ISC-1138
CHEMISTRY-GENERAL

NITROGEN ISOTOPE ABUNDANCE MEASUREMENTS

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November 1958

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UNITED STATES ATOMIC ENERGY COMMISSION • OFFICE OF TECHNICAL INFORMATION

F. H. Spedding, Director, Ames Laboratory.

Work performed under Contract No. W-7405-eng-82.

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Printed in USA. Price $1.00. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

USAEC Office of Technical Information Extension
Oak Ridge, Tennessee

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Nitrogen Isotope Abundance Measurements*

Gregor Albert Junk and H. J. Svec

Abstract

The abundance of the nitrogen isotopes in several sources of nitrogen have been determined. In atmospheric nitrogen the absolute ratio, N^{14}/N^{15}, is 272.0 ± 0.3. Small variations were observed for various sources of compressed gas but the isotopic composition of the nitrogen isotopes of the atmosphere was constant, to 1 part in 7000, in samples collected at different geographical sites and altitudes above these sites.

A procedure for the determination of the absolute abundance by dual collection of the 28^+ and 29^+ ion currents is given along with a method of circumventing the ever present background problem in nitrogen abundance determinations. Proper procedures to be employed when assaying enriched nitrogen preparations and samples containing normal nitrogen mixed with another gas such as oxygen are described.

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*This report is based on an M. S. thesis by Gregor Albert Junk submitted November, 1958, to Iowa State College, Ames, Iowa. This work was done under contract with the U. S. Atomic Energy Commission.

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I. HISTORICAL REVIEW

A general review of the developement of the atomic theory reveals that in 1803, Dalton presented the first correct ideas concerning the elements or "fundamental particals". Prout later suggested that since all elements had atomic weights which were exact multiples of hydrogen, the elements were made up of varying amounts of hydrogen. For some time Prout's hypothesis seemed reasonable because many of the first atomic weight determinations by Berzelius were not exact. When the atomic weights were redetermined more carefully with pure elements and proven to be fractional in some cases, Prout's hypothesis was abandoned.

It was not possible to study the problem of non-integral weights of the elements by chemical means since, by definition, the elements were made up of atoms of similar chemical properties. One must realize that Avogadro's ideas of "integral molecules" and "elementary molecules" were not conclusively proven and accepted during this period and that the chemists of this time had few concrete ideas concerning atomic structure. They were convinced, however, that all elements were separated by their different chemical behavior and, in each case, different atomic weight. Therefore, it was difficult for them to reconcile and accept the hypothesis of Crookes when in 1886 he proposed that it was conceivable that calcium could be a mixture of atoms or unit particles whose atomic weights were 39, 40 and 41 or even 38, 40 and 42. In view of these facts it is not surprising that a controversy centering around fractional atomic weights existed among leading chemists during the 19th century.

After the discovery of radioactivity, chemists realized that atoms which have similar chemical behavior could have different properties such as radioactivity and atomic weight. The idea was soon carried over to the non-radioactive elements and scientists gradually became converted to the concept of isotopes. This conversion was accelerated when J. J. Thomson published his results obtained with neon in a positive ray tube. Any remaining doubt was completely removed when Aston in 1919, proved conclusively that two stable isotopes of neon existed.

After 1910, various researchers in this country and in Europe constructed instruments for the observation of positive rays. Some investigators constructed their instruments in such a manner that absolute atomic masses could be determined. Such instruments are generally known as mass spectrographs. Dempster (3), in 1918 constructed an instrument which was capable of isotope abundance determinations and today similar instruments are generally distinguished from those used for atomic mass determinations by the designation, mass spectrometer. With mass spectrometers, the early researchers were able to make fast and fairly accurate abundance determinations.

By 1935, due primarily to the untiring efforts of the early investigators, the abundance of all the stable isotopes of the elements had been determined. Improved measurements have appeared from time to time since then, but even if the magnitude of the early isotopic compositions were slightly in error, at least the scientists had observed all the stable isotopes of the then known elements less than two decades after the pioneering work of Aston and Dempster.

Following the initial work on the abundance of the atoms of the elements, investigators turned their attention to other applications for mass spectrometers such as direct gas analysis, ionization potential measurements, tracer technique measurements, the determination of bond strengths, and more recently, the reactions of gaseous ions. However, prior to 1950, many results were obtained and interpreted without regard to discriminations and errors in technique which occur and lead to inaccurate observations. Even though all the modern reviews on the subject of mass spectrometry stress technique and discrimination errors which arise due to gas flow, source geometry, and lack of experience with mass spectrometric procedures, some work has been published in the literature where these errors have been ignored or have been assumed negligible without proof. In 1950, Nier (8) was the first to experimentally study gas flow discrimination effects in abundance determinations when he worked with mixtures of separated argon isotopes. A study of the literature on abundance determinations reveals that argon is the only element whose absolute abundance has been determined entirely free of any possible discrimination errors.

A discussion of the developement, the design, the general operation, the theory and the applications of mass spectrometers is not necessary here, since these are well presented in two recent books (1, 5) covering the field.

II. DEFINITION OF TERMS

1. Discrimination--- any effect which yields ion currents not representative of the sample material introduced into the instrument.
2. Source Discrimination--- ion currents whose magnitudes are distorted due to the geometry of the source and the applied fields.
3. Gas Flow Discrimination--- ion currents whose magnitudes are distorted due to a non-representative sample of the gas in the ion source caused by the character of the gas flow into and out of the source region.
4. Viscous Leak--- a device, usually employing a fine metal or glass capillary of suitable dimensions such that no fractionation of the different mass species in a mixture occurs as a result of gas flow.
5. Molecular Leak--- a device consisting of a large volume, low pressure gas reservoir separated from the ion source by means of an orifice. The dimensions of the orifice are so small compared to the mean free path of the gas molecules at the reservoir pressure that effusive flow through the orifice occurs. Under these conditions the rate of flow of any one component of a mixture of gases of different masses is inversely proportional to the square root of its mass and fractionation results.

6. Source--- the component of the mass spectrometer which produces the positive ions and then accelerates and collimates them.

7. Collector--- the component of the mass spectrometer used for the collection of the beam of positive ions.

8. Peak--- a term used synonymously with positive ion current.

9. Background--- the ion currents observed when no gas other than the residual and absorbed gases are present in the mass spectrometer.

10. Abundance--- the composition of the stable isotopes of any one element measured in atom %.

11. Atom % N^{15}--- atom % N^{15} is defined as the

$$\frac{\text{Number } N^{15} \text{ atoms x } 100}{\text{Number } N^{15} \text{ atoms} + \text{Number } N^{14} \text{ atoms}} .$$

12. Ionization Efficiency--- the ratio of the number of positive ionic species to the number of molecular species such as N_2^{28+}/N_2^{28}. Thus, if equal numbers of N_2^{28}, N_2^{29} and N_2^{30} molecules are present in the ion source, one would expect to observe equal numbers of N_2^{28+}, N_2^{29+} and N_2^{30+} ions, provided all three molecular species have exactly the same ionization efficiencies.

III. INTRODUCTION

In 1950, A. O. Nier (8) published a value of 0.366 atom % N^{15} for the absolute abundance of the nitrogen isotopes of the atmosphere. This value was based upon the 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. Of the two instruments used, one employed 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 effusive gas flow out of the ion source, and corrections for this were applied. Nier was able to show, by means of synthetic mixtures of 97 atom % A^{36} and 99.8 atom % A^{40}, that the simple effusive gas flow correction was slightly in error. He extrapolated his correction factor for mass 36 and mass 40 to mass 28 and mass 29 in order to get the absolute N_2^{29}/N_2^{28} ratio for nitrogen. In the instrument which employed the molecular leak, no corrections for gas flow discriminations were applied and the gas in the ion source was assumed to be representative of that in the inlet manifold. This assumption was supported within the experimental limits of detection by the results obtained with the argon isotope mixtures.

The availability of highly enriched isotopes of nitrogen from ion exchange columns (14) at the Ames Laboratory of the Atomic Energy Commission presented the opportunity of using N_2 standards to re-examine the problem of 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+} ion current ratios 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. Schaeffer (11) has shown that fragmentation patterns for the different molecular species of nitrogen are different and it seems reasonable that small differences might also exist in the ionization efficiencies. Re-examination of the nitrogen isotope abundance problem seemed profitable in view of recent mass measurements (10) of increased precision and the large range of values (265 to 274.5) which have been reported (7, 8, 12, 13, 16, 17, 18) for the N^{14}/N^{15} ratio for atmospheric nitrogen. Any agreement between the reported literature values given above is only fortuitous since all the investigators, exclusive of Nier, had no criteria for judging the discrimination effects caused by gas flow and/or source geometry. Even Nier ignored the possible difference in the ionization efficiencies for the isotopic species in all the elements he studied, except argon.

IV. EXPERIMENTAL

A. 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 build at the Ames Laboratory of the Atomic Energy Commission several years ago and, with only a few minor changes was patterned after the design published by Nier in 1947 (9). 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 commercial dual-collector instrument (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.

B. Preparation and Assay of the Standards

Gaseous nitrogen samples were prepared by the hypobromite oxidation of the NH_3 from the N^{14} and N^{15} solutions of ammonium sulfate obtained by neutralizing the eluant from the ion exchange columns. This oxidation has been investigated and reported by Clusius (2) and proceeds by way of equation 1.

$$2NH_3 + 3BrO^- = N_2 + 3H_2O + 3Br^- . \qquad (1)$$

The atomic nitrogen produced by the action of BrO^- on NH_3 combines at random to form the molecular nitrogen. The constant for the expected distribution of the molecular species of nitrogen based on this random combination of N^{14} and N^{15} should have a value of 4. This can be shown mathematically by letting α equal the fraction of N^{14} atoms and $(1 - \alpha)$ equal the fraction of N^{15} atoms before they combine to form the molecular nitrogen. The binomial theorem is applied to these atomic fractions to obtain the molecular fractions of α^2 for the N_2^{28}, $2\alpha(1 - \alpha)$ for the N_2^{29} and $(1 - \alpha)^2$ for the N_2^{30}. Substitution of these molecular fractions in the equation which gives the equilibrium constant,

$$K = \frac{\left[N_2^{29}\right]^2}{\left[N_2^{28}\right] \cdot \left[N_2^{30}\right]} , \qquad (2)$$

gives

$$K = \frac{\left[2\alpha(1 - \alpha)\right]^2}{(\alpha)^2 \, (1 - \alpha)^2} . \qquad (3)$$

This reduces to

$$K = 4 \quad . \qquad (4)$$

Urey and Greiff (15) have made a quantum mechanical calculation of the equilibrium constant and report a value of 3.998 at 25°C.

Because the background at the 28, 29 and 30 mass positions was appreciably lower in MS-1 than it was in MS-2, isotopic assays of the N_2 prepared from the highly enriched ammonium sulfate solutions were made on MS-1 using only the number 2 collector. Thus the uncertainties due to the background were minimized. As a check on the reliability of the isotopic assays of both the enriched N^{14} and N^{15} preparations, a value for K was computed from the observed 28^+, 29^+ and 30^+ peaks. In both cases when the mass spectrometric data were corrected only for the background, a value of less than 4 was obtained. This indicated that small contaminations in the mass 28 and/or 30 positions were present. Because of the small size of the N_2^+ ion currents at these positions in highly enriched N^{14} and N^{15} preparations, the value of K is extremely sensitive to even small amounts of contaminants which produce peaks in the mass 30 and mass 28 positions, respectively. This can be seen by examining equation 2 above.

In the highly enriched N^{15} preparation, the presence of small amounts of impurities producing peaks at the mass 30 position had a negligible effect on the value of K. If part of the ion currents at the 28 and 29 mass positions were assumed to be due to the presence of a small amount of air in addition to the background, the 28^+ and 29^+ ion currents could be corrected by observing the A^{40+} ion current (7) while the sample was in the instrument and the background after it had been removed. The correction for the presence of air using the A^{40+} ion current depends upon a previously determined A^{40+}/N_2^{28+} ion current ratio for air and an approximate knowledge of the isotopic nitrogen composition for air. After the data were corrected for background and the presence of air, the calculation of K gave values very near to, or slightly greater than 4.0. These small variations could be attributed to random reading errors made while taking the data.

A small contamination in the mass 30 position had a similar effect on the value of K computed from the observed peaks of the enriched N^{14} preparation. In assaying this material the height of the mass 30 peak was greater than would be expected from the measured 29 and 28 peaks. The excess 30^+ ion current could be due to the NO^+ fragment produced by electron bombardment of the N_2O which according to Clusius (2) is produced during the hypobromite oxidation in greater or less quantity. For this reason only, the 28^+ and 29^+ ion currents as observed on the number 2 collector of MS-1 were used, along with a value of 4 for K, to compute the isotopic constitution of the enriched N^{14} preparation. With this method of computation, the atom % N^{15} is calculated by substitution in the equation

$$\text{Atom \% } N^{15} = \frac{R}{2 + R}, \qquad (5)$$

where R is obtained by dividing the 29^+ by the 28^+ ion current.

This formula can be easily derived by combining equation 2 with the general equation used for the calculation of the atom % N^{15} from the observed 28, 29 and 30 peaks of a N_2 sample. This general equation is

$$\text{Atom \% } N^{15} = \frac{N_2^{30} + 1/2\ N_2^{29}}{N_2^{28} + N_2^{29} + N_2^{30}}. \qquad (6)$$

No definite proof could be obtained that a contamination was not present at the mass 29 position. However, the consistently low values computed for K and the difficulty of postulating a plausible reaction to produce a species of mass 29 during either the hypobromite oxidation of the NH_3 or in the mass spectrometer while the sample was being assayed, indicated that the detectable 29^+ ion current was produced solely by molecular nitrogen ions.

Despite the fact that discriminations due to gas flow and ion source geometry probably existed during the abundance determinations on the highly enriched N^{14} and N^{15} preparations, neglecting it introduced uncertainties in the final results which had less effect on the mixed standards than did the Kjeldahl distillation used to determine the concentration of NH_4^+ in the N^{14} and N^{15} solutions. The error caused by discrimination is one of constant proportion, that is, the ion currents can be corrected at any isotopic composition by multiplying the observed ion currents by constant factors. With assumed factors the error caused by discrimination can be calculated at various isotopic compositions. Such calculations were carried out using the factors of 1.000, 1.018 and 1.035 for the 28, 29 and 30 isotopes of nitrogen, respectively. Figure 1 shows that the maximum error would be made at 50 atom % N^{15} and that the error decreases as 100 atom % of either atomic nitrogen isotope is approached. Above 99 atom % N^{15} the error is less than 1 part in 4000 for the isotopic composition of the N^{15} isotope. The same is true for the N^{14} isotopic composition if the gas is above 99 atom % N^{14}. Since the enriched N^{14} and N^{15} solutions which were used to prepare the standards in this work were 99.9835 atom % N^{14} and 99.793 atom % N^{15}, it was not necessary to correct the mass spectrometer data for discrimination effects.

A semi-micro Kjeldahl steam distillation was used to determine the total NH_4^+ concentration in the highly enriched N^{14} and N^{15} solutions. The NH_3 liberated by the steam dis-

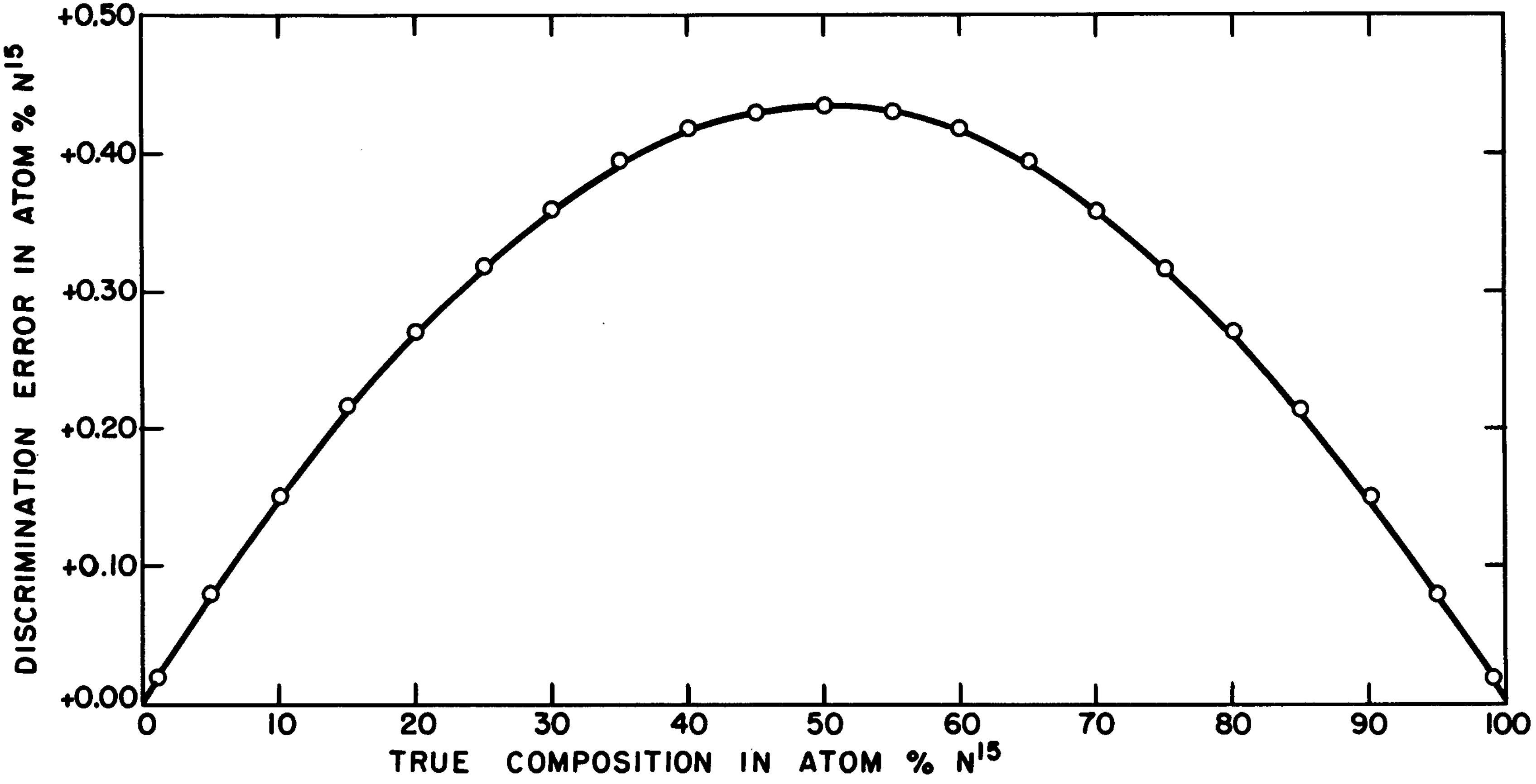

Figure 1. Discrimination error in nitrogen abundance determinations

tillation was absorbed in a boric acid solution containing methyl purple indicator. The first appearance of a grey tinge during the titration with a standard solution of HCl was taken as the end point. Numerous trial runs, using dilute (0.1 N) solutions of reagent grade ammonium sulfate, showed that the Kjeldahl procedure gave consistent and accurate results to 1 part in 1000.

C. Mixing of the Standards

The $(NH_4)_2SO_4$ solutions, which were carefully assayed for both the isotopic composition and concentration of NH_4^+, were mixed by weight to prepare standards #1 and #2, plus a series of solutions containing from 10 to 90 atom % 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 1 and Table 2. 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.

Table 1. Assay of solutions of $(NH_4)_2SO_4$ enriched in N^{14} and N^{15}

Runs	$(NH_4)_2SO_4$ Enriched in N^{15}		$(NH_4)_2SO_4$ Enriched in N^{14}	
	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[a]	2640 ± 1.5	165 ± 4.5[b]

[a] This corresponds to 99.793 atom % N^{15}.

[b] This corresponds to 99.9835 atom % N^{14}.

Table 2. Data used in mixing calibration standards and test solutions

Solution No.	Grams N^{14} soln taken	Grams N^{15} soln taken	Calc'd % $N^{15\,a}$
Standard #1	35.83	0.1387	0.3657
Standard #2	43.01	0.1983	0.4321
10	3.828	0.3997	8.650
20	3.343	0.8913	19.45
30	2.358	1.1081	29.84
50	1.4436	1.4433	47.47
60	1.4346	2.3687	59.85
60	1.2729	2.0803	59.60
70	0.9918	2.5664	69.99
90	0.4235	4.2093	89.83

[a] Absolute to 1 part in 1000.

D. Mass Spectrometric Procedures and Discussion

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 with MS-2 although, as mentioned earlier, the background at the 28 and 29 mass positions was higher than in MS-1. This adverse effect of high background was compensated by the increased stability of MS-2 and the procedure employed. It should be noted that the procedure adopted is such that background corrections are not necessary in the determination of the absolute 29/28 ratio of pure nitrogen gas whose N^{15} abundance is near that of the standard.

If the magnitude of the 28^+ and 29^+ ion currents which yield the $29^+/28^+$ ion current 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. In such case the error which the background causes in the abundance determination of the unknown is exactly the same error which occurs with the standard whose isotopic composition is known. The ideal situation[1] of approximately equal 28^+ ion currents for both the standard and the unknown was achieved in all of the $29^+/28^+$ ion current ratio measurements by preparing standards #1 and #2 (see Table 2) so that their isotopic abundance was near that of atmospheric nitrogen. Equal 28^+ ion currents for atmospheric nitrogen and the standard, when both were run at the same inlet manifold pressure, were achieved by removing the oxygen from the air samples by means of a solution of potassium hydroxide, sodium dithionite ($Na_2S_2O_4$) and the sodium salt of β -anthraquinone

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[1] The situation is called ideal because background corrections are not necessary and a precise knowledge of the behavior of the input resistors of the mass spectrometer amplifiers is not required under these conditions.

sulfonic acid known as Fieser's solution (6). This procedure has been shown to be non-fractionating by Soloway (13), whose observation was corroborated here. Removal of the oxygen greatly improved the mass spectrometer stability during the measurements and aided in attaining higher precision. It also removed the potential production of CO by a reaction of the carbon in the filament of the ion source with the oxygen. The alkaline nature of Fieser's reagent also removed CO_2 which can introduce small errors in the $29^+/28^+$ ion current ratio because of the CO^+ ion fragment which forms when CO_2 is subjected to electron bombardment. After exposing an air sample to Fieser's solution for a period of 1/2 hour, during which time constant stirring was employed, the gas (O_2 removed) was introduced into the mass spectrometer. Its absolute abundance was determined by comparison to a standard of approximately the same isotopic composition. The procedure was as follows.

1. The mass spectrometer was conditioned with pure tank N_2 or atmospheric N_2 (O_2 removed) at 5 cm. inlet manifold pressure for at least 2 hours. This was necessary to stabilize the background in the desired mass region.
2. After the conditioning gas was removed, the sample gas to be measured was introduced into the inlet manifold at 5.00 cm. pressure. Five to eight minutes were allowed to insure gas flow equilibration before any measurements were made.

3. Four individual ratios were taken and the average of these was used as the observed ratio.
4. Three to five minutes were allowed for pump-out of the sample gas and steps 2 and 3 were repeated in detail with the standard gas.
5. The absolute N_2^{29}/N_2^{28} ratio of the sample gas, (R_t), was calculated using the equation

$$R_t = \frac{R_{\text{std calc}}}{R_{\text{std obs}}} \times R_{\text{sample gas obs}} \quad , \qquad (7)$$

where $R_{\text{std calc}}$ refers to the calculated 29/28 ratio of the standard which is a known, absolute value. $R_{\text{std obs}}$ refers to the observed $29^+/28^+$ ion current ratio of the standard.

The isotopic assays of all the nitrogen standards listed in Table 7 were made, using only the #2 collector, by means of both magnetic and voltage scanning. In these assays the background observed after running the sample gas was subtracted from the observed 28^+, 29^+ and 30^+ ion currents. Corrections for discrimination were also applied.

V. RESULTS AND DISCUSSION

A series of measurements of the N_2^{29+}/N_2^{28+} ion current ratio of a sample gas containing an impurity (5% O_2) were made to prove that accurate comparisons with a standard could be obtained if corrections were properly applied for instrumental background. To make this correction it was necessary to measure the $29^+/28^+$ ion current ratio and the 28^+ ion current of both the background and the sample. Measurement of the 28^+ ion current was made at the time the ratio measurement was made. The $29^+/28^+$ ion current ratio of the sample gas, (R_S), corrected for background is obtained by substitution in the following equation 8,

$$R_S = \frac{R_O - R_B\,(X)}{(1 - X)} \quad . \qquad (8)$$

Here R_O equals the observed $29^+/28^+$ ion current ratio; R_B equals the $29^+/28^+$ ion current ratio of the background; X equals the fraction of the total 28^+ ion current due to background at the 28 mass position; (1 - X) equals the fraction of the total 28^+ ion current due to the sample gas. It is assumed that the background doesn't change when a sample gas is in the mass spectrometer. Table 3 shows the results of these measurements.

Table 3. N_2^{29+}/N_2^{28+} measurements on commercial tank N_2 containing 5 per cent O_2[a]

Runs	$R_1 \times 10^6$ [b]	$R_2 \times 10^6$ [c]	$R_3 \times 10^6$ [d]
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

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

[b] R_1 O_2 present, background correction applied to both standard and sample and equation 7 used to calculate R_1.

[c] R_2 O_2 present, background correction not applied to either standard or sample. Equation 7 was used to calculate R_2.

[d] R_3 O_2 removed by means of Fieser's solution; background not necessary because both the standard and tank N_2 were pure. Equation 7 used to calculate R_3.

In this table, R_1 compares to R_3 (the true N_2^{29}/N_2^{28} ratio) within the limits of the 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. An observed $29^+/28^+$ ion current 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 the same total inlet manifold pressure of 5.0 cm. Because of this, R_2 was too high due to the effect of the background.

It can be said that if 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 amount of the contamination, (2) the background ratio and (3) the magnitude of the 28^+ ion current of the background in proportion to the 28^+ ion current due to the sample gas. Thus equation 7 cannot be applied indiscriminately to a N_2 sample containing other gases if an absolute N_2^{29}/N_2^{28} ratio is to be determined. If possible the contaminant should be removed. If removal of the contaminant is not possible then the comparison of the unknown to the standard should be carried out using the procedure for background corrections as outlined above. If the contaminant is not removed or the data are obtained without regard to the background, what appears to be a difference in abundance may not be real as Table 3 illustrates.

It should be kept in mind when considering the data presented in the next section of this paper that the Kjeldahl analysis limited the absolute accuracy of the results to 1 part in 1000. Despite this limitation, the method of comparing the $29^+/28^+$ ion current 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 values given in Tables 3, 4 and 5 are not absolute to the limits quoted. The limits listed are those obtained from a number of comparisons with the standard and are given as such in order to show the small variation in the $29^+/28^+$ ion current ratio observed for nitrogen gas from various sources.

Table 4 gives six individual results of a series of determinations of the $29^+/28^+$ ion current ratio for a particular tank of Matheson prepurified nitrogen which was in the Ames Laboratory of the Atomic Energy Commission.

Table 4. $N_2^{29^+}/N_2^{28^+}$ measurement on Matheson prepurified N_2[a]

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

[a] Measurements on MS-2; comparisons were made to Standard #1.

This Matheson tank was used as a secondary standard in the determination of the absolute abundance of several commercial sources of N_2 and air collected at various geographical sites and altitudes above these sites. These results are listed in Table 5. No corrections for background were necessary in obtaining the data given in Table 4 because comparison was made to standard #1 and the Matheson nitrogen was pure. The standards applied to the data in Table 5 had $29^+/28^+$ ion current ratios which were very close to those of the pure nitrogen samples in question. Again it was not necessary to apply background corrections to obtain these data.

Table 5. N_2^{29+}/N_2^{28+} measurements on N_2 from various sample gases[a]

Nitrogen samples	Runs	MS used	Std used	$R_t \times 10^6$
Matheson[b] 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
Puritan Sales[c] Commercial tank 5% O_2	4	MS-2	#1 - 4 runs	7354 ± 2
Oxidized $(NH_4)_2SO_4$ Baker and Adamson rgt. grade	4	MS-2	Matheson prepurified tank	7630 ± 1
Air[d] Ames, Iowa	4	MS-2	Matheson prepurified tank	7352 ± 1

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[a] These analyses were made during the period starting 2-18-57 and ending 5-30-57.

[b] Summary of data presented in Table 4.

[c] O_2 removed by means of Fieser's solution; summary of data in Table 3.

[d] O_2 removed by means of Fieser's solution.

Table 5. (Continued)

Nitrogen sample	Runs	MS used	Std used	$R_t \times 10^6$
Air[d] Moosonee Bay, Ontario	4	MS-2	Matheson Prepurified tank	7351 ± 1
Air[d] 3000 ft above Kansas City, Missouri	4	MS-2	Matheson Prepurified tank	7351 ± 2
Air[d] 18,000 ft above Leavenworth, Kansas	4	MS-2	Matheson Prepurified tank	7350 ± 1
Air[d] 36,000 ft above Des Moines, Iowa	4	MS-2	Matheson Prepurified tank	7350 ± 2

The #3 and #4 standards cited in Table 5 were prepared from a solution of ammonium sulfate much less enriched in the N^{15} isotope (25 atom % N^{15}) and a solution containing 99.9835 atom % N^{14}. 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 observed agreement of the #3 and #4 with the #1 and #2 standards may have been fortuitous since no absolute assurance could be obtained that the mass spectrometric analysis of the N_2 gas obtained from the moderately enriched $(NH_4)_2SO_4$ solution (25 atom % N^{15}) did not contain measurable discrimination errors. Had MS-1, instead of MS-2, been chosen to analyze the nitrogen used to prepare the #3 and #4 standards the abundance results obtained by using these standards would have been in error because, as will be shown later, the gas flow conditions in MS-1 were not the same as in MS-2.

From the absolute N_2^{29}/N_2^{28} ratio for the nitrogen of the air given in Table 5, an absolute N^{14}/N^{15} ratio of 272.0 ± 0.3 is computed. This compares favorably with Nier's value of 273 ± 1 for the same measurement. The present limits of precision however produce a value for the physical atomic weight of nitrogen in which the uncertainty in the calculated value is no longer due to uncertainties in the abundance data when the most recent mass measurements for the N^{14} and N^{15} isotopes are applied (10). The results of these calculations, in which Nier's value and the value 272.0 ± 0.3 reported here were used, are given in Table 6. 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 using the #2 collector for the various other mixtures of N^{14} and N^{15} solutions listed in Table 2 appear in Table 7. The amount

Table 6. Physical atomic weight of nitrogen[a]

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

[a] Masses of N^{14} = 14.007551 ± 4 and N^{15} = 15.004905 ± 6 of Ogata and Matsuda (10) were employed to calculate the physical atomic weight.

of N^{15} was calculated from the observed 28^+, 29^+ and 30^+ ion currents corrected for the background observed 3 to 5 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 root of the ratio of the masses under consideration. This correction is applied by assuming the 30^+ ion current representative of the N_2^{30} in the inlet manifold and multiplying the 29^+ ion current by 1.018 (the sq. root of 30/29) and the 28^+ ion current by 1.035 (the sq. root of 30/28).

The distribution constant (K) was calculated for each sample gas listed in Table 7. Its value was 3.99 ± 0.02 for all the samples except the 8.65 and 89.83 atom % N^{15} samples. With these latter two samples a greater deviation from 4 was caused by random reading errors made while taking the data. This observation is in excellent agreement with the statistically computed value of 4.00 (see page 11) and the quantum mechanically calculated value of 3.998 at room temperature (15).

In making the assays of the sample gases listed in Table 7, sufficient time was allowed for the 28^+, 29^+ and 30^+ ion currents to stabilize 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 a replacement of some of the adsorbed gases by the incoming molecules. An apparent elution of absorbed gases occurs on the various components of the instrument. This was indicated by the results of an experiment where purified argon was introduced into the mass spectrometer at 5.0 cm. inlet manifold pressure and the 28^+ peak monitored. Immediately after introducing the argon the magnitude of the 28^+ ion current increased sharply, approximately doubling in size. Only after 10-15 minutes did this ion current return to the value it had before the argon was introduced.

The peaks observed during any gas assay include ions originating from both sample and absorbed gases, plus any

Table 7. Atom % N^{15} in mixtures made with separated isotopes

Calc'd Atom % N^{15}[a]	A[b]		B[c]		C[d]	
	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	89.59

[a] Data from Table 2.

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

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

[d] C - Corrections made for background, air contamination and the assumption that the observed peak heights were distorted according to the square root of the ratio of the masses involved due to gas flow out of the ion source of the instrument. It is assumed that gas flow into the source is purely viscous.

residual gas present due to an imperfect vacuum system. This residual gas is usually air and is the cause of the high 28^+ background observed in all mass spectrometers. When assaying the samples of varying composition shown in Table 7, 10 - 15 minutes were usually required before a stable spectrum was achieved. By this time the distribution of molecules representing the adsorbed gases approachs those of the sample. For this reason any background corrections subsequently made, should be based upon peaks 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 of Table 7 indicated 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 significantly alter the flow characteristics in the capillaries. Consequently the simple assumption that correction for molecular gas flow out of the ion source can be made by using the square root of the ratio of the masses involved is not completely valid. These data imply that flow through the leak of MS-1 was not purely viscous while that through the leak of MS-2 was viscous. Thus it appears that in the absence of calibrating media as presented here, corrections based on simple assumptions regarding the nature of gas flow in various mass spectrometers may lead to greater errors than those which might arise if no correction were applied.

The close agreement between Nier's results for the normal isotopic abundance of the nitrogen isotopes and those reported here indicated that the correction he made for discrimination errors was very close to the true correction necessary to yield accurate values for the nitrogen abundance. It should be kept in mind however that Nier ignored or assumed negligible the error which could be caused by a difference in the ionization efficiencies for the N_2^{28}, N_2^{29}. N_2^{30} molecules. Also, his method of observing the ion currents on a single collector is not nearly as precise for determining ratios as the method of dual ion current collection reported here.

It must be admitted that Nier's correction factor and the assumptions he had to make in treating his data turned out to be valid, but the deviations in the other reported values for the isotopic abundances of nitrogen which have appeared in the literature are due to variations in gas flow conditions and source geometry existing in the various mass spectrometers on which those measurements were made.

It is impossible to determine the relative ionization efficiencies of the molecular nitrogen isotopes without a precise knowledge of the gas flow conditions existing in the mass spectrometer. While it may be possible to determine whether a leak yields true viscous flow, it is extremely difficult to exactly describe the flow conditions under which the gas leaves the ion source. Hence no relative ionization efficiencies are given here.

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