SPECTRAL ANALYSIS OF COMPLEX GAS MIXTURES BY ISOTOPE DILUTION

III. Determination of Hydrogen, Nitrogen, Oxygen, and Carbon Present Together

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Hydrogen, oxygen, carbon, and nitrogen have been determined separately in complex gas mixtures [1,2], as have nitrogen and hydrogen together [3]. Here we describe a method for simultaneous determination of hydrogen, oxygen, carbon, and nitrogen in these mixtures.

Measurements were made with a three-channel grating monochromator, with the mixture excited in an uncooled discharge tube. The wavelengths used were Hα 4861 Å; CO 4835.3 Å; N2 8169.3 Å. The isotopic composition of the hydrogen was determined from a calibration curve (Fig. 1a).

The ratio IH/ID is constant over the pressure range 5–20 mm Hg, with IH/ID > cH2/cD2 (Fig. 1a)*. Third components had less effect on IH/ID than in [1] (Fig. 2a), so only the total content of other components was used in determining cH2/cD2 [1].

Relative intensities of the isotopic bands of nitrogen were determined with allowance for overlap [5, 6], and then the result is almost independent of third components and experimental conditions [3]. A calibration curve (Fig. 1b) was used to determine the isotopic composition of nitrogen in a mixture.

The isotopic bands for CO were the most affected by third components, because of changes in the discharge conditions and of overlap with the CO band. Hydrogen, oxygen, nitrogen, and inert gases substantially narrow the CO band and so decrease the overlap. Various impurities have almost identical effects, so a single curve was used to correct for them (Fig. 2b). The relative intensities of the heads were independent of the composition up to tenfold dilution of CO2 with nitrogen, alone or with other gases. Larger degrees of dilution gave rise to distortion due to overlap of the nitrogen spectrum with the 4855.3 Å CO band, but the effect of the overlap was substantially reduced if a wide discharge tube was used. A calibration curve (Fig. 1c) was used to determine the proportions of oxygen or carbon isotopes.

The results should, therefore, be processed starting with determination of the nitrogen content, followed by the hydrogen and then the oxygen (or carbon). The overlap coefficient for the CO bands may (Fig. 2b) be introduced on the basis of the total amount of nitrogen and hydrogen.

The concentration of component i is given by

\[
c_i = \frac{\left[\left(\frac{c_1}{c_2}\right)_{ii} - \left(\frac{c_1}{c_2}\right)_{ii} \right] P_i V_1}{1 - \gamma_i \left(\frac{c_1}{c_2}\right)_{ii} \left[1 + \left(\frac{c_1}{c_2}\right)_{ii} \right] P_i V_2},
\]

in which (c1/c2)i and (c1/c2)ii are the initial and final relative concentrations of the light and heavy isotopes in the gas used for dilution, while γi is a correction factor for the natural content of the heavy isotope, with

\[
\gamma_H = 0.00016; \gamma_O = 0.002; \gamma_C = 0.01; \gamma_N = 0.0038,
\]

and P_i is the partial pressure of the i-th isotope-bearing gas taken for dilution in a vessel of volume V_i, while P_2 is the pressure of the mixture taken for dilution in a vessel of volume V_2.

\*In a cooled tube [1,4] IH/ID < cH2/cD2.

\[
\frac{I_1}{I_2} = \frac{c_{H_2}}{c_{D_2}}; \quad \frac{I_N}{I_{N_2}} = \frac{c_{N_2}}{c_{N}}; \quad \frac{I_{CO}}{I_{CO_2}} = \frac{c_{CO_2}}{c_{CO}};
\]

I < 1 is a coefficient related to the method of allowing for overlap of the bands of the isotopic molecules.
In our case, \((c_1/c_2)_{01}\) was 0.01 for hydrogen, 0.39 for oxygen, 4.55 for carbon, and 6.67 for nitrogen.

As \(\gamma\) is small and the relative concentration of the isotopes in the mixture was close to 1, we may assume that \(\gamma \cdot c_1/c_2 \ll 1\), whereupon (1) becomes

\[
c_i = \frac{\left[ \frac{c_1}{c_2} \right]_i - \left( \frac{c_1}{c_2} \right)_{0i}}{1 + \left( \frac{c_1}{c_2} \right)_{0i}} \cdot P_{H_i} V_1.
\]

This formula has been used to calculate the contents of oxygen, carbon, and nitrogen. As \((c_1/c_2)_{01} \ll 1\) and \(c_1/c_2 \approx 1\) for hydrogen, (2) becomes

\[
c = \frac{c_1}{P_i/V_1} \cdot P_{H_i} V_1.
\]

Formulas (2) and (3) give the correct result only if the number of atoms of the element in a molecule of the isotope-bearing gas equals that in the corresponding molecules in the mixture to be analyzed. This condition was obeyed here in our previous work. In the general case, the form of the compound of the element in the mixture is unknown, and so the concentration should be expressed via the number of atoms in unit volume of the mixture at NTP, and the formula becomes

\[
c_i = \frac{n}{k} \frac{P_0}{T_0} \left[ \frac{\left( \frac{c_1}{c_2} \right)_{i} - \left( \frac{c_1}{c_2} \right)_{0i}}{1 + \left( \frac{c_1}{c_2} \right)_{0i}} \cdot P_{H_i} V_1 \right].
\]

in which \(n\) is the number of atoms of the element in a molecule of the isotope-bearing gas, \(P_0\) and \(T_0\) are standard pressure and temperature, and \(k\) is Boltzmann's constant.