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ABSTRACT

The absolute abundance of the isotopes in atmospheric and commercial compressed N_2 from various sources has been determined. Nitrogen gas standards, prepared by mixing separated nitrogen isotopes in the form of $(NH_4)_2SO_4$ solutions, were employed to calibrate two 60° sector mass spectrometers. As a result, the absolute ratio of N^{14}/N^{15} in atmospheric nitrogen was found to be 272.0 ± 0.3. Small variations from this value were found for commercial compressed gas.

The mass spectrometric procedure used in determining the N_2^{29+}/N_2^{28+} ratio allowed for detection of differences to 1 part in 3500. However, the absolute accuracy of the abundance measurements was limited to 1 part in 1000 because of the semimicro Kjeldahl distillation employed to determine the amount of $(NH_4)_2SO_4$ present in the solutions of the separated isotopes.

In these measurements instrumental background played a very significant role. A reliable method of correcting the observed N_2^{29+}/N_2^{28+} ratio for the contribution of the background at these mass positions was developed.

INTRODUCTION

In 1950, A. O. Nier[1] published a value of 0.366% N^{15} for the absolute abundance of the nitrogen isotopes of the atmosphere. His result was based upon calibration of two mass spectrometers with mixtures of separated A^{36} and A^{40}. The basic assumptions made were that instrumental discriminations for the nitrogen isotopes were proportional to those observed for the argon isotope mixtures. Two instruments were used by Nier, one employing a viscous leak and one a molecular leak. In the case of the former, the assumption was made that ratio measurements were distorted because of gas flow according to the square root of the masses being measured, and corrections for this were applied. In the latter instrument, no correction for gas flow discrimination was applied and the gas in the ion source was assumed to be representative of that in the inlet manifold.

The availability of highly enriched isotopes of nitrogen from ion exchange columns[2] at the Ames Laboratory of the Atomic Energy Commission presented the opportunity of using N_2 standards to re-examine the absolute abundance of the nitrogen isotopes in the atmosphere and in other sources. Use of nitrogen standards required only the reasonable assumption that any discrimination errors made in obtaining the N_2^{29+}/N_2^{28+} ratio of the standards were of the same order of magnitude as those for the sample gas whose absolute N_2^{29+}/N_2^{28+} ratio was to be determined. Thus the assumptions made are reduced to a minimum and the error which could result from a possible small difference in the ionization efficiencies of the molecular nitrogen isotope species was eliminated. Re-examination of the nitrogen isotope abundance problem seemed profitable in view of recent mass measurements[3] of increased precision and the large range of values (265 to 274.5) which have been reported[1,4,5,6,7,8,9] for the N^{14}/N^{15} ratio of atmospheric nitrogen.

EXPERIMENTAL

Instruments

Two mass spectrometers were used in these experiments. Both were equipped with dual ion current collectors and "viscous" leaks. One of the instruments, MS-1, was built here several years ago and, with only a few minor changes, was patterned after the design published by Nier in 1947.[10] Changes made were the elimination of plate J_3 in the ion source; mounting the ion source directly on the analyzer instead of the tube flange; using Faraday cups instead of the flat plates for ion collectors and doubling the inverse feedback amplifier sensitivity by means of 8×10^{10} ohm input resistors. The second instrument, MS-2, was a Consolidated-Nier, Model 21-201 (Consolidated Electrodynamics Corporation, Pasadena, California) which was unaltered from the specifications given in the manufacturer's handbook supplied with the instrument. Both instruments make use of the null method for comparing ion currents but have provisions for single ion current collection.

Any difficulties in making absolute abundance measurements which depend upon a precise knowledge of the linearity of the input resistors were eliminated by employing calibration standards whose ion currents ratio were very close to those of the samples being measured. The background in the two instruments in the mass positions 28, 29 and 30 were different. In MS-1, the background at 28 was 5 parts in 10000 when a normal nitrogen pressure of 5.0 cm Hg was employed in the sample manifold, while that in MS-2 was 30 parts in 10000 under the same conditions. Backgrounds at the 29 and 30 positions in both instruments were 1 to 2 per cent of that in the 28 position. Because of the lower background, MS-1 was employed to assay the highly enriched N^{14} and N^{15} preparations. Only one collector was used in these analyses.

Preparation of the Standards

(1) Assay of N^{14} and N^{15} Solutions

Gaseous nitrogen samples were prepared by the hypobromite oxidation of the NH_4^+ ions in the N^{14} and N^{15} solutions of ammonium sulphate obtained by neutralizing the eluant from the ion exchange columns. Isotopic assays of N_2 prepared from these solutions were made on MS-1 because the background at the 28, 29 and 30 mass positions was appreciably lower than it was in MS-2, thereby decreasing uncertainties due to background. Since peaks due to N_2^{29+} and N_2^{30+} were very small in the N^{14}

preparations, and peaks due to N_2^{29+} and N_2^{28+} very small in the N^{15} preparations, corrections were made only for background and possible air contamination in the assays of these materials. Despite the fact that discrimination due to gas flow in the instruments probably existed in these cases, neglecting it introduced uncertainties in the results which had less effect on the mixed standards than did the Kjeldahl distillation used to determine the concentration of the NH_4^+ in the N^{14} and N^{15} solutions.

The constant for the expected distribution of the molecular species of nitrogen based on a random combination of N^{14} and N^{15} should have a value of 4. This has been shown to be true at room temperature from quantum mechanical considerations[11] for the equation $N_2^{28} + N_2^{30} \rightleftharpoons 2N_2^{29}$. It was experimentally demonstrated to be 3.99 ± .01 by work in these laboratories on mixtures containing 10 to 50% N^{15} where the uncertainties due to background were negligible. As a check on the reliability of the isotopic assay of both the N^{14} and the N^{15} preparations, a value for K was computed from the observed 28, 29 and 30 ion peak heights. In both cases a value less than 4 was obtained, which indicated the possibility of small contaminations in the mass 28 and 30 positions. Because of the size of peaks at these positions in highly enriched N^{14} and N^{15} preparations, the value of K is extremely sensitive to contaminants in the mass 30 and 28 positions, respectively.

In the N^{15} preparations, small amounts of impurities in the mass 30 position had a negligible effect on the value of K. If contaminations at 28 and 29 positions were assumed to be due to background and the presence of air, the 28 and 29 peaks could be corrected by observing the background after pumping out the sample gas and the A^{40+4} peak while the sample was in the instrument. Calculation of K using the corrected values gave values very near to or slightly greater than 4.0. These small variations were attributed to random reading errors made while taking the data. Despite these precautions, the actual value of the $\%N^{15}$ was changed less than 0.20% in all assays made on the enriched N^{15} preparations.

A small contamination in the mass 30 position had a similar effect on the value of K computed from the observed peaks of the N^{14} preparation. In assaying these materials the height of the 30 peak was greater than would be expected from the measured 29 and 28 peaks. For this reason only the 28 and 29 peaks were used, along with an assumed value of 4 for K, to compute the isotopic constitution of the N^{14} materials. No definite proof could be obtained that a contamination was not present at the 29 mass position. However, the consistent computed values of K and the difficulty of postulating a plausible reaction to produce a species of mass 29 during either the hypobromite oxidation of the NH_4^+ ions or in the mass spectrometer while the sample gas was being assayed, seemed to indicate that the detectable 29 mass current was produced solely by molecular nitrogen ions. A semi-micro Kjeldahl distillation was used to analyze these same N^{14} and N^{15} solutions for their total ammonium ion content. Numerous trial runs showed that the procedure gave consistent and accurate results to 1 part in 1000.

(2) Mixing of the Standards

The carefully assayed $(NH_4)_2SO_4$ solutions were mixed by weight to prepare standards #1 and #2, plus a series of solutions containing from 10 to 90% N^{15}. All of the information necessary to calculate the N^{15} abundance in the two standards and other mixed solutions is tabulated in Table I and Table II. Deviations stated in these tables and all subsequent tables, except where noted, are average deviations. Standard deviations were calculated only when sufficient data warranted such calculations.

Portions of the #1 and #2 solutions were oxidized by the hypobromite reaction and the gases produced were used as standards to establish the absolute isotopic abundances of several sources of nitrogen. As subsequent tables show, most of the measurements were made on MS-2 although, as mentioned earlier, the background at the 28 and 29 mass positions was much higher than on MS-1. This adverse effect of high background was partially compensated by the increased stability of MS-2 and the reliability of the background corrections, when these were necessary.

Table I

Assay of solutions of $(NH_4)_2SO_4$ enriched in N^{14} and N^{15}.

	$(NH_4)_2SO_4$ Enriched in N^{15}		$(NH_4)_2SO_4$ Enriched in N^{14}	
Runs	Kjeldahl analysis millieq/ gram soln x 10^4	At $\%N^{14}$ x 10^3 data from MS-1	Kjeldahl analysis millieq/ gram soln x 10^4	At $\%N^{15}$ x 10^4 data from MS-1
1	2398	198	2638	165
2	2393	207	2641	163
3	2393	212	-	165
4	-	207	-	166
5	-	210	-	176
6	-	-	-	152
Average	2395 ± 2.3	207 ± 4*	2640 ± 1.5	165 ± 4.5**

* This corresponds to 99.793 atoms % N^{15}

**This corresponds to 99.9835 atoms % N^{14}

If the magnitude of the 28 and 29 ion currents which yield the 29/28 ion ratios of both the standard and the sample gas whose abundance is to be determined are of the same order, then corrections for the background contribution to the observed ratios need not be applied. This ideal situation was achieved in most of the measurements by preparing standards #1 and #2 (see Table II) so that their isotopic abundance was near that of air and by removing the oxygen from the air samples by means of a mixture of sodium dithionite and the sodium salt of β-anthraquinone sulfonic acid known as Fieser's solution.[12] This procedure

Table II

Data used in mixing calibration standards and test solutions.

Solution No.	Grams N^{14} soln taken	Grams N^{15} soln taken	Calc'd % N^{15}*
Standard #1	35.83	0.1387	0.365_7
Standard #2	43.01	0.1983	0.4321
10	3.828	0.3997	8.650
20	3.343	0.8913	19.4_5
30	2.358	1.1081	29.8_4
50	1.4436	1.4433	47.4_7
60	1.4346	2.3687	59.8_5
60	1.2729	2.0803	59.6_0
70	0.9918	2.5664	69.9_9
90	0.4235	4.2093	89.8_3

* Absolute to 1/1000

has been shown to be non-fractionating by Soloway[9] whose observation was corroborated here. Removal of oxygen improves the mass spectrometer stability during the measurements and aids in attaining higher precision. It also removes the potential production of CO by reaction of carbon with O_2 in the ion source. The alkaline nature of Fieser's reagent removes CO_2 which might also introduce a small error in the 29/28 ratio measurement of atmospheric nitrogen. Then the absolute N^{14}/N^{15}

ratio of air (O_2 removed) or pure tank nitrogen was determined by comparison to the standard according to the following procedure:

1) The mass spectrometer was conditioned with pure tank N_2 at 5 cm pressure for at least two hours. This was necessary to stabilize the background in the desired mass region.
2) The sample gas to be measured was introduced into the inlet manifold at 5.00 ± 0.02 cm pressure and 5-8 minutes were allowed before making any measurements.
3) Four individual ratios were taken and the average of these was used as the observed ratio.

Three to five minutes were allowed for pump-out between samples and steps 2 and 3 of the above procedure were repeated in detail with the standard gas. The absolute ratio of the sample gas, (R_t), was then calculated using the equation:

$$R_t = \frac{R_{\text{std calc}}}{R_{\text{std obs}}} \times R_{\text{sample gas obs}}. \qquad (1)$$

A series of measurements of the N_2^{29+}/N_2^{28+} ratio of a sample gas containing impurities (5% O_2) were made to prove that accurate comparisons with a standard could be obtained if corrections were made for instrumental background. To make this correction it was necessary to measure the $29^+/28^+$ ratio and the 28^+ ion current of both background and the sample. Measurement of the latter was made at the time the ratio measurement was made. The $29^+/28^+$ ratio of the sample gas, (R_s), corrected for background contribution is given by

$$R_s = \frac{R_o - R_B(x)}{(1 - x)} \qquad (2)$$

where R_o = the observed $29^+/28^+$ ratio; R_B = $29^+/28^+$ ratio of background; x = fraction of total 28 ion current due to background at the 28 mass position; (1 - x) = fraction of total 28 ion current due to the sample gas. Table III shows the results of these measurements.

In this table, R_1 compares to R_3 within the limits of precision of the measurements. R_2 does not compare within these limits due to the systematic error caused by failure to correct for the background contribution to the observed ratios. The observed $29^+/28^+$ ratio of 0.015 for the background in MS-2 contributed to the observed ratio of both the standard and the tank containing the O_2 impurity, but to a different degree since the two gases were run at 5.0 cm total inlet manifold pressure. Thus the $R_{(t)}$ as determined by equation (1) was high due solely to the background.

If other contaminations are present in the sample, the error (caused by failure to correct for the background when making comparisons to a pure standard at the same inlet manifold pressure) will depend upon (1) the % contamination, (2) the background ratio and (3) the magnitude of the 28^+ ion current of the background with reference to the 28^+ ion current due to sample gas.

It should be kept in mind when considering data presented in the next section of this paper that the Kjeldahl analysis limited the absolute accuracy of results to 1 part in 1000. Despite this fact, the method of comparing the $29^+/28^+$ ratio of two sample gases with a standard was capable of precision much better than 1 part in 1000 during any series of determinations. Consequently the limits quoted in Tables III, IV and V are average deviations and are given as such in order to show the small variation in the $29^+/28^+$ ratio observed for nitrogen gas from various sources.

Table IV gives six individual results of a series of determinations of the $29^+/28^+$ ratio for a tank of Matheson prepurified nitrogen which was in our laboratory.

No corrections for background were necessary here because comparison was made to standard #1 and the gas was pure. This would also apply to the data in column three of Table III. The standards applied to the data in Table V had 29/28 ratios which were very close to those of the pure nitrogen samples in question. Therefore, it was also not necessary to apply background corrections to obtain these data. Table V shows the results for several commercial sources of nitrogen and air collected at various geographical sites and altitudes above these sites.

The #3 and #4 standards cited in Table V were prepared from solutions of ammonium sulfate less enriched in N^{15} than those used to prepare the #1 and #2 standards. The results obtained with these standards showed that their calculated ratios were consistent with the #1 and #2 standards. Like the "Matheson tank", they are actually secondary standards and the agreement of the #3 and #4 with the #1 and #2 standards may have been fortuitous since we had no absolute assurance that the mass spectrometric analysis of the N_2

gas prepared from the moderately enriched $(NH_4)_2SO_4$ solutions did not contain measureable discrimination errors.

Table III

N_2^{+29}/N_2^{+28} measurements on commercial tank N_2 containing 5 percent O_2*.

Runs	$R_1 \times 10^6$	$R_2 \times 10^6$	$R_3 \times 10^6$
1	7358	7362	7355
2	7352	7353	7355
3	7355	7359	7351
4	7359	7363	7353
5	7355	7359	
6	7356	7360	
7	7357	7361	
8	7363	7367	
9	7361	7369	
Average	7357 ± 2.6	7361 ± 3.1	7354 ± 1.5

* MS-2 was employed in these measurements and comparisons were made with Standard #1.

R_1 O_2 present, background correction applied to both standard and sample.

R_2 O_2 present, background correction not applied to either standard or sample.

R_3 O_2 removed by means of Fieser's solution; background correction not made.

Table IV

N_229^+/N_228^+ measurement on Matheson prepurified N_2*.

Date	$R_t \times 10^6$	Date	$R_t \times 10^6$
2-18-57	7326	2-20-57	7328
2-18-57	7323	2-20-57	7325
2-18-57	7325	3-14-57	7326
		Average	7326

Average deviation = 1.1

Standard deviation = 1.6

* Measurements on MS-2; comparisons were made to Standard #1.

Table V

N_229^+/N_228^+ measurements on N_2 from various sample gases*.

Nitrogen sample	Runs	MS used	Std used	$R_t \times 10^6$
Matheson** prepurified tank	6	MS-2	#1 - 6 runs	7326 ± 1
Matheson prepurified tank	5	MS-1	#1 - 3 runs #2 - 2 runs	7329 ± 6
Linde purified tank	3	MS-2	#4 - 2 runs #3 - 1 run	7303 ± 4
Linde purified tank	4	MS-1	#3 - 4 runs	7303 ± 5

Table V (Continued)

Nitrogen sample	Runs	MS used	Std used	$R_t \times 10^6$
Puritan Sales≠ Commercial tank 5%O_2	4	MS-2	#1 - 4 runs	7354 ± 2
Oxidized $(NH_4)_2SO_4$ Baker and Adamson reag. grade	4	MS-2	Matheson prepurified tank	7630 ± 1
Air# Ames, Iowa	4	MS-2	Matheson prepurified tank	7352 ± 1
Air# Moosonee Bay, Ontario	4	MS-2	Matheson prepurified tank	7351 ± 1
Air# 3000 ft above Kansas City, Missouri	4	MS-2	Matheson prepurified tank	7351 ± 2
Air# 18,000 ft above Leavenworth, Kansas	4	MS-2	Matheson prepurified tank	7350 ± 1
Air# 36,000 ft above Des Moines, Iowa	4	MS-2	Matheson prepurified tank	7350 ± 2

* These analyses were made during the period starting 2/18/57 and ending 5/30/57.

** Summary of data presented in Table IV.

≠ O_2 removed by means of Fieser's solution; summary of data in Table III.

\# O_2 removed by means of Fieser's solution.

From the abundance data for the nitrogen of the air given in Table V, an absolute N^{14}/N^{15} ratio of 272.0 ± 0.3 was computed. This compares favorably with Nier's value of 273 ± 1 for the same measurement. The present limits of precision however produced a value for the physical atomic weight of nitrogen where the uncertainty in the calculated value was not due to uncertainties in the abundance data if the most recent mass measurements[3] for N^{14} and N^{15} were employed. The results of these calculations, in which Nier's value and the N^{14}/N^{15} ratio of 272.0 ± 0.3 reported here were used, are given in Table VI.

Table VI

Physical atomic weight of nitrogen*.

N^{14}/N^{15} Ratio	Physical atomic wt
273 ± 1	14.011190 ± 14
272.0 ± 0.3	14.011204 ± 4

* Masses of N^{14} = 14.007551 ± 4 and N^{15} = 15.004905 ± 6 of Ogata and Matsuda[3] were employed to calculate values given in this table.

The value of the chemical atomic weight is not affected by these results due to the greater uncertainty of the conversion factor.

The results obtained on MS-1 and MS-2 for the various other mixtures of N^{14} and N^{15} solutions listed in Table II appear in Table VII. The amount of N^{15} was calculated from the observed 28, 29 and 30 ion currents corrected for the background ion currents observed 3 minutes after pump-out of the sample gas. The amount of N^{15} calculated after correcting the observed data for air contamination is also given as well as the results calculated when the observed data were corrected for gas flow discrimination using the assumption that the magnitudes of the observed ion currents are distorted according to the square roots of the masses under consideration.

Table VII

Atoms $\%N^{15}$ in mixtures made with separated isotopes.

Calc'd % N^{15} *	A		B		C	
	MS-1	MS-2	MS-1	MS-2	MS-1	MS-2
8.65	8.68	8.77	8.68	8.80	8.55	8.67
19.45	19.42	19.65	19.42	19.75	19.16	19.48
29.84	29.90	30.09	29.90	30.16	29.55	29.80
47.47	47.58	47.70	47.58	47.86	47.15	47.43
59.85	60.02	59.95	60.02	60.33	59.61	59.91
59.60	59.66		59.87		59.46	
69.99	69.91	69.92	69.91	70.12	69.54	69.75
89.83	89.74	89.45	90.00	89.76	89.58	89.83

* Data from Table II

A - Corrections made for background at 28, 29 and 30 mass positions.

B - Correction made for background and air contamination based on measurement of A^{40+} peak.

C - Correction made for background, air contamination and the assumption that the observed peak heights were distorted according to the square root of masses involved due to gas flow in the instrument.

In making the assays of the sample gases listed in Table VII, sufficient time for the background to stabilize was allowed after the sample was admitted and before data were taken. In a tight vacuum system, under conditions where no reactions take place in the instrument, this instability is due primarily to adsorbed gases. During this time, exchange takes place between the incoming molecules and those adsorbed in the various components of the instrument. An apparent elution of adsorbed gases takes place. This was indicated by the results of an experiment where purified argon[13] was introduced into the mass spectrometer at 5.0 cm manifold pressure and the 28^+ peak monitored. Immediately after introducing the argon, the height of the 28^+ peak rose sharply, approximately doubling in size. Only after 10-15 minutes did the peak height fall to a size near its original value when it remained constant, even after pump-out.

The peak heights observed during any gas assay include ions originating from both sample and adsorbed gases. When assaying gases of varying composition in the instruments at this Laboratory, 10-15 minutes were usually required before the spectrum stabilized. At this time the distribution of molecules representing the adsorbed gases approach those of the sample. For this reason any background corrections should be based upon peak heights measured after the sample has been pumped from the instrument. Consistent results are obtained in this manner and the background correction is reliable.

The data in Table VII indicate that it may not be strictly valid to assume that gas flow in viscous leaks is the same for all leaks. Rather, gas flow may vary according to the exact conditions existing in particular instruments. The basic difference between MS-1 and MS-2 was that the amplifiers in the former were twice as sensitive as those in the latter. Since the mode of operation involved observing 28^+ peaks of similar size on both instruments, the constriction at the end of the capillary comprising the "viscous leak" of MS-1 was smaller than that in MS-2. Sample pressure in the manifold was the same for both instruments as were the lengths and diameters of the capillaries. The difference in constriction size was apparently great enough to alter sufficiently the flow characteristics in the capillaries so that the simple assumption is not completely valid that correction for molecular pump-out from the ion source can be made by using the square roots of the masses involved. Thus flow through the leak in MS-1 was not purely viscous while that through the leak of MS-2 probably was viscous. In the absence of calibrating media as presented here, corrections based on simple assumptions regarding the nature of gas flow in various mass spectrometer inlet systems may lead to greater uncertainties than those which might arise if no corrections were applied.

The close agreement between Nier's results for the normal isotopic abundance of the nitrogen isotopes and those reported here indicate that uncertainties in his basic assumptions were not great. However, deviations in other values for the isotopic abundances of nitrogen which have appeared in the literature are probably due to variations in gas flow conditions existing in the various mass spectrometers on which those measurements were made, in addition to other discriminating factors which may result from source geometry.

SUMMARY

The abundance of the nitrogen isotopes in several sources of nitrogen have been determined. In atmospheric nitrogen the absolute ratio of N^{14}/N^{15} is 272.0 ± 0.3. Small variations were observed in various sources of compressed gas. The abundance of the N_2 isotopes in air, which is constant to 1 part in 7000 in samples collected from various sites and altitudes, supports the findings of Dole et al.[14]

ACKNOWLEDGEMENTS

The authors wish to acknowledge the cooperation and assistance of Drs. F. H. Spedding and J. E. Powell who aided in obtaining the separated isotopes. The assistance of Drs. Harvey Diehl and John F. Smith for their help in collecting some of the air samples is also acknowledged.

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