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MASS SPECTROMETRIC ANALYSIS OF BORON TRIFLUORIDE

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ABSTRACT

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A mass spectrometer and an analytical method for measuring the abundance of the boron isotopes in boron trifluoride are described. Heretofore, "memory" has prevented rapid measurements of isotopically different samples; a system has been devised that reduces memory to an acceptable level at which a correction factor can be accurately determined and applied.

The accuracy of isotopic measurements of boron in boron trifluoride has always been seriously impaired by "memory" effects resulting from sample sorption on the surfaces of the inlet system and ion source. Exchange occurs between this residual and the following sample, so that the measured isotopic difference between two samples is much less than the real difference. For example, Bhide and Saxena (2) followed a boron trifluoride sample containing 44.3% B^{10} by another containing 83.0% B^{10}. The first spectrometer measurement indicated the latter sample contained only 59.0% B^{10}; even after purging the spectrometer nine times with the latter sample, its apparent value had increased to only 66.8%.

Previous efforts to control this problem have included purging between samples to remove the boron chemically (4, 6), extensive baking of the inlet system between samples (9, 10), and careful design of the inlet system (1).

INSTRUMENTATION

The memory problem was reduced to a workable level by a combination of instrument design, operating procedures, and pumping techniques. Figure 1 is a schematic diagram of the mass spectrometer, a Nier type six-inch radius instrument equipped with a dual collection system, so the $B^{10}F_2^+$ and $B^{11}F_2^+$ ions were measured simultaneously with a stabilized feed-back system (3). A null balance ratio recorder system (7) was used to measure the ratio of the two

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ion currents. The input resistors for the high-current (mass 49) beam and the low-current (mass 48) beam were 2×10^{10} and 1×10^{11} ohms, respectively.

Glass was eliminated from the entire sample inlet system to avoid isotopic exchange with boron in the glass, as well as chemical production of silicon tetrafluoride. The high-pressure portion of the nickel-and-monel manifold had a volume of only 10 ml. Boron trifluoride was admitted to this region at atmospheric pressure or greater, so the adsorbed gas was a very small fraction of the total sample. Since most of the isotopic exchange occurs in the low-pressure region following the leak in conventional systems, the adjustable leak was placed directly at the entrance to the collimating tube through which the sample stream is directed into a molecular beam formation. The sides of the ionization chamber of the molecular beam source were completely open, in contrast with the one described by McKnight (5) in which the ionization region was bounded by perforated sides.

The area above the liquid nitrogen in the metal cold trap, against which the un-ionized portion of the molecular beam impinges, was partially evacuated and continuously pumped with a mechanical pump, reducing the liquid nitrogen temperature approximately 14°C. The vapor pressure of boron trifluoride at this reduced temperature is only 8×10^{-10} torr, compared to 3×10^{-6} torr at the usual liquid nitrogen temperature. It was necessary to throttle the pump line so the liquid nitrogen did not solidify and reduce the surface contact with the trap.

SPECTROMETER OPERATION

Two samples to be compared were attached to the mass spectrometer manifold as shown in Figure 1. By closing either valve A or B, the amount of manifold line common to both samples was reduced. The gas sample to be analyzed was valved into the manifold, and the leak was adjusted to give a ten volt high-current amplifier signal. The sample was then pumped out and readmitted, purging twice with the gas to be measured before taking data on the third admission. No more than one minute was required for one purging operation. This same procedure was followed with the second sample, and the samples were alternated until two isotopic ratios of one sample were bracketed by three of the other. If conservation of sample had been important, satisfactory data could have been obtained using only one measurement of each sample, with only moderate sacrifice of precision.

Memory Factor Determination

The memory factor M is defined as the true ratio of mole ratios (W) minus one, divided by the observed ratio (R_o) minus one, or

$$M = \frac{W - 1}{R_o - 1}$$

An observed ratio is corrected for memory by increasing the difference between the ratio and unity by the memory factor M:

$$W = M(R_o - 1) + 1$$

The memory was evaluated by measuring two standards whose isotopic compositions were determined by surface ionization of sodium borate. One standard, prepared by blending boron trifluoride containing 96% B^{10} with boron trifluoride in which the boron was unaltered, contained 26.6% B^{10}. The measured B^{10} content of the other was 20.0%. These two isotopically different gas standards were alternately measured in the mass spectrometer and a memory factor was established from analyses extending over a period of two weeks. The memory level was also confirmed periodically during the analysis of unknown samples. The average ratio of isotopic ratios, 1.425 ± 0.0002 (standard deviation), corresponded to a memory factor of 1.06. This factor was used in correcting all sample ratios.

RESULTS AND DISCUSSION

Since BF_2^+ ions were measured, it was necessary to carefully exclude water vapor, silicon tetrafluoride and sulfur dioxide from the samples and the sample inlet system, since ions of interfering mass can result from their presence. Samples were kept at above-atmospheric pressure; and periodic mass scans, with particular attention to mass 47, showed the impurity level was too low to interfere. It was thus not necessary to chill the samples with solid carbon dioxide to remove objectionable compounds, as suggested by Palmer (8).

The relative method compares the isotope ratio of one sample to that of another sample. In our work, the only information needed was the ratio of isotope ratios of two samples. To determine the absolute isotopic composition of a sample, a standard of known value would be used for comparison.

Approximately 150 sample pairs of varying isotopic composition were analyzed. During these analyses, analytical precision was evaluated by regularly rerunning a pair of control samples. For ten of these control pair determinations, with an average ratio of mole ratios of 1.169, the standard deviation of a single ratio of ratios was 0.0014.

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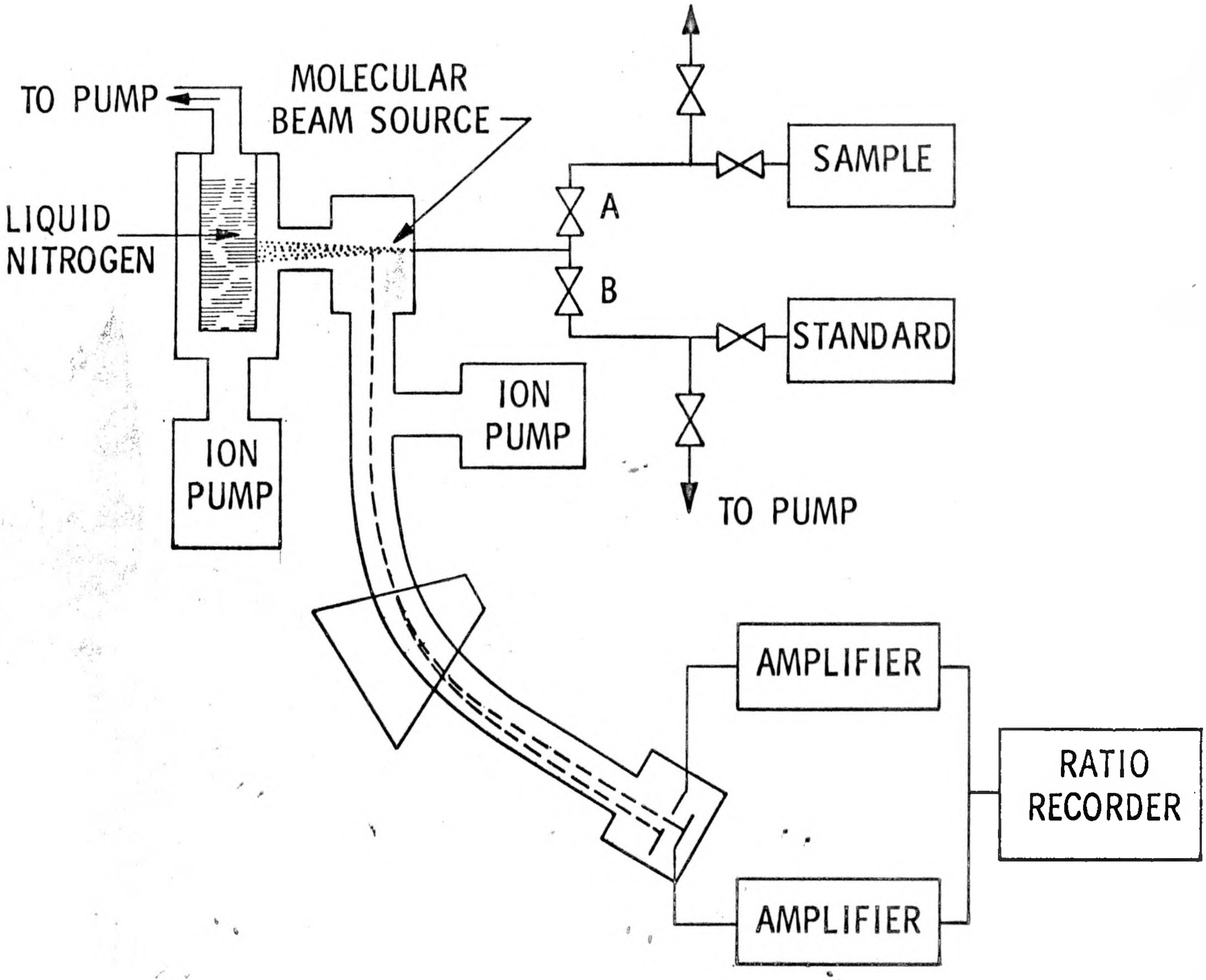

Figure 1

MASS SPECTROMETER FOR BORON TRIFLUORIDE