CALIBRATION OF A FLYABLE MASS

SPECTROMETER FOR N AND O ATOMS

R. S. Narcissi, H. I. Schiff, J. E. Morgan and H. A. Cohen

H. I. Schiff

McGILL UNIVERSITY
DEPARTMENT OF CHEMISTRY
MONTREAL, CANADA

MARCH, 1963

Requests for additional copies by Agencies of the Department of Defense, their contractors, and other Government agencies should be directed to the:

Armed Services Technical Information Agency
Arlington Hall Station,
Arlington 12, Virginia

Department of Defense contractors must be established for ASTIA services or have their 'need-to-know' certified by the cognizant military agency of the project or contract.

All other persons and organizations should apply to the:

U.S. Department of Commerce
Office of Technical Services,
Washington 25, D.C.

ABSTRACT

Atomic nitrogen and atomic oxygen were produced in a flow system by subjecting N_2 to a microwave discharge. The concentration of N atoms was accurately measured by titration with NO. The O atoms were generated by the titration reaction $N + NO \rightarrow N_2 + O$. The gas in the flow system was sampled through a leak into a time-of-flight mass spectrometer which had been developed for upper atmosphere sampling. Various experiments were conducted to find the optimum conditions for the detection of these atoms. It was found that the O-atom response of the mass spectrometer was most affected by the entrance geometry of the ion source while the N-atom response was hardly changed. The most sensitive mass spectrometer variable for atom determination in the presence of molecular atmospheric gases was found to be the energy of the ionizing electrons; the optimum electron energy was found to be 16 e.v. to 24 e.v.

INTRODUCTION

Mass spectrometric measurements of atomic oxygen and nitrogen concentrations have been made in the atmosphere above 100 km[1,2]. A quantitative estimate of concentration from these measurements may have been hindered due to lack of a direct calibration of sensitivity for atomic species, therefore, in preparation for a flight the sensitivity of a mass spectrometer to oxygen and nitrogen atoms was determined; a microwave discharge was used in conjunction with a nitric oxide titration technique[3]. This method was used since the flow of the atomic species into the spectrometer could be accurately measured, and atomic oxygen could be produced without using molecular oxygen. The results of one set of calibrations are described in this report.

MASS SPECTROMETER

The mass spectrometers calibrated were time-of-flight units, constructed by the Bendix Corporation, for use on satellites. The physical system is shown in Fig. 1, and a block diagram of the circuitry is shown in Fig. 2. In the spectrometer, after the neutrals are ionized, masses are separated by giving all ions in a bunch the same energy and allowing all the ions to traverse the same distance:

(a) $\frac{1}{2} mv^2 = e\,V$

(b) $t_m = [\dfrac{S}{\frac{2\,e\,V}{m}}]^{\frac{1}{2}}$

Figure 1

Mass Spectrometer Physicsl System

ELECTRON MULTIPLIER
AND GATE

DRIFT TUBE

ION SOURCE

MULTIPLIER
CATHODE

DYNODE STRIP

SOURCE FILAMENT

CONTROL GRID

DRIFT TUBE LINER

FIELD STRIP

ION FOCUS GRID

ION ENERGY GRID

ANODES

GATES

OUTPUT
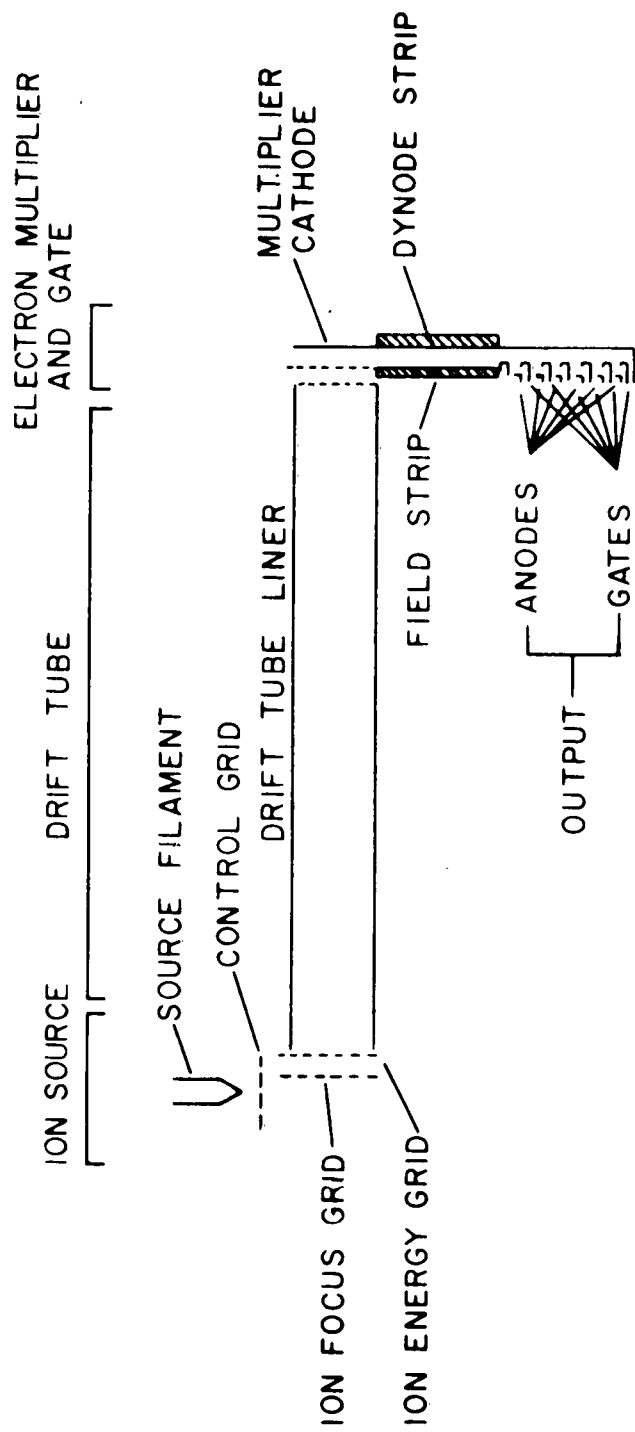
Figure 2

Block Diagram of the Mass Spectrometer

VACUUM HOUSING

TRAP CURRENT CIRCUIT

OUTPUT AMPLIFIER

GATING ASSEMBLY

ELECTRON MULTIPLIER

DRIFT TUBE

ION SOURCE

GAS INLET

GATE PULSE GENERATORS

DELAY LINE

TIMER AND SOURCE PULSE GENERATOR

ELECTRONICS PACKAGE

TEMPERATURE COMPENSATION

HIGH VOLTAGE POWER SUPPLY

SOURCE FILAMENT POWER SUPPLY

LOW VOLTAGE POWER SUPPLY

CONTINUOUS POWER

POWER SUPPLY PACKAGE
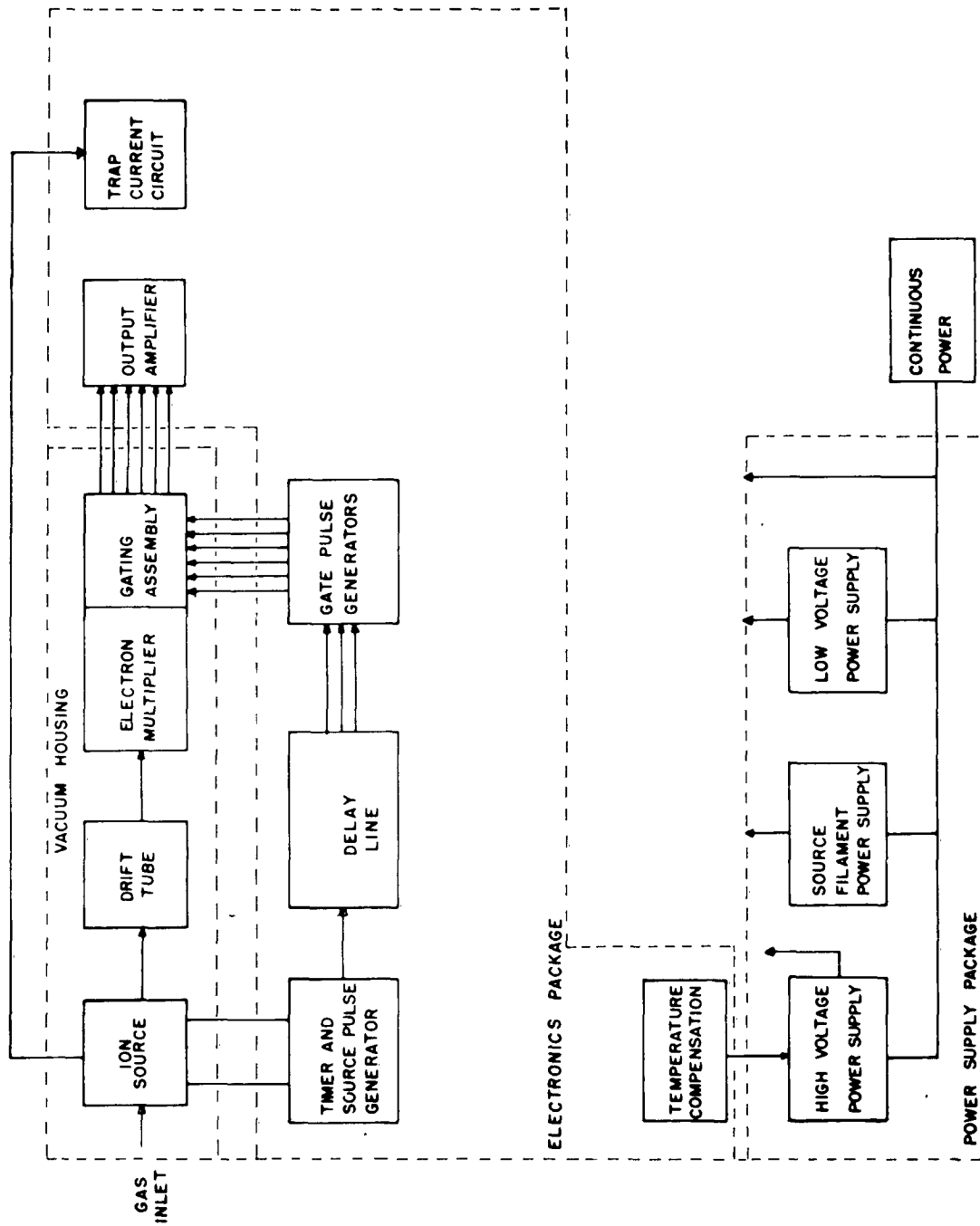
where m is the ion mass, e the ion charge, V the accelerating
voltage, v the final ion velocity, t_m the time for travelling
the distance S.   It is seen from (b) that the lighter masses
take the shortest time to traverse the drift tube distance.
On a linear time sweep at the detector the mass peaks get closer
together toward higher masses due to the square root dependence
shown in the second equation.   Operation of the system can
best be described by referring to the chart of waveforms in
Fig. 3, and the physical system diagram in Fig. 1.   The
filament, biased with respect to spectrometer ground, is kept
continually heated by means of a 1.5 volt p.p. square wave
voltage.   Electrons from the filament are prevented from
reaching the ionization chamber by means of a control grid kept
at a higher negative bias than the filament.   Electrons enter
the ionization chamber when the control grid is pulsed at a 10
kc rate to filament potential.   The fall of the control grid
generates the ion focus grid pulse which accelerates the ions
through the ion focus grid.   The ion energy grid imparts a
400 electron volt energy to all the ions which then travel with
equal kinetic energy down the drift tube.   The electron
multiplier amplifies the currents due to each ion but does not
alter the time between signals.   By running the basic timing
pulse into a delay line which has multiple taps, delay times
can be selected corresponding to arrival times of the ions of
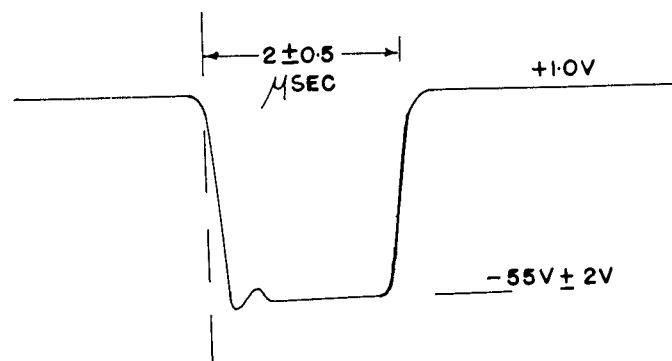different mass at the electron multiplier.   The signal from a

Figure 3

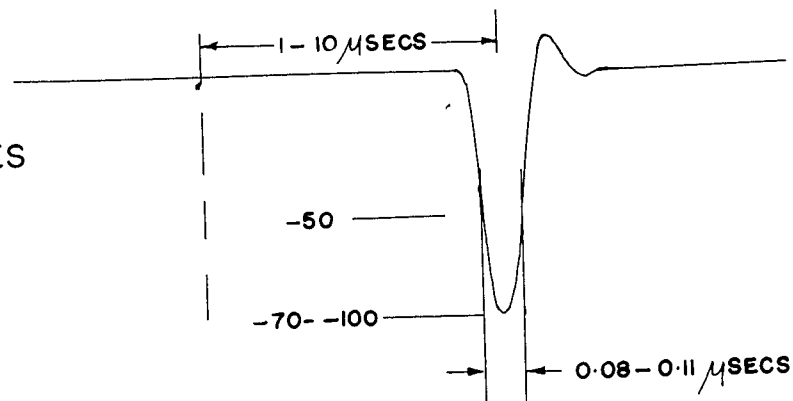Chart of Waveforms Generated in Mass Spectrometer

CONTROL GRID
PULSE

16– 22V

≈ – 80 V

|–0·8± ·1–|
μSECS

ION GRID
PULSE

2±0·5
μSEC

+1·0V

–55V ± 2V

GATE PULSES

1– 10 μSECS

–50

–70– –100
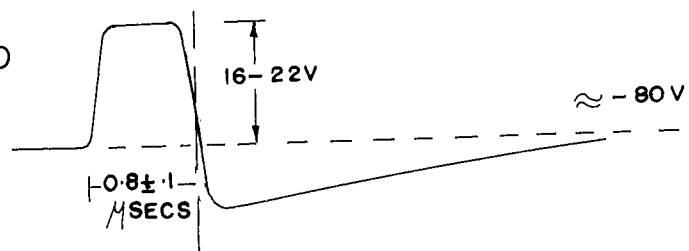
0·08 – 0·11 μSECS

delay tap is then fed to gate pulse generators which generate
pulses to deflect to an anode the amplifed electron bunches
corresponding to ions of a particular mass.   In these
particular spectrometers there were six gates and anodes, so
that six mass peaks could be measured simultaneously with
ammeters during operation.

SPECTROMETER GEOMETRY

Two different types of spectrometers were calibrated:
one with a head-on entrance port for oriented satellite, Fig.
4A;   the other with a backing plate for tumbling satellites,
Fig. 4B.   With the head-on entrance port neutrals may reach
the ionization region (1) directly without striking any walls;
(2) by diffusing around the entrance structures or (3) going
into the drift tube and multiplier region after (1) and (2) and
then diffusing back.   With the backing plate entrance port the
neutral molecules cannot enter the ionization region directly
but must diffuse around the entrance structures;   molecules
which are not ionized or pumped out can enter the drift tube
and multiplier region and then diffuse back to the ionization
region.   A mercury diffusion pump was used to keep the
spectrometer pressure at 2×10^{-5} Torr during the calibrations.
From the dimensions of the spectrometer it was estimated that
the pumping speed at the spectrometer entrance port was
approximately 4 liters/second.   The spectrometer had a total
volume of one liter;   most of the surface area is stainless

Figure 4

Physical Dimensions of Satellite Time-of-Flight
Mass Spectrometer Showing Leak System Used
During Calibration.   All dimensions in cms.

   4A   -   Head-on Entrance Chamber

        4B   -   Backing Plate Entrance Chamber

2.0

5.90

2.

4.0

21.90

ELECTRON
MULTIPLIER

31.0

3.20

DRIFT TUBE

ION ENERGY
GRID

4A

1.65

5.40

.36

CONTROL
GRID

AMBIENT ION
REPELLER GRIDS

TO
PUMP

ION FOCUS
GRID

4.40

4B

BACKING
PLATE
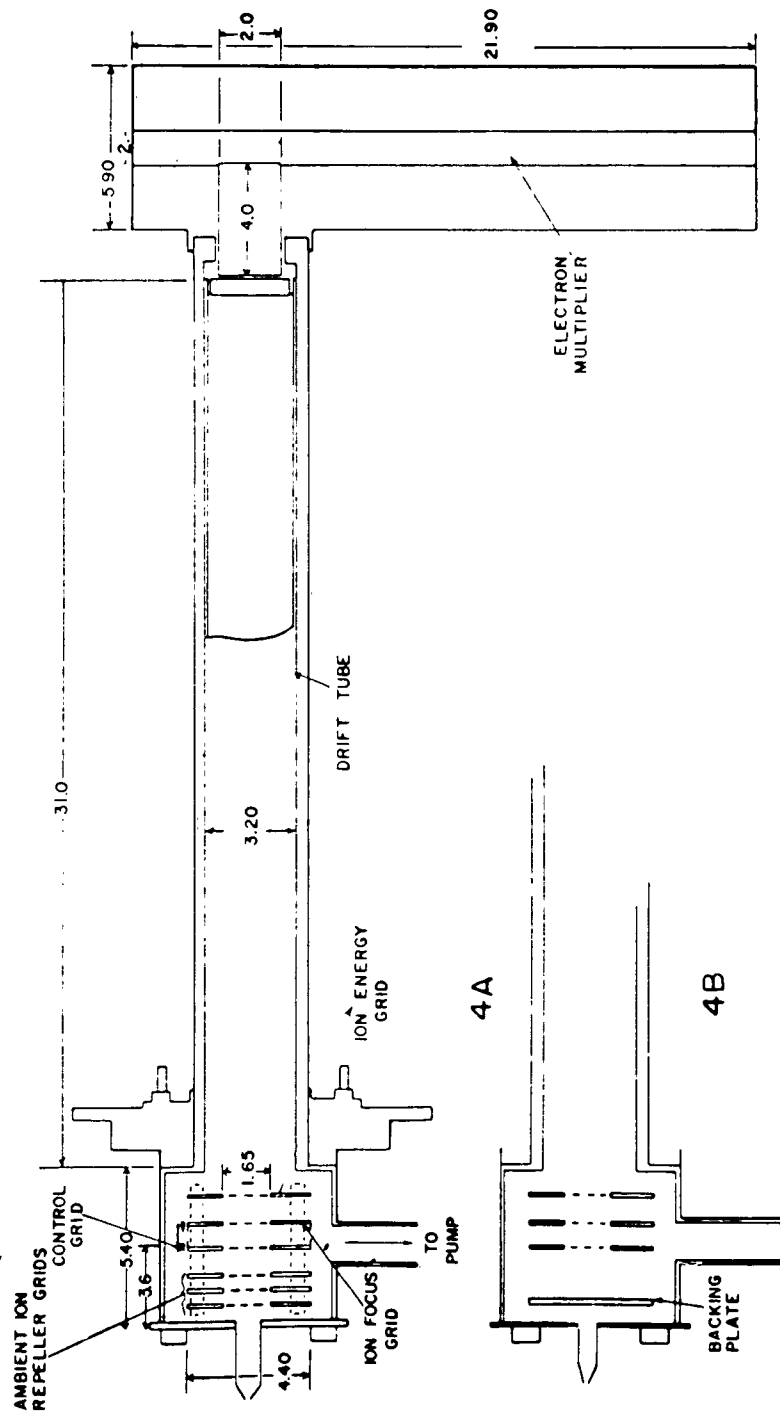
steel with the exception of the .005" tungsten filament, lavite insulators, and sapphire rods.

PRODUCTION OF OXYGEN AND NITROGEN ATOMS

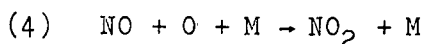The method of producing known concentration of O and N atoms[3] utilizes the reaction of nitric oxide with nitrogen atoms according to the following mechanisms:

(1) $N + NO \rightarrow N_2 + O$
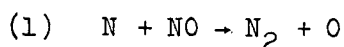
$$k_1 = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1} \quad (4,5)$$

(2) $N + O + M \rightarrow NO + M + h\nu$

$$k_2 = 5 - 15 \times 10^{-33} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1} \quad (6,7)$$

(3) $NO + O \rightarrow NO_2 + h\nu$
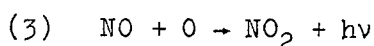
$$k_3 = 1.7 \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1} \quad (8)$$

(4) $NO + O + M \rightarrow NO_2 + M$

$$k_4 = 6 \times 10^{-32} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1} \quad (9,10,11)$$

With concentrations of (N), (NO) and (O) of the order of 10^{14} molecules cm^{-3} and (M) [= (N_2)] of the order of 10^{16} molecules cm^{-3}, it is readily seen that the rate of reaction (1) is of the order of $10^5 - 10^6$ times faster than (2), (3), and (4).

Therefore, under conditions where the concentration of nitric oxide satisfies the stoichiometry of (1), all the nitrogen atoms will be quantitatively consumed to produce an equivalent amount of oxygen atoms. In a flow system this implies that the flow rate of nitrogen atoms can be 'titrated' with nitric oxide to produce an equivalent flow of oxygen atoms.

Since the stoichiometry of reaction (1) has been established[12,13,14], the oxygen atom flow will be equal to the nitric oxide flow necessary to titrate the nitrogen atom stream. The end point of this reaction is readily obtained by visual observation of the light emission downstream from the nitric oxide inlet. It will be seen from the reaction mechanism that an excess of nitric oxide will result in the greenish-yellow emission associated with reaction (3). Conversely, insufficient nitric oxide will result in the blue emission associated with reaction (2). The end point is then sharply defined by the **absence** of either of these two emissions.

Alternatively, in this particular case, the end point can be obtained mass spectrometrically, since at the equivalence point of reaction (1), the concentration of nitric oxide downstream from the inlet will be ideally, zero.

The advantages of this system over simple dissociation of O_2 are obvious:

(a) It produces oxygen atoms in a system free from O_2.

(b) The oxygen atom concentration is readily obtained from the nitric oxide flow rate.

(c) An equivalent nitrogen atom flow can be rapidly and conveniently produced by shutting off the nitric oxide.

(d) By reduction of the nitric oxide flow, mixture of nitrogen and oxygen atoms can be obtained in any desired ratio.

EXPERIMENTAL

Materials:

Nitrogen - Dinsmore 'premium grade' was used directly from the cylinder.

Nitric Oxide - Matheson nitric oxide (purity 98%) was freed from NO_2 and water vapor by trap-to-trap distillation through a column of ascarite, the final fraction of the last distillation being discarded.

Apparatus:

A conventional flow system was used as shown in Fig. 5. Atomic nitrogen was produced by subjecting dry nitrogen to an electrodeless discharge in the quartz tube by means of a Raytheon microwave generator (2450 mc/sec 0-100 watts of C.W. power). Nitric oxide from the reservoir, R, was added to the discharged nitrogen stream through a multiple jet located in the mixing chamber C. The flow rate of nitric oxide was then adjusted to an approximate end point and the system allowed to stabilize for ten minutes.

Final adjustment to the end point was then made by varying the input power to the discharge. Under these conditions, the flow system downstream from C contained oxygen atoms and undissociated nitrogen molecules only. The nitrogen flow was determined by means of the calibrated capillary flow meters. The nitric oxide flow was determined independently at the end of every experiment by measuring the

Figure 5

Nitrogen and Oxygen Atom Generating System
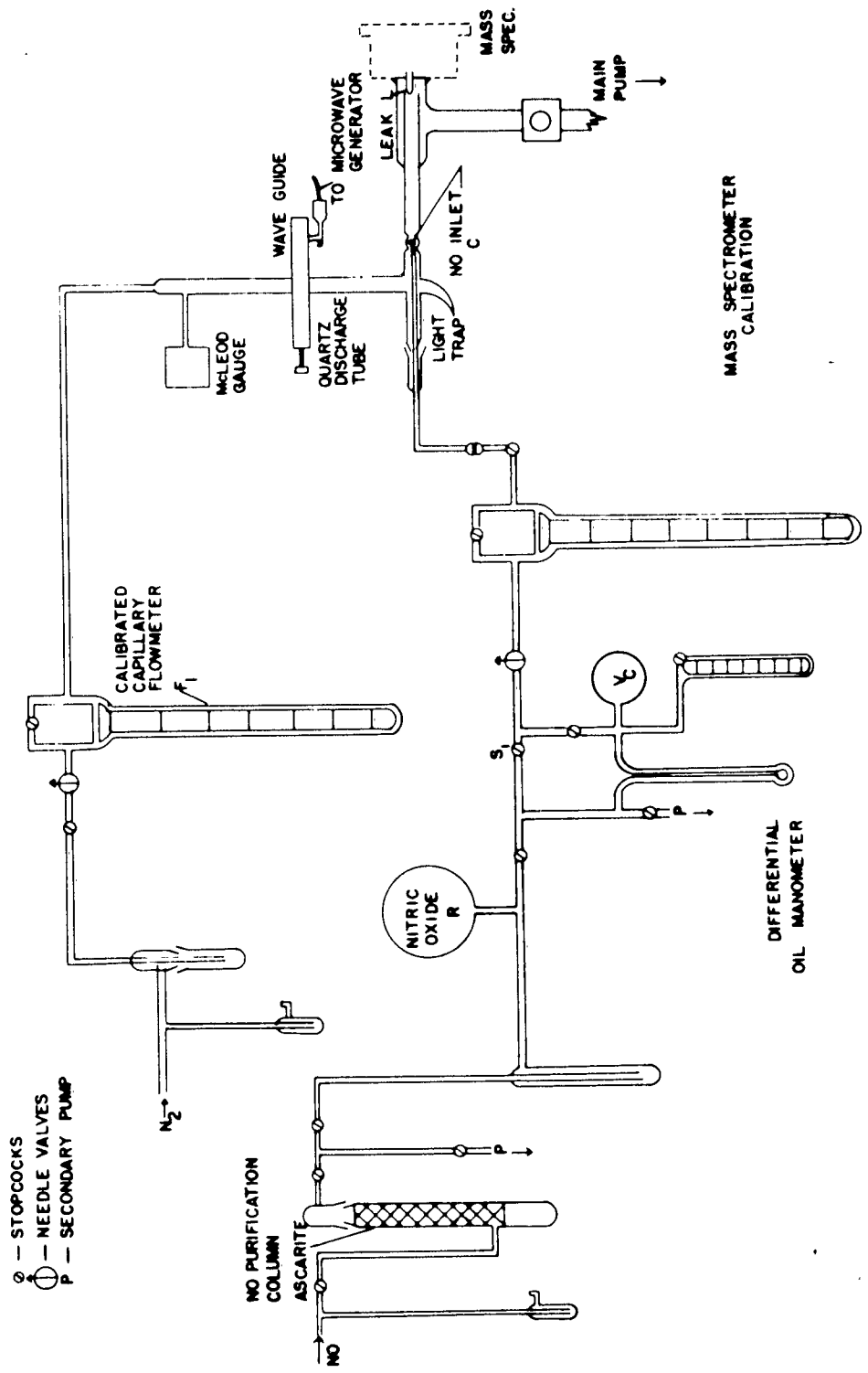
MASS SPECTROMETER CALIBRATION

rate of differential pressure drop on the oil manometer
consequent to isolation of the reservoir R by closure of the
stopcock S_1.   This, in conjunction with a knowledge of the
volume V_c, enabled the flow rate to be determined by application
of the gas law.

These flow rates were of the order of 60 - 100
micromoles sec^{-1} for nitrogen and 1 - 2 micromoles sec^{-1} for the
nitric oxide.   The ratio of these two flows then gives
directly the percentage of atomic oxygen relative to the
undissociated nitrogen at the mixing point C.   The linear
velocity in this system was of the order of 1500 cms/sec.
Since the sampling point was approximately 20 cms downstream
from C, this corresponds to an elapsed time of about 16 m secs.
From the known rate constant for oxygen atom recombination[3,15],
it can be shown that negligible recombination occurs between the
point C and the sampling leak, L.

The atomic oxygen was sampled continually into the
mass spectrometers by means of the leak L.   This leak was
constructed from a pyrex thimble with a wall thickness of
approximately 20 microns in which a 20 micron hole was punched
by means of an electric spark.   At the pressures prevailing in
the flow system (0.2 mm Hg), this hole diameter ensures
molecular flow into the mass spectrometer.   During measurements
the spectrometer pressure as measured by a Veeco ionization
gauge was 2×10^{-5} Torr.

As mentioned earlier, production of a known nitrogen atom flow was obtained by shutting off the nitric oxide. Under these conditions, the system contained nitrogen atoms and undissociated nitrogen molecules only. As before, the nitrogen atom flow will be equal to the nitric oxide flow.

RESULTS

1. An attempt was first made to measure the spectrometer efficiency for N and O atoms, with head-on geometry, at electron ionization energy of 91 electron volts; this is near the maximum ionization efficiency for these atoms[16]. No changes were found between discharge off and on for either the current at mass 14 $i(N^+)$ or that at mass 16 $i(O^+)$, although there was a significant change in the current at mass 30 due to NO. The first three grids, the ambient ion repeller grids, were removed with the same results when the measurements were repeated. Typical data **are** shown **in** Table I and the results of all the measurements summarized in Table III.

2. The ionization efficiencies of N and O are not significantly different from that of NO at 91 volts electron energy[16,17]; in addition, the multiplier selectivity is not significantly different for masses 14 and 16 as compared to mass 30[18]. Therefore the preceding results could be explained only by assuming that the atoms are destroyed in the spectrometer or that the high dissociative ionization background due to the flowing N_2 and to the background species in the

Table I

TYPICAL CURRENT READINGS WITH 91 VOLTS IONIZATION ENERGY

Discharge	$i\ (N_2^+)$ $(10^{-8}$ amps$)$	$i\ (N^+)$ $(10^{-9}$ amps$)$	$i\ (O^+)$ $(10^{-10}$ amps$)$	$i\ (NO^+)$ $(10^{-10}$ amps$)$
Off	5.1	3.0		
On	5.0	3.0		
Off	5.0	2.9		
On			8.6	6.3
Off			8.4	17

spectrometer mask the results.   To test the latter hypothesis, the amount of N^+ produced by dissociative ionization was measured as a function of electron energy, **Fig. 6.**   These measurements showed that the optimum detectability for a change in $i(N^+)$ was at an ionization energy below 21 volts.

3.   The measurements of sensitivity were repeated as in (1) with the ion repeller grids out (the first three grids) and using 18 volt ionization electrons.   Significant changes were found in $i(N^+)$ and smaller changes were found for $i(O^+)$ with and without discharge.   Typical data are shown in Table II and the results summarized in Table III.

4.   The measurements were repeated with the ambient ion repeller grids out but with a longer entrance tube to increase

Figure 6

Ratio of Mass 14 to Mass 28 Ion Current

● -· Discharge On

O - Discharge Off

N^+/N_2^+

ELECTRON VOLTAGE
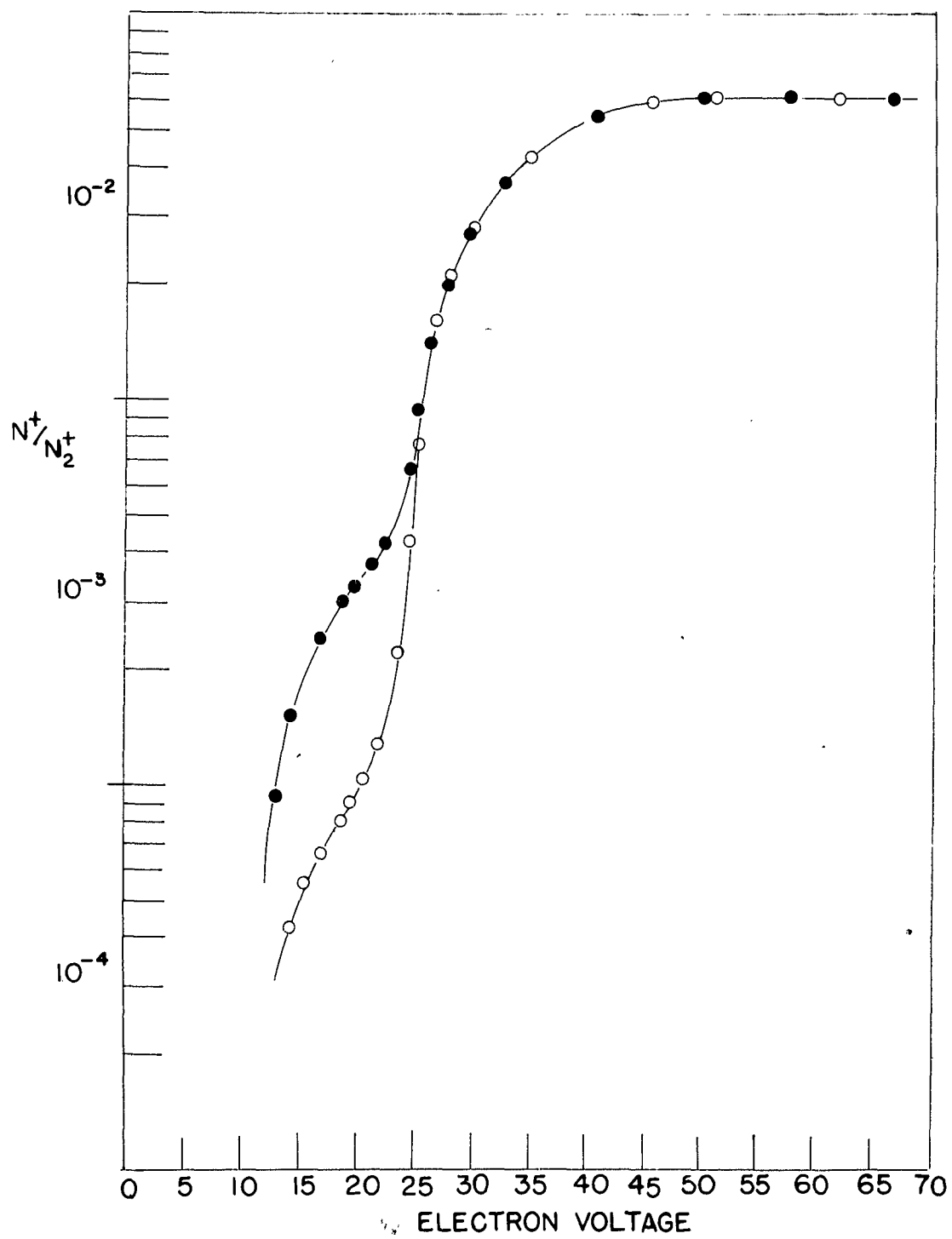
Table II

TYPICAL CURRENT READINGS WITH 18 VOLTS IONIZATION ENERGY

Discharge	$i\ (N_2^+)$ (10^{-8} amps)	$i\ (N^+)$ (10^{-10} amps)	$i\ (0^+)$ (10^{-11} amps)	$i\ (NO^+)$ (10^{-10} amps)
Off			0.92	22
On			2.65	2.0
On	3.4	1.0		
Off	3.4	0.55		

Table III

T.O.F. CALIBRATION RESULTS

Spectrometer Type	Entrance Modification	Ionization Voltage	$\dfrac{\Delta i\ [N]}{\Delta i\ [NO]}$	$\dfrac{\Delta i\ [0]}{\Delta i\ [NO]}$
H – O	Grids On	91 volts	$< 2 \times 10^{-1}$	$< 3 \times 10^{-1}$
H – O	Grids Off	91 volts	$< 2 \times 10^{-1}$	$< 3 \times 10^{-1}$
H – O	Grids Off	18.12	$(4.1 \pm 0.2) \times 10^{-2}$	$(7 \pm 2) \times 10^{-3}$
H – O	Inlet Extended	18.1	4.0×10^{-2}	8.8×10^{-3}
H – O	Grids On (normal)	18.2	$(3.2 \pm .2) \times 10^{-2}$	8×10^{-3}
B – P	Normal	17.5 – 18.1	4.2×10^{-2}	2×10^{-3}
B – P	Normal	16.5	2.5×10^{-2}	6×10^{-4} 1.3×10^{-3}

H – O   Head On

B – P   Backing Plate

the jet component of the atoms, Fig. 7. There was no significant change from previous measurements as seen in Table III. The measurements were also repeated with a normal size tube but with ambient ion repeller grids in place. Again there appeared to be no major change from the results of (3).

.   5.   The measurements were repeated near 18 volts ionization energy for the backing plate spectrometer with little change from previous results for $i(N^+)$ using the head on spectrometer. There appeared to be a significant change in $i(O^+)$ from the previous measurement with the head on spectrometer but the measurements were made close to the noise limit for the electrometer used.

6.   One further measurement was made to determine whether the flow into the spectrometer was viscous or molecular. The pressure on the high pressure side of the leak was 0.2 mm and therefore there was a mean free path λ, of 2.5×10^{-2} cm. The hole diameter, d, was 20 microns, $\lambda = 12$ d. For λ greater than 15 to 40 d, molecular flow is expected[19]. When the pressure on the high pressure side of the leak was increased from 0.2 Torr to 0.4 Torr, it was found that the pressure in the spectrometer was linearly related to it. This indicates that the flow was molecular[20].

Figure 7

Jetting Tube Geometry

CONTROL GRID

ION ENERGY GRID

SPECTROMETER

LEAK

0·5 CM

0·6 CM

5 CM
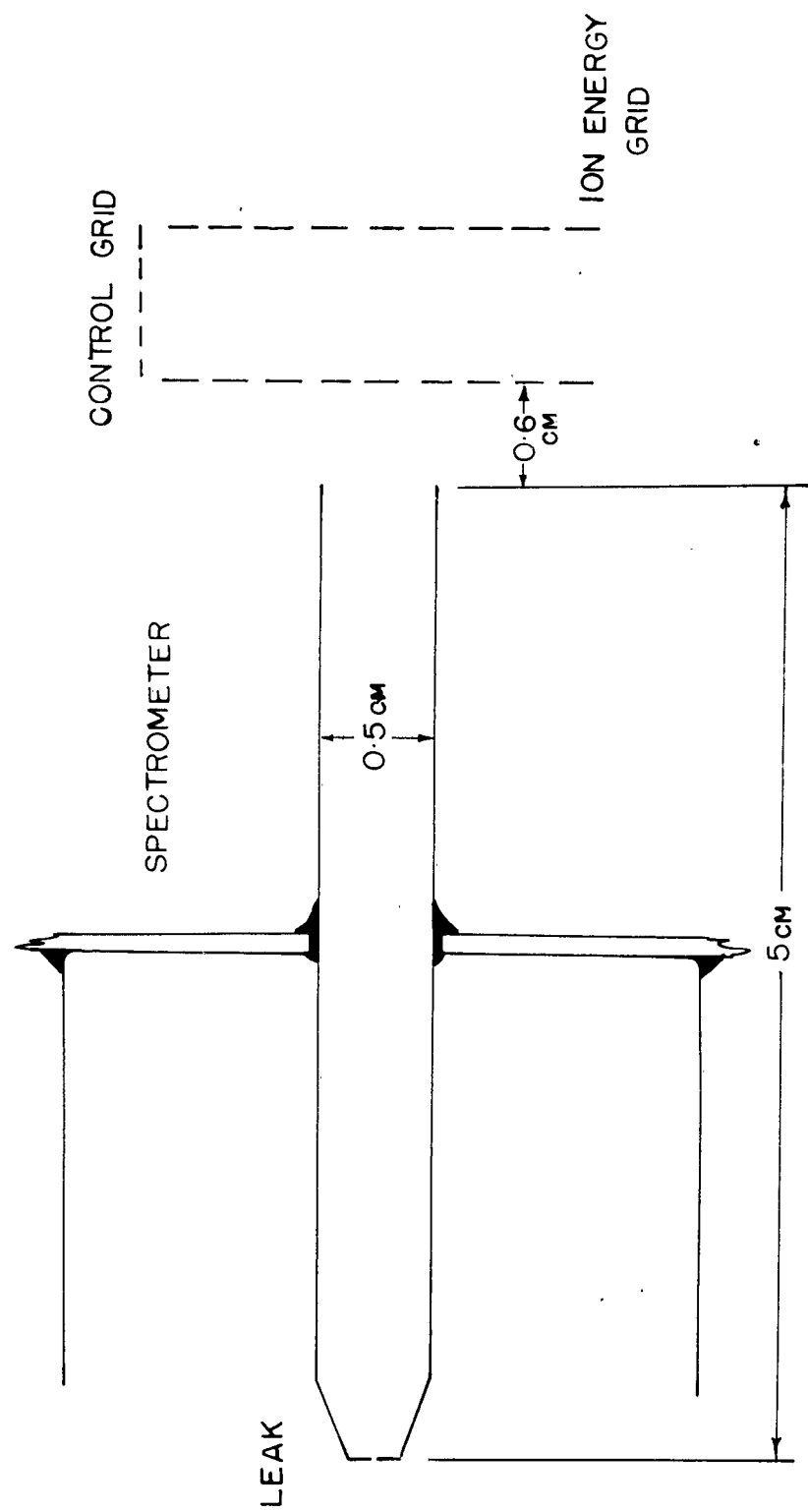
CONCLUSIONS

1.   At an ionization energy of 18 electron volts with both the backing plate and head-on arrangements, the spectrometer has a sensitivity for N atoms of 4×10^{-2} that for NO molecules.

2.   Increasing the number of wall collisions does not materially affect the sensitivity of the spectrometer for N atoms.

3.   When it is desired to measure the concentration of N atoms and where a large N_2 background is expected, the ionization voltage must be chosen to reduce optimally the background produced by dissociative ionization.

4.   The sensitivity of the spectrometer for O atoms is at least a factor of 5 less than for N atoms and depends on the number of wall collisions.

PUBLICATIONS UNDER PARTIAL SPONSORSHIP
OF THIS CONTRACT

Calibration of a flyable mass spectrometer for N and O atom
    sensitivity.
        R.S. Narcissi, H.I. Schiff, J.E. Morgan, and H.A. Cohen.

        Space Research III, Washington, 1962.
        (North-Holland Publishing Company, Amsterdam - In press).

REFERENCES

1. E.B. Meadows and J.W. Townsend, Jr., Space Research Proc. of First International Space Science Symposium, Nice, Jan. 1960. Edited by H. Kallman-Bijl, (North Holland Publishing Co., Amsterdam,1960).

2. A.A. Pokhunkov,   Ibid.

3. J.E. Morgan, L. Elias and H.I. Schiff, J. Chem. Phys., 33, 930 (1960).

4. J.T. Herron, J. Res. Nat. Bur. Standards, 65A, 411 (1961).

5. L.F. Phillips and H.I. Schiff, J. Chem. Phys., 36,1509(1962).

6. C.E. Barth,'Chemical Reactions in Lower and Upper Atmosphere' (Interscience, New York,1961) p.306.

7. C. Mavroyannis and C.A. Winkler, Can.J.Chem., 39, 1601(1961).

8. A. Fontijn and H.I. Schiff, 'Chemical Reactions in Lower and Upper Atmosphere' (Interscience, New York, 1961) p. 239.

9. F. Kaufman, J. Chem. Phys., 28, 352 (1958).

10. P. Harteck, R.R. Reeves and G. Manella, J. Chem. Phys., 29, 1333 (1958).

11. L. Elias, E.A. Ogryzlo and H.I. Schiff, Can. J. Chem., 37, 1680 (1959).

12. G.B. Kistiakowsky and G.G. Volpi, J. Chem. Phys., 27, 1141 (1957).

13. F. Kaufman and J.R. Kelso, J. Chem. Phys., 27, 1209 (1957).

14. J.E. Morgan, Ph.D Thesis, McGill University.

15. R.R. Reeves, G. Manella and P. Harteck, J. Chem. Phys., 32, 632 (1960).

16. M.J. Seaton, Phys. Rev., 113, 814 (1959).

17. J.T. Tate, P.T. Smith, Phys. Rev., 39, 270 (1932).

18. M.G. Inghram and R.J. Hayden, 'Mass Spectrometry' Nuclear Science Series No. 14, National Acad. of Science, National Research Council, (Washington, D.C., 1954) p. 43.

19. R.E. Honig, J. Appl. Phys., $\underline{16}$, 646 (1945).

20. G.P. Barnard, 'Modern Mass Spectrometry', The Institute of Physics (London 1935) p. 101.

UNCLASSIFIED

AF Cambridge Research Laboratories, Bedford, Mass. Geophysics Research Directorate. Rept. No. AFCRL-63-437. CALIBRATION OF A FLYABLE MASS SPECTROMETER FOR N AND O ATOMS. Final Report, March 1963, 22 pp. incl., illus., tables.
Unclassified Report

N atoms, produced by microwave discharge, were measured by titration with NO. O atoms were generated by the titration reaction $N + NO - N_2 + O$. The gas stream was sampled through a leak into a time-of-flight mass spectrometer developed for upper atmosphere sampling. The O-atom response of the mass spectrometer was most affected by the entrance geometry of the ion source while the N-atom response was hardly changed. The optimum electron energy was found to be 16 e.v. to 24 e.v.

1. Mass Spectrometer
I. Project 6687, 7676
   Task 668700, 767302
II. Contract AF 19(604) 8807
III. McGill U, Montreal, Canada.
IV. Narcissi, R.S., Schiff, H.I., Morgan, J.E., Cohen, H.A.

UNCLASSIFIED

UNCLASSIFIED

AF Cambridge Research Laboratories, Bedford, Mass. Geophysics Research Directorate. Rept. No. AFCRL-63-437. CALIBRATION OF A FLYABLE MASS SPECTROMETER FOR N AND O ATOMS. Final Report, March 1963, 22 pp. incl., illus., tables.
Unclassified Report

N atoms, produced by microwave discharge, were measured by titration with NO. O atoms were generated by the titration reaction $N + NO - N_2 + O$. The gas stream was sampled through a leak into a time-of-flight mass spectrometer developed for upper atmosphere sampling. The O-atom response of the mass spectrometer was most affected by the entrance geometry of the ion source while the N-atom response was hardly changed. The optimum electron energy was found to be 16 e.v. to 24 e.v.

1. Mass Spectrometer
I. Project 6687, 7676
   Task 668700, 767302
II. Contract AF 19(604) 8807
III. McGill U, Montreal, Canada.
IV. Narcissi, R.S., Schiff, H.I., Morgan, J.E., Cohen, H.A.

UNCLASSIFIED