Chapter V

VARIOUS METHODS OF ANALYSIS OF GAS MIXTURES

22. QUALITATIVE AND SEMIQUANTITATIVE ANALYSIS OF GAS MIXTURES*

To start with, the light source and a discharge tube of appropriate design must be selected on the basis of considerations set forth in Section 16.

The discharge tube is sealed to a vacuum unit of the type described in Section 7. This is followed by a period of "conditioning" of the tube. This procedure is used because air is strongly adsorbed on the electrodes and the walls of the discharge tube, as are gases present in the tube before the introduction of the sample. If not removed, these gases evolve during the discharge, with the result that lines of foreign elements will appear in the sample spectrum. To avoid this, the discharge tube is filled with some gas known to be present in the sample (usually, the primary component). The discharge is then switched on for a few minutes. Its color, as well as the characteristic bands or lines in the

*See also general handbooks on spectral analysis [25, 317, 375].
spectrum, immediately indicates whether such impurities as nitrogen, oxygen, hydrogen, carbon monoxide, C₂OH, CH or CN are present in the tube.

The current used in the conditioning of the tube is somewhat higher than is required under the analytical conditions. The gas pressure is maintained at a level approximating that required during the analysis. After this conditioning, the unit is evacuated (5-10 min) and a new portion of the conditioning gas is introduced. At first, no lines or bands indicating impurities may appear in the spectrum, but as such impurities continue to evolve from the electrodes and walls of the tube, both lines and bands will gradually be seen. The discharge is again maintained for several minutes and then the tube is reevacuated. Tube conditioning is continued until all of the lines excited by adsorbed impurities disappear completely from the spectrum. The conditioning time varies with the type of discharge. When internal electrodes are used in a glow discharge, the conditioning may require several days, but the tube, once free of impurities need not be subjected to another such long conditioning during subsequent use. On the other hand, use of a high frequency discharge tube with external electrodes requires only that the gas in the tube be replaced a few times, after which the tube is ready for use either in qualitative or in quantitative analysis.

In cases where large quantities of the sample are available, it is convenient to use the flow method of analysis. The optimum gas pressure in the discharge tube and the flow rate must be determined experimentally. The recording of the spectrum can start a few minutes after the current has been switched on, and one obtains several spectrograms in succession. The spectrogram which does not show any lines of stray impurities is used in analysis. If one uses short current bursts produced by a discharge
of a capacitor, the tube need not be conditioned since neither the walls nor the electrodes heat up sufficiently to evolve adsorbed gases.

Interpretation of spectrograms consists in identifying every one of the spectral lines visible in the photograph. To speed up a qualitative analysis it is necessary to have on hand a set of photographs showing the spectra of most of the common gases, obtained on the same spectrograph that will be used in the analysis, and if possible, with the same light source. By superposing the analytical and reference spectrograms, one can identify at once a number of lines. Verifying the presence of hydrogen in a gaseous mixture is a most difficult problem, since this gas evolves not only from the walls of the tube but also from the greases and sealing compounds. This is especially true during the first few days after regreasing of stopcocks when the persistent hydrogen line, \( H_a \), can be detected in virtually all spectrograms. Rigorous precautionary measures are therefore necessary when determining traces of hydrogen; specifically, it is advisable to work with weak currents. The spectrum of the gas sample is photographed along with the spectrum of its primary component. The presence of hydrogen cannot be unequivocally established unless the analytical spectrogram displays greater intensity of the hydrogen lines than the reference photograph.

Historically, the first paper on qualitative analysis of gas mixtures, which dates back to 1896, described the determination of hydrogen in air [403]. Then Moureu and Lepape [404] determined the krypton and xenon concentrations in argon by visual photometry. They adjusted the pressures so as to obtain a match between the intensities of the krypton and xenon lines and those of the argon lines at various concentrations of krypton and xenon in argon. Tables of homologous line pairs were then compiled for the concentration range of 0.05 to 0.5%. Pentcheff [405] used the
Moureu-Lepape technique for the analysis of gas from water originating from various natural sources and improved the sensitivity of the method, achieving a limit of detectability of 0.01%.

Heyes [406] worked with condenser spark discharges between metal electrodes at atmospheric pressure. The gas mixture was introduced by suction into a discharge tube in which aluminum electrodes were mounted 8 mm apart. An induction coil (this was the excitation source in many early experiments) with the breakdown gap of 15 cm supplied the current. A capacitance \( C = 8260 \, \mu \text{F} \) and an inductance \( L = 2.3 \times 10^{-5} \, \text{henry} \) were connected in the circuit of the secondary, with a 7 A current flowing through the primary. Analysis, carried out by the method of persistent lines as well as by the method of homologous pairs (internal standard), yielded the following results:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration range, %</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen in hydrogen</td>
<td>0.037-7.8</td>
<td>Persistent lines and homologous pairs</td>
</tr>
<tr>
<td>Hydrogen in nitrogen</td>
<td>1-20</td>
<td>Homologous pairs</td>
</tr>
<tr>
<td>Nitrogen in oxygen</td>
<td>0.057-12.5</td>
<td>Both methods</td>
</tr>
<tr>
<td>Oxygen in nitrogen</td>
<td>1.25-12.5</td>
<td>Both methods</td>
</tr>
</tbody>
</table>

The intensities of nitrogen lines were compared with those of iron lines, since the electrodes contained iron as an impurity. However, this procedure is not too good, because the intensity of lines of the electrode material varies (with the discharge conditions). As seen from the table, the sensitivity was poorest in the case of determinations of impurities in nitrogen. The sensitivity of hydrogen determinations in nitrogen is improved if helium is added. This sharply increases the intensity of the \( \text{H}_2 \) lines. Thus, the intensity of the \( \text{H}_2 \) line at a concentration of 1.75% \( \text{H}_2 \) in \( \text{N}_2 \) is the same as when 10% \( \text{H}_2 \) is present in the absence of He. The Heyes method is still extensively used in spectral analysis of gas mixtures,
because addition of large quantities of an element with a high excitation potential increases the electron temperature in the discharge gap and, consequently, the analytical sensitivity for the difficult-to-excite components.*

Somewhat earlier, interesting results were reported by Paneth and Petters [407] during analysis of helium and neon in air. They used an induction coil connected in parallel to a spark gap. The discharge tube was a narrow capillary. The thin wire electrodes could be moved in the capillary, thus materially altering the discharge conditions.

In later experiments, Paneth and Günther [408] abandoned the induction coil, because the method failed to produce spectral lines of sufficient intensity. They then worked with high frequency electrodeless discharges from a Tesla transformer and determined small quantities of hydrogen and neon in helium. The gases were excited in 0.1-0.4 mm capillaries. Hydrogen was detected in helium in concentrations as low as 0.1%, with the appearance of H lines being strongly dependent on pressure. Best results were obtained at pressures ranging from 2-4 mm Hg. In determining neon in helium, the pressure range of 2-4 mm Hg was again used, and the limit of detection was 0.002%.

Qualitative analysis of inert gases in helium is described by Karlik [358]. An h-f tube oscillator was used for spectrum excitation [409]. The quartz discharge tube, 1-1.5 mm in diameter, carried external electrodes set 3.5 cm apart. The range of pressures investigated was 0.01 to 0.1 mm Hg. The tube was connected to the remainder of the unit by means of a mercury seal so that it could be rotated alternately toward one of two spectrographs, one

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*The optimum quantities of helium added to the mixture were selected by experiment. It would appear that it is undesirable to dilute the mixture more than by a factor of 10.
of which was used for the visible and the other the UV spectrum. Long low pressure discharge was associated with a fatigue effect, which was apparent from the fact that it became more and more difficult to start the discharge. The fatigue was removed upon introduction of air or oxygen into the tube. Prior to analysis the tube was conditioned in pure helium. Karlik tabulated the limits of detection (in %) for argon, krypton, xenon and neon in helium, both in the visible and the UV regions:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Spectral region</th>
<th>Absolute quantity cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ultraviolet</td>
<td>Visible</td>
</tr>
<tr>
<td>Argon</td>
<td>5·10$^{-3}$</td>
<td>3·10$^{-2}$</td>
</tr>
<tr>
<td>Krypton</td>
<td>3·10$^{-3}$</td>
<td>2·10$^{-2}$</td>
</tr>
<tr>
<td>Xenon</td>
<td>3·10$^{-3}$</td>
<td>3·10$^{-3}$</td>
</tr>
<tr>
<td>Neon</td>
<td>2—6·10$^{-3}$</td>
<td>2—3·10$^{-3}$</td>
</tr>
</tbody>
</table>

Traces of a difficult-to-excite impurity of a gas mixture can be detected in the cathode regions of a glow discharge. Thus, Frisch and Konovalov [366] were able to detect a few tenths of one percent of argon in nitrogen.

To determine argon in nitrogen, Van Liempt and Visser [410] photographed radiation emitted by the positive column of a glow discharge and studied the argon line $Ar \lambda$ 4159 Å. When the glow is photographed in the vicinity of an internal electrode, the sensitivity for the difficult-to-excite component in a high-frequency discharge is no higher than in analysis confined to the positive column of a glow discharge. However, with external electrodes the sensitivity can be improved to a point where argon can be detected in nitrogen at concentrations of a few tenths of one percent.

Monfils and Posen [411] developed a method for determining traces of nitrogen in argon. The analysis was carried out in a
hollow cathode and in the anode portion of the discharge, using a pointed anode. In using the hollow cathode portion and pressures of the order of $10^{-1}$ mm Hg, the authors were able to detect argon in concentrations of the order of $10^{-2}\%$. The authors noted that, while the sensitivity for nitrogen increases with pressure in the tube, the discharge becomes unstable. In the anode region, the limit of detection was $0.01\%$. However, neither in the anode region nor in the hollow cathode were the discharge conditions favorable for excitation of nitrogen in argon.

Duffendack and Wolfe [381] obtained high sensitivity for nitrogen and hydrogen in helium. In the positive column of a glow discharge, hydrogen was detectable in concentrations as low as $0.005\%$, and nitrogen in concentrations of about $0.02\%$. (In a high frequency discharge, the limit of detection was of the order of $10^{-4}\%$.)

In a pulse discharge [271], helium can be determined in nitrogen or argon, and neon in air, when present in concentrations of the order of $10^{-2}\%$.

The above summary shows that, given a judicious selection of the excitation source, discharge conditions and the discharge tube dimensions, the limit of detection for the difficult-to-excite component can reach $10^{-1}\%$, and in some cases even $10^{-2}\%$, whereas the same limit for the easily excited component of the mixture is of the order of $10^{-4}\%$.

Spectrograms for qualitative analysis can be obtained readily and speedily with the aid of a very compact device described in [412]. This device consists of a pocket-size Zeiss direct vision spectroscope combined with a camera for recording the spectrum on film (see Fig. 68). The excitation of the gas mixture is achieved by means of a standard 2450 Mc, 10-100 W magnetron oscillator.

In many cases, it is relatively simple to obtain a rough quantitative estimate of the composition of a mixture. This is done
semiquantitatively either on the basis of persistent lines or with homologous pairs. The accuracy of the method of persistent lines is not better than the order of magnitude, since the discharge conditions must be very exactly reproduced. More accurate results are obtained via the method of homologous pairs. As a preliminary step, one prepares a table of lines of equal intensities at various concentrations in the mixture. This is done at strictly specified discharge conditions which are then maintained constant. This method can be used both with photographic recording or visual examination of the spectrum. At the present time, it is used mainly in semiquantitative analysis performed with the aid of a styloscope.

When checking the purity of a gas, it is often sufficient to establish only the upper or lower concentration limits for such impurities present. This amounts to, in effect, to a visual semiquantitative evaluation of the impurity content, an evaluation which can be successfully accomplished by means of a styloscope or some other type of visual spectroscope. The visual methods of
semiquantitative metal and alloy determinations by means of a styloscope or stylometer are well developed [413] and are widely used in the industry. Styloscopic determinations of gas mixtures are, in fact, less complicated than those of alloys because gas spectra show fewer lines. Thus, in an actual case of gas mixture analysis with the aid of a styloscope, minute quantities of neon were determined in helium [414]. A high-frequency oscillator was used to generate the discharge. The discharge tube (8 mm I.D.) was made of quartz and contained the sample at a pressure of 8 mm Hg. The light emerging from the discharge capillary was allowed to fall directly upon the styloscope slit, obviating a condenser lens. The most sensitive neon line in the visible spectrum was the $\lambda 6402$ A line. The only helium line displayed in this region ($\lambda 6678$ A) was used as the comparison line. When neon is added to pure helium, its line $\lambda 6402$ A begins to appear in the spectrum only at concentrations of 0.001% or greater. When neon is present in a concentration of 0.08%, the neon and helium lines show equal intensity. Helium spectra are characterized by the scarcity of lines, hence it is extremely difficult to find helium and neon lines of equal intensity at low neon concentrations in the sample. For this reason, the relative line intensities of neon and helium were compared by viewing the spectrum through an optical step attenuator, set up in front of the styloscope slit and at some distance from it. If the attenuator is placed directly on the slit, then the astigmatism of the instrument causes the vertical spectral lines and the horizontal steps of the filter to focus in different planes, so that it is impossible to see clearly and simultaneously both the spectrum and the individual steps of the attenuator. By placing the attenuator in front of the styloscope slit, it is possible to focus in one plane the individual steps of the attenuator and the spectral lines. Comparison of neon and helium
line intensities gave the following results for different degrees of attenuation:

<table>
<thead>
<tr>
<th>Neon concentrations, %</th>
<th>Steps of the optical attenuator (on the left, Ne λ 6402 Å; on the right, He λ 6678 Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>The 6402 Å line becomes visible</td>
</tr>
<tr>
<td>0.009</td>
<td>1 = 2</td>
</tr>
<tr>
<td>0.014</td>
<td>1 = 3</td>
</tr>
<tr>
<td>0.030</td>
<td>1 = 4</td>
</tr>
<tr>
<td>0.050</td>
<td>1 = 5-6</td>
</tr>
<tr>
<td>0.070</td>
<td>1 = 7</td>
</tr>
<tr>
<td>0.080</td>
<td>1 = 1</td>
</tr>
<tr>
<td>0.095</td>
<td>8 = 1</td>
</tr>
<tr>
<td>0.150</td>
<td>7 = 1</td>
</tr>
<tr>
<td>0.220</td>
<td>5 = 1</td>
</tr>
<tr>
<td>0.470</td>
<td>3 = 1</td>
</tr>
<tr>
<td>0.940</td>
<td>2 = 1</td>
</tr>
</tbody>
</table>

Logarithms of the transmission values for the attenuator steps are: 2.0; 1.86; 1.74; 1.64; 1.51; 1.38; 1.24; 1.12.

The concentration range of 0.001-0.01% can be calibrated if a step attenuator of greater optical density is available. Styloscopic determination of neon in helium thus becomes possible at concentrations ranging from 0.001 to 1%. However, other analytical line pairs must be used to determine higher neon concentrations, since at those concentrations the neon line $\lambda$ 6678.28 Å superposes on the helium line $\lambda$ 6678.15 Å. When neon is present in low concentrations, this neon line is weak and cannot affect the results. At neon concentrations of 1% and higher, the analysis should be based on the line pair $\text{He} \, \lambda \, 5876 \, \text{Å} - \text{Ne} \, \lambda \, 5852 \, \text{Å}$.

The determination of the composition of other gas mixtures by the visual semiquantitative technique is also relatively simple.

23. QUANTITATIVE ANALYSIS OF BINARY GAS MIXTURES

The analysis of binary gas mixtures can be divided into the following groups:

I. Determination of molecular gases in inert gases.
II. Analysis of mixtures of inert gases.

III. Determination of inert gases in molecular gases.

IV. Analysis of mixtures consisting of two molecular gases.

The first group of analysis can be classified as determination of an easily excited component in a difficult-to-excite primary constituent, while the third group, is the opposite, that is, determination of a difficult-to-excite minor component in an easily excited primary constituent. In groups II and IV, the primary constituent can be either an easily or a difficult-to-excite gas.

We shall discuss a few typical cases which illustrate the analytical approach to each of the above groups. The gas mixtures as well as the analytical pairs used are listed in Appendix II.

I. Determining nitrogen, oxygen, hydrogen and hydrocarbon impurities in inert gases

This is the simplest case of analysis of an easily excited component in a difficult-to-excite gas, and there are no major difficulties in achieving relatively high sensitivity. The light source is the positive column of a DC or a high-frequency discharge. The most reproducible results are achieved with a high frequency discharge in a tube with external electrodes. In the determinations of nitrogen, oxygen and hydrogen in inert gases, the maximum relative sensitivity (of the order of $10^{-3}$-$10^{-5}\%$) can be obtained only when the gas pressure in the discharge tube is high. Increasing the pressure in large-diameter discharge tubes causes a compression of the positive column, which results in a significant decrease in the brightness of the radiation. Therefore, there is nothing to be gained by operating at pressures higher than 20 mm Hg, because the relative sensitivity under these conditions does not exceed a few hundredths of one percent. On the other hand, in narrow capillaries (0.5-1 mm bore), pressures of several
hundred mm Hg do not reduce the brightness of the emitted radiation, so that one can determine impurities in concentrations of $10^{-3}-10^{-5}\%$ [415].

**Nitrogen determination in helium**

Nitrogen determinations in inert gases require special attention to the condition of surfaces in the discharge tube. Nitrogen adsorption from the sample has been observed even in discharge tubes subjected to efficient preliminary conditioning. It was noted, for example, that nitrogen bands in helium spectra become detectable only at concentrations of about $10^{-3}\%$. However, if the tube has been flushed several times with a mixture containing $10^{-3}\%$ nitrogen in helium, the intensity of nitrogen bands will increase appreciably upon addition of only $2 \cdot 10^{-5}\%$ $N_2$ to this mixture. The calibration curves for nitrogen in helium (see Fig. 69) were obtained under

![Calibration curves for determination of nitrogen in helium. The curves were obtained under several discharge conditions.](image)
the following conditions. The mixture was excited by a high frequency discharge (f = 6 Mc) in a 1 mm I.D. capillary, at a pressure of 600 mm Hg and a current of 300 mA. Under these conditions the visible spectrum of the mixture (see spectrum X in Appendix VI) displays lines of atomic helium as well as bands of molecules He₂, N₂ and N₂⁺. Analytical pairs such as He₂ λ 4648 Å—N₂⁺ 4600 Å, He₂ λ 4626 Å—N₂⁺ λ4278 Å, N₂ λ 3998 Å—He I 3889 Å may then be used. Pressure variations of 100 mm Hg do not affect the variation in the relative intensities of the He₂ and N₂⁺ bands. Analytical results are reproducible to within 5%.

**Nitrogen determination in neon**

Over the concentration range of 10⁻⁴ - 10⁻²%, nitrogen admixtures in neon are determined from the bands of the second positive nitrogen system C³Π — B³Π lying in the 3500 Å region (see Appendix VI, spectrum XI). At nitrogen concentrations in the sample of the order of one tenth of one percent, the first positive system of nitrogen bands B³Π — A³Σ can likewise be used for nitrogen determination.

If the nitrogen-containing sample also containing small quantities of carbon dioxide and hydrocarbons, the nitrogen can be determined in neon from the CN bands, whose intensity varies linearly with changes in nitrogen concentration. The analytic conditions are the same as in the case of nitrogen in helium or argon. The mixture is excited at a pressure of the order of 100 mm Hg, using a high frequency discharge and a 0.5-1 mm I.D. capillary. An appropriate interference filter can be used to separate the neon bands.

**Nitrogen determination in argon**

The analytical procedure for determination of nitrogen in argon with a high frequency discharge as an excitation source is described in Section 26.
If the sample is flowing through the discharge tube, the nitrogen-argon mixture can be excited not only in a high frequency discharge, but also in the positive column of an AC discharge [416] or in a hollow cathode [366]. However, the order of magnitude of the relative sensitivity of nitrogen determination in these sources does not exceed 0.01%, with the average analytical error amounting to about 20%.

When traces of nitrogen are determined in a hollow cathode it is advisable to base the analysis on the $\lambda_{4236}$ Å band. At nitrogen contents ranging upward from 0.1%, the $\lambda_{4709}$ Å band can be conveniently employed. The use of analytical pairs $\text{Ar} \lambda_{3949}$ Å—$\text{N}_2 \lambda_{3943}$ Å or $\text{Ar} \lambda_{4044,42}$ Å—$\text{N}_2 \lambda_{4059,4}$ Å is recommended by one experimenter [416].

It was shown [417-420] that the determinations of traces of nitrogen in argon can be conveniently based on the total intensity of bands II of the positive nitrogen system. These bands are located in the 3900-3600 Å region, which is easily separated by means of filters. This technique has been employed by a number of authors in developing automatic gas analyzers [358, 359, 421, 422]. A description of such analyzers was given in Section 14.

**Oxygen determination in inert gases**

Oxygen concentrations of $10^{-4}$% and higher can be determined in neon and helium if the sample is excited by means of a high frequency discharge in 0.5-1 mm I.D. capillary at a pressure of $\sim 600$ mm Hg. The analysis is based on the lines of atomic oxygen in the infrared spectrum. When neon or helium are the principal constituents, the analytical line pairs are $\text{OI}\lambda_{7772}$ Å—$\text{NeI}\lambda_{7839}$ Å and $\text{OI}\lambda_{7772}$ Å—$\text{HeI}\lambda_{7281}$ Å, respectively.

Again, the discharge tube should be flushed with the sample prior to analysis, since oxygen is adsorbed on the discharge tube to an even greater extent than nitrogen.
The limit of detection of oxygen in argon is lower than in helium or neon, it being no higher than 0.01%. The analysis should be based on the analytical pair OI $\lambda$ 7772 A—Ar $\lambda$ 7624 A.

Figure 70 shows the calibration curves for oxygen in inert gases. The shallow slope of the curves and their deviations from linearity over the range of low concentrations can be attributed to the presence of a background as well as traces of oxygen which remain adsorbed on the walls of the tube even after flushing with pure inert gas.

The sensitivity of oxygen determinations can be improved by using equipment of high dispersion. The above results were obtained with an ISP-51 spectrograph, $\lambda = 270$ mm (see Appendix IV). Simplified analytical techniques can be used provided one also employs a monochromatic filter with a very narrow passband for the OI $\lambda$ 7772 A line.

**Hydrogen determination in inert gases**

In this case, both the vacuum unit and discharge tube should be thoroughly outgassed, and all water vapor should be removed. Outgassing the equipment does not remove all the water: over 18-25
hours, the amount of water vapor evolving from the walls of even a carefully outgassed tube is sufficient to increase the hydrogen content of the sample by several hundredths of one percent (the discharge dissociates the water). In addition, the release of water vapor from the walls is accelerated by the discharge, and the rate of evolution increases with the discharge current. To add to the difficulties, the tube adsorbs hydrogen from the sample. Thus, if the sample in the tube is replaced by a pure gas, the latter will show traces of hydrogen. The latter cannot be completely removed unless the tube is heated by means of a gas burner. These complications are encountered with all mixtures containing hydrogen.

Hydrogen analysis in helium is described in [384, 419, 423, 424]. A helium-hydrogen mixture is excited by a high frequency discharge in a 1-2 mm I.D. capillary, the maximum working pressure being ~20 mm Hg. The limit of detection can be as low as $10^{-3}\%$ [384]. Hydrogen determinations in helium can be carried out both in sealed and open discharge tubes, under conditions of continuous passage of the gas [384, 423]. The analytical line pairs used are $H_\beta \lambda 4861 \text{A} - \text{He} \lambda 4922 \text{A}$, $H_\beta \lambda 4861 \text{A} - \text{He} \lambda 5047 \text{A}$. The red hydrogen line $H_\alpha \lambda 6562 \text{A}$ can also be used. In the concentration range of $10^{-3}-10^{-2}\%$, the analytical errors amounted to about 25% and to 10% for concentrations ranging from $10^{-2}$ to $10^{-1}\%$.

To obtain reproducible results, especially at low hydrogen concentrations, the discharge tube should be thoroughly conditioned by heating with a gas burner after each analysis [384]. When working in a stream of gas, the conditioning of the tube is done with the sample during preliminary firing.

According to [419], an alternative method of hydrogen determination in helium consists of isolating the analytical lines by means of monochromatic interference filters. The limit of detection is in this case determined by the quality of the filter used to separate the hydrogen line. Filters with $\lambda_m = 486$ millimicrons, $\Delta\lambda = 10$
millimicrons at $T_r/T_m$ of the order of several percent, allow the determination of hydrogen in helium when the former is present in amounts of not less than a few hundredths of one percent.

The methods of hydrogen determination in argon and neon are the same as those used in analyzing helium for its hydrogen content.

**Determination of total hydrocarbon content in inert gases**

Emission spectroscopy can only determine the total hydrocarbons in an inert gas, without identifying the compounds. Analysis is based on the CH $\lambda4315$ A or $C_2$ $5165$ A bands, which are easily excited in any type of discharge.* The limit of detection ranges from $10^{-4}$ to $10^{-5}$%. However, if the hydrocarbon content is greater than 0.01%, the analysis becomes virtually impossible, because the spectrum of the sample shows nothing but $C_2$ and CH bands whose intensities do not vary with concentration of the hydrocarbon. If the inert gas also includes hydrogen, the hydrocarbon analysis becomes ambiguous, since the intensities of $C_2$ and CH bands become greater as the concentration of the hydrogen impurities in the sample increases. In such cases, one can establish only the range of the hydrocarbon content in the sample, and even that, more often than not, will involve large errors.

In these paragraphs we discussed only the determination of single minor components of samples consisting mainly of an inert gas. Such analyses are seldom encountered in practice, because what is generally required is the simultaneous determination of several components.

Various techniques for simultaneous determination of several components of a sample are described in Sections 18, 25 and 26.

**II. Analysis of mixtures of inert gases**

Analyses involving binary mixtures of inert gases are required in the manufacture of these gases. For instance, helium of spectral

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*The vapors of the sealing compound (grease) interfere in this analysis because they are decomposed in the discharge, producing high-intensity CH bands.
purity is known to invariably contain traces of neon which cannot be removed by the usual methods. Conversely, neon always contains some helium. It is also very difficult to separate krypton and xenon. Furthermore, a krypton-xenon mixture invariably contains traces of argon.

**Determination of neon in helium**

Neon can be quantitatively determined in a helium-neon mixture when present in concentrations ranging from 0.001 to 99.9%. The standard deviation of a single analysis varies between 3.5 and 7.5%, depending on the concentration. Figures 71 a and b show calibration curves for determination of neon in helium when the former is present in low concentrations (0.002 to 0.01%). The spectra were obtained in a high-frequency discharge using an 8 mm I.D. capillary.
a pressure of 10 mm Hg, and a discharge current of 200 mA. The analytical line pair used was Ne\(\lambda\) 6402 Å—He\(\lambda\) 6678 Å. Figure 71c shows calibration curves plotted on the basis of various analytical pairs for neon concentrations in helium ranging from 18 to 75%. It is evident from this graph that electron temperature variations associated with changes in the composition of the mixture alter the ratios of intensities of different lines of one of the components. Thus, when neon is present in helium at a concentration of 18%, lines Ne\(\lambda\) 5852 Å and Ne\(\lambda\) 5038 Å have about the same intensity, while at a concentration of 75%, the first line is far more intense. Because of this, there is no need for using the lines of a second element as a reference, and the analysis of a mixture can be based on calibration curves plotted from the relative intensities of different lines of the same element, which are changed to a different extent by variations in the discharge conditions. The most conspicuous variation of intensity ratios is noted in the arc and spark lines of one and the same element.

The relative sensitivity of quantitative analysis of helium–neon mixtures is lower than that for helium in nitrogen. This is because an increase in the total pressure in the discharge tube to 600 mm Hg drastically alters the spectral pattern of helium. Thus, at pressures of 100 mm Hg and higher, the spectrum shows, in addition to atomic lines, high intensity He\(_2\) bands (6399, 6310, 5862, 4649, 4626 Å) slightly shaded to the red region of the spectrum. The He\(_2\)\(\lambda\) 6399 Å band becomes superimposed on the sensitive line Ne\(\lambda\) 6402 Å. For this reason, the pressure in the discharge tube should not exceed 100 mm Hg for neon determinations in helium. The limit of detection for neon in this case is \(10^{-3}\%\).

The procedure of neon determination in helium is readily simplified if the neon lines are separated by means of monochromatic filters with a broad passband for 200 Å and \(\lambda_m\) 6400 Å [419].
The limit of detection of helium in neon is 0.1% or less. The 5876 Å analytical line for helium is very close to the neon line 5882 Å. For this reason, the simplified analytical procedure based on the use of filters is not very sensitive. For direct determination of neon in helium in gas discharges, see Section 27.

**Xenon determination in krypton**

This analysis involves no particular difficulties. Limits of detection of about \(10^{-2} - 10^{-3}\%\) can be attained, if the sample is excited in the positive column of a high frequency discharge (1-5 mm I.D. capillaries and pressures of 5-10 mm Hg).

The determination of traces of krypton in xenon is considerably more complicated. The limit of detection, even with a high frequency discharge produced in 0.5 mm I.D. capillary at pressures of 0.4-0.5 mm Hg, does not exceed a few tenths of one percent. The analysis is based on the analytical line pairs Kr 5871 Å—Xe 5875 Å, Kr 5871 Å—Xe 5976 Å, Kr 5571 Å—Xe 5419 Å, etc. Calibration curves for krypton determination in xenon are shown in Fig. 72.

Krypton determination in xenon can be based on the electrode regions of the discharge, or the glow inside the external electrode (which is an analog of a hollow cathode in a high frequency discharge). Both arc and spark krypton and xenon lines in the 4000-4800 Å region can be used as the analytical pairs (see Appendix V, spectrum V).

**Argon determination in a krypton-xenon mixture**

Determination of traces of argon in a krypton-xenon mixture, as well as of traces of krypton in xenon, are typical examples of analysis for a difficult-to-excite component in an easily excited primary constituent. There is little difference between the excitation potentials of Kr and Xe lines, but argon lines require considerably higher excitation potentials. A further difficulty associated with the
determination of argon in krypton-xenon mixtures lies in the fact that
the sensitive argon lines which appear during transitions to meta-
stable levels $^3P_2$ and $^3P_0$ are located in the infrared region. Neverthe-
less, a high frequency discharge, using a 0.5 mm I.D. capillary and
pressures of 0.3–0.5 mm Hg, allows determination of argon in con-
centrations of a few tenths of one percent. The analytical line
pairs used are Ar 6965 Å–Kr 6905 Å, Ar 7067–Kr 6905 Å. In
the concentration range of 0.3–0.1%, the calibration curves have
slopes close to unity, while for concentrations ranging between
1–20%, the slopes are greater than 2.* The error of a single de-
termination does not exceed 10%.

III. Determination of inert gases in molecular gases.
Determination of argon in nitrogen

Frisch and Konovalov [366] were the first to attempt the analysis
of a nitrogen–argon mixture. They used a discharge tube with a
hollow cathode (see Fig. 25b).

*The large slope is apparently due to the fact that the intensity of lines of the primary
constituent also varies with the concentration of the minor component.
As we pointed out earlier (Section 4), a tube with a hollow cathode tends to confine the entire glow region to the interior of the cathode, where both the bands of the molecular nitrogen and the spark lines of argon are excited simultaneously. Frish and Konovalov compared lines $\text{Ar} \text{I} \lambda 4765$ Å and $\text{Ar} \text{I} \lambda 4736$ Å with a line in the band $\lambda 4709$ Å in the rotational structure of nitrogen. The ratio of intensity of the nitrogen band to these argon lines was shown in special experiments to be practically independent of both the current and pressure. Figure 73 shows the calibration curve for argon concentrations in nitrogen ranging from 2 to 96%. The spectra were recorded at 0.65 mm Hg and 65 mA. The analytical sensitivity is very high at low concentrations, where the curve is steep, but it is not so high in the middle region where the slope is shallow. When using a hollow-cathode tube, one can detect argon in nitrogen at concentrations of the order of 0.1%.

Traces of argon in nitrogen can also be detected if the mixture is excited in a high frequency discharge, using the positive column region. For high analytical sensitivity, it is necessary to use small-diameter capillaries (0.4 mm) and low pressures (0.2 mm Hg). In a small-bore capillary the nitrogen molecule dissociates into atoms, and a line spectrum is excited as a result. The calibration curve for argon concentrations in nitrogen ranging from 0.2 to 1.5% is
shown in Fig. 74. For a single determination, the standard deviation is 6%. The intensity of the glow decreases sharply at low pressures. Thus, to increase the intensity of light falling upon the spectrograph slit, the discharge tube was not set up parallel to the slit, but was mounted at right angles to it (the end facing the slit). The tube end consisted of a flat quartz window, and a sharply enlarged image of the capillary was projected upon the slit. This permitted reduction of the exposure to 1/3 or 1/4 of what would have been otherwise necessary.

The nature of the glow produced by a high-frequency discharge is similar to the glow in a hollow cathode [367]. To observe this high-frequency discharge we used a 12 mm diameter tube (Fig. 25a). The spectra were photographed in the middle and lower portions of the tube (as indicated by the arrows). When photographing the lower part of the tube, the light falling on the spectrograph came from the portion of the tube enclosed by the external electrode. The spectra from the middle part differed markedly from those from the lower part of the tube. The former were identical with the normal positive column spectra, while the glow in the lower
section of the tube produced spectra similar to those obtained in hollow-cathode glow. Thus, in the case of nitrogen, molecular spectra predominated in the middle, while atomic spectra were most frequent in the lower part. The high frequency 'hollow cathode' can be used in determining traces of a difficult-to-excite component in an easily excited primary constituent. Figure 75 shows the calibration curve for traces of argon in nitrogen. The curve was plotted at $p = 6 \cdot 10^{-2}$ mm Hg and $i = 300$ mA. The 'hollow cathode' diameter was 12 mm. The slope of this calibration curve is very small, but it is nevertheless convenient to work with a large-diameter tube.

![Figure 75. Calibration curve for determining traces of argon in argon-nitrogen mixtures.](image)

Analysis of argon in air was described in [361, 366, 382 and 415]. The results of these experiments are described in Section 25.

*Krypton determination in oxygen*

The high frequency discharge is also suitable for this analysis. While developing methods for krypton determination in oxygen, we noticed that the first few photographs taken after the sample had been admitted to the discharge tube showed krypton lines of far greater intensity than any of the subsequent photographs. Thus, the difference in optical density (blackening) $\Delta S$ for the analytical pair Kr$\lambda$ 5870 A–O1$\lambda$ 5437 A in three consecutive photographs at 1.5% krypton
in oxygen was 0.28, 0.11 and 0.12, respectively. The respective values for 2.3% krypton in oxygen were 0.55, 0.34 and 0.32. The second and third photographs gave results of excellent reproducibility, while the first photos yielded values with large scatter. It follows that some time should be allowed to elapse after admission of the sample to the discharge tube before photography is started. In the above case the discharge should be maintained for not less than 5 min. An identical effect is observed in the analysis for low nitrogen concentrations in argon.

The calibration curve for determining traces of krypton in oxygen is shown in Fig. 76. The photographs were obtained at \( p = 0.60 \text{ mm Hg, } i = 350 \text{ mA, capillary bore of } 0.5 \text{ mm.} \) The analysis was based on the atomic oxygen line, since the emission spectrum of a neutral oxygen molecule is extremely difficult to obtain.

\[ \text{FIG. 76. Calibration curve for determining krypton concentrations in a krypton-oxygen mixture.} \]

**Helium determination in hydrogen**

The limit of detection of helium in hydrogen in a high frequency discharge produced in a 0.5 mm I.D. capillary under a pressure of 1 mm Hg does not exceed 0.1%. Alongside the atomic hydrogen and helium lines, the spectrum shows a highly intense spectrum of the \( \text{H}_2 \) molecule. A suitable pair of analytical lines is \( \text{He}\lambda 4471 \text{ A—H}_1\lambda \)
The slope of the calibration curve is flat over the low concentration section. The mean error of the analysis can be as high as 8%.

IV. Analyzing mixtures of two molecular gases

Emission spectra from a mixture of molecular gases produced by conventional light sources as a rule do not correspond at all to the composition of the sample. The electric discharge causes dissociation of the majority of molecules into atoms or free radicals, with the result that even a single molecular gas will actually contain two components. Thus, the spectrum shows lines of atoms as well as molecular bands corresponding to excited molecules or free radicals. In addition, the discharge may produce new compounds in the mixture; their spectra may then also appear [367, 425].

All these factors greatly complicate the quantitative analysis of molecular gas mixtures by means of emission spectra. Thus, it is not possible to differentiate between CO and \( \text{CO}_2 \), \( \text{H}_2\text{O} \) and \( \text{H}_2 \), to separate the individual gaseous hydrocarbons, etc. Nevertheless, aside from free radicals which may be present in the sample, emission spectroscopy is capable of determining the components of a number of mixtures consisting of molecular gases with fairly high accuracy.

\textit{Determination of nitrogen in carbon dioxide}

As an example, we shall discuss the analysis of a nitrogen-carbon dioxide mixture. Its high-frequency discharge spectrum will display \( \text{N}_2 \), CO and CN bands. The CO is the result of dissociation of the \( \text{CO}_2 \), while the CN is produced on reactions of CO with N. An equilibrium is established a few minutes after the start of the discharge. The nitrogen content in the carbon dioxide can be determined from both the nitrogen and the CN bands. Calibration curves are plotted from relative intensities of the molecular head band. The width of
the spectrograph slit must be kept strictly constant throughout the calibration and analysis, since the head band intensity is a function of this width (one records a group of overlapping lines in the rotational structure of the band).* Calibration curves for concentrations ranging from 0.5 to 25% are shown in Fig. 77. The spectra were recorded at $p = 3.5$ mm Hg, $i = 350$ mA, $d = 5$ mm, exposure 2-5 min [367]. An alternative illustration of analytical procedures used with mixtures of molecular gases is provided by the analysis of air samples taken near the ground (see Section 25).

![Calibration curve for determining nitrogen in a nitrogen-carbon dioxide mixture.](image)

**FIG. 77. Calibration curve for determining nitrogen in a nitrogen-carbon dioxide mixture.**

### 24. QUANTITATIVE ANALYSIS OF MULTICOMPONENT MIXTURES

Analysis of multicomponent mixtures inevitably involves the effect of the third and subsequent components. The third component effect is especially pronounced in cases where critical potentials of the minor constituents are lower than that of the primary component.

*It follows that in cases where the lines of the rotational structure are sufficiently intense for photometry, the analyst should use one of the components of the rotational structure rather than the head band.*

**The pressure in this case was selected on the basis of incidental considerations. A higher sensitivity of analysis could have been attained at greater pressures.*
Such effects are also involved in analysis of alloys, ores and minerals, and were pointed out time and again by various researchers. Spectral analysis of gases is usually more affected by the third component factor than analysis of alloys and minerals which uses a spark or an arc discharge. In the case of gas samples, the third component effect may 1) alter the discharge conditions (i.e., produce an electron temperature drop) due to the presence of additional elements with low ionization potentials; 2) afford conditions conducive to chemical reactions in the discharge; 3) produce conditions favorable to collisions of the second kind.

Several methods have been developed for analyzing multicomponent mixtures. One such procedure, designed for analysis of ternary mixtures, may be used only when the line intensities are affected by only one of the components [371]. An example of this method is the case where helium is the primary component, while neon and argon, in concentrations ranging from 0.8 to 7%, are the minor constituents. The addition of neon does not appreciably alter the ratio of line intensities of argon and helium, whereas the addition of argon causes a change in the corresponding ratio for helium and neon. This is because the critical potentials of helium and neon differ far less than do the critical potentials of helium and argon, and thus the addition of neon to helium has little effect on the electron temperature (this temperature is already sharply reduced by the presence of argon in the mixture).

In the actual analytical procedure, a calibration curve was established for determination of argon in helium (see Fig. 78a). In constructing the curve, the absence of a neon effect on the ratio of line intensities of argon and helium was verified. The calibration curve was plotted from photographed spectra taken under the following conditions: a high frequency discharge; \( p = 1.4 \text{ mm Hg} \); \( i = 300 \text{ mA} \); tube diameter = 5 mm. Next, the calibration curves
for neon in an argon-neon-helium mixture were plotted under the same conditions but at varying argon concentrations (see Fig. 78b) [371]. Thus, the method boils down to the following: the argon concentration is determined from the first calibration curve, after which one knows which curve from the second family of graphs in Fig. 78b can be used to determine the concentration of neon.

The method of plotting a family of curves was also used to determine argon in air when argon and oxygen concentrations were variable [382] (see Section 25). It was possible to analyze the mixture because changes in argon concentration did not affect the oxygen determination, and a change in oxygen concentration caused only a parallel displacement of the calibration curves for the argon-nitrogen mixture.

However, the third component effect does not always produce a mere parallel shift of the calibration curves: sometimes, it also causes a change in the slope of the curves. Thus, Krasnova and Schreyder observed such changes while developing an analytical
As we stated earlier, this method for analyzing ternary mixtures has a limited application. In cases where both minor components affect each other, one should select another gas as the reference element. The line intensities of that gas should not vary with changes in concentration of the other components. Duffendack and Wolfe [381] used this technique in analyzing mixtures of nitrogen, carbon monoxide, hydrogen and oxygen. The discharge tube (a quartz capillary 3 mm I.D.) had internal nickel electrodes.

FIG. 79. Calibration curves for determining nitrogen (a) and oxygen (b) in an oxygen-nitrogen-hydrogen mixture.
and the discharge current was 25 mA. To reduce the adsorption of gas during the discharge, large amounts of helium were introduced (the helium pressure varied between 2 and 8 mm Hg in different experiments). Helium was used because it is adsorbed on the electrodes and walls of the tube to a lesser extent than the other gases, and its ionization potential is also higher. Hence, the addition of helium does not reduce the electron velocity. However, helium could not be used as an internal standard, since its line intensities vary sharply with the concentration of the other components. The best internal standard proved to be argon, which was used at partial pressures ranging from 0.01 to 0.07 mm Hg. (Naturally, the immunity of the argon line to other components was prechecked.) The argon-helium mixture was admitted to the thoroughly evacuated discharge tube through a trap cooled with liquid air. The purity of the mixture was checked by photographic recording of the discharge. The first photographs displayed some impurity lines, but as the discharge continued these lines vanished.

To obtain a plot of the analytical curves, known quantities of hydrogen (partial pressures of 0.0001 to 0.0075 mm Hg), nitrogen (0.004 to 0.25 mm Hg), oxygen (0.002 to 0.12 mm Hg) and carbon monoxide (0.001 to 0.10 mm Hg) were introduced into the discharge tube. The calibration curve for small nitrogen concentrations in helium is shown in Fig. 80. Similar curves were obtained for hydrogen, oxygen and carbon monoxide in helium.

To determine the composition of an unknown mixture, an accurately known quantity of the sample was introduced into the discharge tube containing a helium-argon mixture (of the same composition as used in plotting the calibration curve) and the spectrum was photographed. If the helium-argon spectrum showed no additional lines or if such lines were of low intensity, another portion of the unknown mixture was admitted the tube, and the
spectrum was rephotographed. The sequence was repeated until all the additional elements were determined from the calibration curves. The composition of the unknown mixture could then be determined using the known ratio of partial pressures of helium and the unknown sample.

Helium dilution is also useful in microanalysis of air because such dilution circumvents the mutual interference of air components [419].

It would seem that if the primary component of a mixture is an inert gas with a high excitation potential and the minor components, which have lower excitation potentials, are present in relatively insignificant amounts, then the mutual interference of the components can be neglected, within the limits of experimental error. In this case, the analysis of a multicomponent mixture involves, in effect, nothing more than a simultaneous determination of several binary mixtures. The correctness of this hypothesis was confirmed by Bochkova and Chernysheva [384] in determining traces of nitrogen and hydrogen in helium. The mixtures were excited by means of a high frequency discharge in a 1-1.5 mm I.D. capillary, the hydrogen and nitrogen concentrations being in the $10^{-3}$ and $10^{-1} \%$ range. The hydrogen was determined by means of
the $H_\beta \lambda 4861 \text{ A} - He \lambda 5047 \text{ A}$ line pair and the $N_2^+ \lambda 4278 \text{ A} - He \lambda 5047 \text{ A}$ pair was used for nitrogen. Line intensities were measured successively by means of an FEU-17 photomultiplier installed in back of the exit slit of an ISP-51 spectrograph (see Appendixes III and IV). The photomultiplier was powered by a stabilized rectifier, and the photocurrent was read off from a microammeter. The analytical procedure used three standards, with helium of spectral purity used in the preparation of standard mixtures. The residual nitrogen and hydrogen in helium was determined by the method of additions. In preparing the calibration curves, the ratios of line intensity for hydrogen-helium and nitrogen-helium mixtures (proportional to the respective photocurrent ratios) were plotted on the ordinate with the minor component concentrations on the abscissa. This procedure gave a series of linear calibration plots at a given pressure, each curve covering a range of minor component concentrations varying by a factor of 10. It was shown that if the nitrogen concentration does not exceed $2 \cdot 10^{-2}\%$, this component does not affect the analysis of $H_2$ in $He$. When the nitrogen content is of the order of $0.1\%$, the error in determining hydrogen concentrations (in helium) of the order of $0.01\%$ is within the limits of the accuracy of the procedure ($\sim 10\%$). However, the error in determining concentrations of the order of $0.001\%$ hydrogen may be as high as $40-50\%$.

The limit of detection of hydrogen in helium is $10^{-3}\%$ (at a pressure of 20 mm Hg). This limit is not, however, imposed by limitations of spectral analysis per se, but by the hydrogen purity attained in the tube. The evolution of hydrogen and water vapor from the tube walls during discharge reduces the analytical sensitivity for traces of hydrogen, thus adversely affecting the accuracy of the method.
In testing for the effect of hydrogen on the determination of nitrogen in a ternary helium-nitrogen-hydrogen mixture [384], it was found that the addition of 0.1% hydrogen to a helium-nitrogen mixture has no effect on detection of nitrogen concentrations of the order of 0.01 to 0.1%. In the nitrogen concentration range of $10^{-2} - 10^{-3}\%$, hydrogen concentrations of the order of $10^{-2}\%$ do not hinder the nitrogen detection. The limit of detection for nitrogen is $10^{-4}\%$. The percentages of nitrogen and hydrogen do not differ by more than an order of magnitude, and therefore the mixture can be analyzed simultaneously for both components. Under industrial conditions the analysis is most conveniently carried out in a stream of gas, using an arrangement of the type shown in Fig. 19. The time required for simultaneous analysis for both components does not exceed 5 minutes.

In some instances the third component effect can be eliminated by a trick, as in analysis of the He-Ne-Ar-Kr and He-Ne-Kr-Xe mixtures [383]. The method resorted to was the familiar spectroscopic technique of stabilizing the excitation conditions by introducing known quantities of a component whose excitation potential is lower than that of any of the other components. This technique, while useful on many occasions, is not altogether advantageous since it lowers the sensitivity.

The problem of analyzing multicomponent gas mixtures has been successfully solved in many cases. Some of these successes were described in this section, and others will be discussed in Sections 25 and 26.

25. ANALYSIS OF AIR

Since air is a multicomponent gas mixture, its quantitative analysis is difficult. Air consists of nitrogen and oxygen (basic constituents), as well as some hydrogen, carbon dioxide, water
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vapor and inert gases (total about 1%) of which argon is the most abundant (about 0.95%).

The composition of air near the ground is generally determined by chemical and physicochemical methods, which are fairly accurate in identifying the active components (O₂, N₂, H₂O, H₂, CO₂). The chemical procedures are, however, not suitable for analyzing inert gases. Fractional distillation with subsequent measurements of gas volumes is accurate only when relatively large gas samples are available [1]. The chemical and physicochemical methods become completely unsuitable for analyzing the composition of upper atmospheric air, a case where the samples are usually extremely small. In this case, optical spectroscopy and mass-spectrometry are the only available means of analysis.

**Analysis of surface air. Determination of hydrogen and moisture in air**

Hydrogen and water vapor in air are determined from the intensities of lines of atomic hydrogen (Balmer series). These lines are produced in the discharge tube by atomic or molecular hydrogen, as well as water vapor. If the water is frozen out, then one can determine the hydrogen content alone.

The direct analysis of hydrogen in air is capable of determining only concentrations not lower than ~1% [370, 403]. The limit of detection can be lowered by one order of magnitude by adding helium in quantities ranging from 10 to 50% of the sample [426].

Microspectroscopic analysis of traces of moisture in air at reduced and at normal pressures was described by Garger [427]. The spectrum was excited in a glow discharge produced in a Frisch all-purpose tube, using an induction coil generating 10-30 kV when combined with the Sventicki arc activator [315]. A condenser discharge can also be used, according to Garger. The discharge tube was filled with a mixture of air and water vapor. The partial pressure of the water was determined by measuring the temperature
in a tube extension containing distilled water, which was placed in a Dewar flask filled with a cooling mixture. The $H_\alpha$ line was used for determining water in concentration of the order of $10^{-3}\%$. Moisture contents of the order of $0.01\% - 0.2\%$ lead to the appearance of the $H_\beta$ and $H_\gamma$ lines as well as the OH $\lambda$ 3064 A band. Upon increasing the moisture content to $3.5\%$, the OI $\lambda$ 6158 line of oxygen appeared and the nitrogen bands decreased in intensity. Garger developed a procedure for determining water in air both at reduced and at normal pressures. The limits of reliable measurements were $0.02 - 2\%$, with an error of $4 - 10\%$.

*Determinations of carbon dioxide and carbon monoxide*

Both the carbon dioxide and the carbon monoxide present in the air are identified in the spectrum by means of the CO bands, since during the discharge carbon dioxide dissociates into carbon monoxide and oxygen. As a result, it is impossible to differentiate spectroscopically between CO and CO$_2$. Where each of these gases must be determined separately, spectroscopy is combined with some technique based on chemical absorption of one of the components. Occasionally simple freezing out of CO$_2$ will suffice, since it is virtually impossible to remove CO by this method.

The limit of detection of carbon dioxide and carbon monoxide in air, when a high frequency discharge is used, is about $1\%$. The analytical pairs are CO $\lambda$ 4835 A $- N_2 \lambda$ 4709 A and CO $\lambda$ 5198 A $- N_2^+ \lambda$ 5228 A; the analysis is carried out in a 0.5 mm I.D. capillary at a pressure of $1 - 2$ mm Hg. The analytical error is of the order of $5\%$. In the concentration range of $1 - 30\%$, calibration curves are linear.

Wignen and Van-Tiggelen [425] determined carbon dioxide in air in which the oxygen concentration was variable. An r-f oscillator generating an 11 meter wave was used for excitation. The discharge was produced in a 5 mm I.D. glass Geissler tube at a pressure of
2.5 mm Hg. The sample-filled tubes were fused to the remainder of the system. These experiments showed that nitrogen is more intensively adsorbed on the discharge tube walls than carbon dioxide. To improve the reproducibility of the results, the spectra were photographed during the first 2-5 min after the discharge current had been switched on. The pressure in the discharge tube varied from 2 to 3.1 mm Hg, but this did not alter the relative intensities of the \( \text{N}_2 \lambda 3159.3 \) Å and \( \text{CO} \lambda 3127 \) Å bands. Variations in the oxygen concentration also failed to alter the ratio of band intensities of \( \text{N}_2 \) to \( \text{CO} \), provided the oxygen content was below 20%.

The procedure developed in [425] allows nitrogen determination over the 3.5-37.5% concentration range, and carbon dioxide determination at concentrations ranging from 46 to 95%. The mean error of analysis amounted to 3% in the case of nitrogen and 1% in the case of \( \text{CO}_2 \). The reported accuracy of the carbon dioxide determination appears doubtful, considering that during fusion of the glass tubes to the system large quantities of \( \text{CO}_2 \) must have evolved from the glass and must have contaminated the sample. Such sources of impurities are very difficult to control.

A very high analytical sensitivity for carbon monoxide in air is obtained in the procedure of [428], which is based on liberation of Hg in the reaction

\[
\text{CO} + \text{HgO} \rightarrow \text{Hg} + \text{CO}_2.
\]

The CO content was determined from the amount of liberated mercury, measured in terms of absorption of the mercury resonance line \( \lambda 2537 \) Å. The limit of detection for CO in this method is \( 10^{-6} \% \).

**Determination of oxygen**

The oxygen content in air is easily determined in the concentration range of 5 to 50%, using the line pair \( \text{O} \lambda 7772 \) Å—\( \text{N} \lambda 7468 \) Å.
The mixture is excited by a high frequency (6 Mc) discharge in a 1 mm I.D. capillary at pressures of a few mm Hg. Lower pressure in the discharge tube improves the analytical sensitivity. Hydrogen, water vapor and carbon dioxide affect the results. Water and carbon dioxide dissociate during the discharge, releasing additional oxygen. The presence of CO$_2$ in amounts below 1% was shown to have no effect on the oxygen analysis. When the CO$_2$ content is higher than 1%, the third component effect, which leads to a displacement of the calibration curves, must be taken into consideration.

Nitrogen and oxygen are intensively adsorbed on the tube walls during the discharge. As a result, the ratio of line intensities of oxygen and nitrogen varies with time. To achieve good reproducibility, this ratio should always be recorded at some fixed time after the start of the discharge. As the oxygen concentration is increased, the intensity of both the molecular bands and atomic lines of nitrogen decreases. As a result, the calibration curves invariably have slopes greater than unity. Future methods for checking rapid changes in the O$_2$ content of the air can be based on these intensity variations of nitrogen bands. In addition, the nitrogen radiation may be separated for photoelectric recording by means of a filter with a fairly wide passband in the 3900-4200 Å region, thus affording the basis for a compact, simple design.

Ozone determination in air is described in Chapter VI.

*Analysis of inert gases in air. Determination of argon*

The air contains relatively large amounts of argon (up to 1%). Therefore argon can be readily detected by any type of discharge: in a hollow cathode [366], a high frequency hollow cathode [367], a pulse discharge [371], the positive column of a high frequency discharge [362, 382], and a high-voltage spark discharge at
pressures close to the atmospheric [415]. The smallest argon concentration in air which is detectable by high frequency discharge without preliminary enrichment of the sample is 0.1%.

Analyses of argon in air are affected by the oxygen concentration. As shown in [382], this effect is negligible when such concentrations do not exceed 10%. However, higher concentrations cause a parallel displacement of the calibration curves for the argon-nitrogen mixture (see Section 23). The experiments were carried out in a high frequency discharge, using a 0.5 mm I.D. capillary and a pressure of several mm Hg. The accuracy, based on the analytical pair Ar λ 7504 Å — Ni λ 7468 Å, is of the order of 5%.

A rapid and accurate procedure (taking less than 1 min) for argon determination in air, with photoelectric readout and recording of the results, was developed by Lee [361] (see Fig. 81). A high frequency oscillator was used to excite the discharge in a capillary. A continuous air stream was drawn through the discharge tube by means of a circulating system similar to the one proposed by Broida and Moyer (see Section 29). The discharge tube capillary was cooled with water. A photomultiplier was used to detect the radiation from argon line λ 4158 Å and nitrogen line λ 3998 Å. This radiation was separated by a monochromator with a diffraction grating.

In the concentration range of 0.9 to 1.1%, argon can be determined with high accuracy by measuring either the ratio of line intensities of argon and nitrogen or the absolute line intensities of argon. Lee has thoroughly explored the factors responsible for deviations of the ratio of the two signals (argon and nitrogen) from normal, and selected optimal excitation conditions and gas pressures in the discharge tube. In analyses based on the absolute intensities and on the ratio of intensities of the argon and nitrogen
lines, the analytical accuracy was as high as $95 \pm 0.43\%$* and $95 \pm 1.4\%$, respectively. Analysis based on absolute measurements thus appears to be the more accurate. This is because the intensities of the nitrogen lines vary markedly with the discharge conditions, while the intensities of the argon lines remain constant. In such cases, there seems to be no point in relying on relative

*This means that $95\%$ of the measurements involved errors not exceeding $0.43\%$. 
measurements. According to Lee the analytical accuracy is improved by using a 2450 Mc oscillator. Since the concentration ratio of nitrogen to oxygen remained constant in these experiments, Lee did not need to consider possible changes in nitrogen and argon line intensities at varying oxygen concentrations.

**Determination of helium**

The helium content of air is very small. It cannot be detected spectroscopically even after all the active gases have been removed and the inert gas residue is analyzed. Helium concentration in a natural inert gas is of the order of $5 \cdot 10^{-4}\%$, while its limit of detection in argon is no higher than 0.05-0.1%. It follows that the helium content in air cannot be determined spectroscopically unless the argon is removed. In some gases escaping from oil wells the helium content is higher, and can be determined without freeing the gases of argon.

The least helium concentration detectable in a high frequency discharge without freeing the air of active gases is of the order of 0.1%. The mixture is excited in a 0.5 mm I.D. capillary at pressures of 1-2 mm Hg, using the analytical pair He$\lambda$ 5876 A–Na$\lambda$ 5800 A. At low concentrations, the calibration curve is not linear. The two factors responsible for the change of slope reduced relative sensitivity, and the presence of a background arising from molecular nitrogen bands. Helium can be determined in air in a pulse discharge [271]. The limit of detection is 0.05% at the following discharge parameters: tube I.D. = 15 mm; pressure = 8 mm Hg; voltage = 3000 V; $C = 12$ microfarads. The system had no discharge gap, and the discharge was fired by means of a Tesla transformer. The spectrum was photographed over an interval of a few pulses, without time scanning. Isolation of a specified time interval corresponding to a proper pulse should considerably
increase the intensity of the helium lines with respect to the background, and will thus improve the analytical sensitivity.

Gladushchak and Schreider used a discharge inside a pulsed hollow cathode to determine low helium concentrations in air. A bank of condensers, capacity 5 microfarads, potential 10 kV, was discharged by thyatron switches and thereby sent a current flowing through the discharge tube. The hollow cathode (diameter—10 mm) was made of aluminum, a metal that has no great tendency to sputter, so that the discharge largely took place in the sample, rather than in a metal vapor. The tube pressure was of the order of 0.5 mm Hg. The limit of detection was about 0.02%.

Pulse sources appear to ensure a higher relative sensitivity in analysis of helium in air than high frequency discharges. One reason for this is that the end helium line $\lambda 5876$ Å superposes on nitrogen bands, which are strongly excited in a high frequency discharge, but fail to do so in a pulsed discharge.

**Determination of krypton**

The krypton of the air can be detected spectroscopically in any concentration up to the normal one provided all active impurities have been removed, leaving a residue of inert gases. The smallest air sample sufficient for a krypton determination is $\sim 10 \text{ cm}^3$. The initial purification (lasting 5 min) is carried out in an arc using calcium electrodes. The complete removal of the residual nitrogen and oxygen is effected in Na or K vapor, while maintaining the discharge in the tube over a period of 20 min. Following such purification the high-frequency discharge spectrum will show nothing but an Ar line and the line Kr $4319$ Å, on which determination is based. Our analysis showed $1.5 \cdot 10^{-4}$% in air, which, within the limits of
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experimental error, agrees well with other data. Higher Kr concentrations in air (above 0.2%) are easily detected without a preliminary purification.

Analysis of air samples from the upper atmosphere

The upper atmosphere air can be analyzed for only three components—nitrogen, oxygen and argon. The analysis differs little from that for surface air. The difficulty lies in the fact that the gases in the sample are easily adsorbed in the discharge tube, and only minute samples are available. To obtain reliable analytic results, two factors must be given careful consideration: 1) sampling of the air and storage of the sample; 2) analysis of microquantities of the gas.

Sampling and storage of air samples are described in detail by Mirtov [389]. Although his studies were of a rather specific nature, much of what had been found applies generally to the preliminary steps necessary for any gas microanalysis.

The procedure for determining oxygen, nitrogen and argon admixtures in microvolumes of air is described in [382]. The analysis used a unit designed for microdeterminations of gases (see Section 19). The microsample (from a cylinder containing all the available gas) was drawn by suction into a 200-250 cm$^3$ vessel and was compressed into a 15 cm long, 0.5 mm I.D. capillary. The glow was excited by means of a high frequency oscillator. The line pairs $\text{O} \lambda 7772 \text{ A} - \text{N} \lambda 7468 \text{ A}$ and $\text{A} \lambda 7503 \text{ A} - \text{N} \lambda 7468 \text{ A}$ were used for oxygen and argon, respectively. Calibration curves for oxygen and argon ions in air are shown in Fig. 82. Changes in argon concentration do not alter the ratio of intensities of lines $\text{O}$ and $\text{N}$ and therefore do not affect the shape of the calibration curves. Changes in the oxygen concentration, on the other hand, alter the ratio for Ar and N lines, causing a parallel displacement of the calibration curves, a factor that must be reckoned with in analysis.
The mean error in determining oxygen was 15%, while for argon it was 8%. These large errors proved due to the averaging of results obtained in analyzing the air samples in a "weak" and a strong discharge (see Section 5). The actual error does not exceed 3.5-5% in the case of argon and 5-8% in the case of oxygen.

![Calibration curves for analysis of oxygen (a) and argon (b) in air without diluting the mixture with helium.](image)

These errors are considerably reduced with larger gas samples. Mirtov [389] analyzed 0.5 liter samples of the upper atmosphere at $p = 10^{-3}$ mm Hg. The analytical error averaged 5% for oxygen and 3% for argon.

An alternative technique useful in analyzing minute air samples consists in adding an inert gas to the original mixture. The most suitable gas—which is a discharge carrier—is helium. It has the highest excitation potential of all the gases present, and consequently the latter are more readily excited than helium; for this reason, their detection limits in helium are $10^{-3}-10^{-5}$%. In addition, the total gas mass of the sample is increased by the helium. This reduces the adverse effects associated with changes in the composition of the mixture, as well as the sorption and desorption of gas by the discharge tube walls.
To improve the reproducibility of results, the pressure of the helium added to the original air sample \( (p = 1 \cdot 10^{-4} \text{ mm Hg}, V = 250 \text{ cm}^3) \) must exceed the pressure of the sample by a factor of more than 3 and not more than 100. The best results were obtained on adding a fivefold excess of helium. The addition of helium in 100-fold (or still greater) excesses allows quantitative spectroscopy of gas mixtures in volumes that could scarcely be analyzed otherwise. The minimum air sample required for a single-component determination can be reduced to \( 3 \cdot 10^{-5} \text{ mm Hg} \) in a volume of 250 cm\(^3\) (i.e., 0.01 mm\(^3\) at STP).

Figure 83 shows calibration curves for analysis of argon and oxygen in air, obtained on diluting the original air mixture with an 80-fold amount of helium. Atomic nitrogen as well as helium lines can be used as the reference lines in the case of oxygen. The error in quantitative oxygen analysis is 10-12%. It should be pointed out that when helium is added to the mixture, changes in the oxygen concentration cease to cause shifts in the calibration curves used in analysis for argon. The absolute sensitivity of Ar analysis in air amounts to \( 5 \cdot 10^{-5} \text{ mm}^3 \text{ at STP} \).

**FIG. 83.** Calibration curves for analysis of oxygen (a) and argon (b) in air following dilution of the mixture with helium. The negative \( \Delta S \) values relate to the helium line, and the positive values to the nitrogen line.
The ionic and isotopic composition of upper atmosphere air may be analyzed with the aid of a mass spectrometer. Quantitative analytical data on the composition of the upper air are given in [389, 429-432].

26. FAST ANALYSIS OF GAS MIXTURES

In the preceding sections we have discussed various methods of quantitative spectral analysis where spectrographs or monochromators were used as dispersing systems. Since all such procedures involve a vacuum unit and complex spectroscopic equipment, most techniques designed for spectral gas analysis are too cumbersome for use outside a large laboratory. However, there is a great need for simple and rapid methods of analysis of gaseous media. Such procedures must be adaptable to use by semi-skilled personnel under plant conditions, and should ensure a sufficiently high accuracy and sensitivity of analysis. The so-called "fast" methods of spectral gas analysis meet such requirements. In many cases, especially where binary gas mixtures are analyzed, complex spectroscopic equipment can be replaced by a suitable monochromatic filter [417, 433]. This technique, widely practiced in absorption spectroscopy (see Chapter IV), is now being occasionally used in emission spectral analysis of metals. If a continuous gas flow is available, the vacuum unit can be considerably simplified [416]. Separation of radiation of desired wavelength by means of monochromatic filters, in turn, allows the use of simpler photometric units because the relative intensity of the light flux becomes sufficiently high [358, 359, 418]. In theory, most procedures of quantitative spectral analysis of gases can be simplified through such modifications.

Let us now review in some detail the few reported attempts at developing such methods. Servigne, de Montgareuil and Dominé
[417] worked out a simplified technique for analysis of nitrogen in argon and neon. The unit included a magnetron oscillator ($f = 2450 \text{ Mc}$), an interference filter ($\lambda_m = 3998 \text{ Å}$) and a vacuum photocell. The limit of detection was $10^{-4}\%$, gas consumption, $100 \text{ cm}^3$, and the analysis was finished within a few minutes. According to the authors, similar methods can be used for hydrogen in inert gases, whereby the line H$_\beta$ ($\lambda = 4861 \text{ Å}$) is used.

The same method and equipment were used by Vernotte [312].

Simplified procedures for determination of nitrogen in argon and other inert gases, based on use of interference filters, are described by Bochkova, Razumovskaya, Frisch, Chernysheva and Sagaydak [418-420]. A vacuum unit such as shown in Fig. 19 was used, and the analysis was of the flow type. The gas is drawn by means of a forepump from the distributing manifold and through the discharge tube capillary. The pressure in the tube is regulated by means of valves and a manometer. The glow is excited by an r-f oscillator. The discharge radiation is projected by a condenser lens upon the photocathode of the photomultiplier FEU-19 (see Appendix IV) and is indicated (without amplification) by a microammeter. A glass light filter, with a transmission peak of about $3700 \text{ Å}$ and $\Delta \lambda \approx 400 \text{ Å}$, is employed to separate the nitrogen bands in the $\lambda 3600 \text{ Å}$ region.

A working calibration chart is prepared on the basis of known standard mixtures, with nitrogen concentrations plotted along the abscissa and microammeter readings $\alpha$, along the ordinates. The values of photocurrents $\alpha$ are proportional to the light flux of the radiation emitted by nitrogen bands, and isolated by means of the light filter. The light flux ratio $\alpha/\alpha_0$ can also be used, where $\alpha_0$ is the photocurrent produced by the total radiation from the discharge tube. Since the nitrogen band intensity in argon is strongly dependent on the total pressure, it is essential that the pressure in
the discharge tube be optimum (see Fig. 84) for every range of nitrogen concentrations in argon.

We shall next describe a method for determining the nitrogen content of argon of various purities.

**Technical-grade argon**

Technical-grade argon contains from 9 to 15% nitrogen. At these nitrogen concentrations, high intensity molecular bands appear already at discharge tube pressures of 1-3 mm Hg. This pressure corresponds to curve 5 in Fig. 84; the curve is linear for all nitrogen concentrations below 20%, but has a relatively shallow slope. As the pressure is increased to 10 mm Hg the curve becomes non-linear; its slope is high in the nitrogen concentration range of 1-10% and then markedly decreases in the 10-20% N₂ range. This curve may be used for analyzing nitrogen concentrations in the range of 1-10%. Above 10%, nitrogen must be determined at a lower pressure.

**Pure and spectrally pure argon**

The nitrogen content of pure argon should not, as a rule, exceed 0.5%. A discharge tube pressure of about 50-80 mm Hg is then required for the excitation of strong nitrogen bands. The so-called
spectrally pure argon should contain less than 0.01% nitrogen. To determine such nitrogen traces, the pressure in the discharge tube must be several hundred mm Hg.

Linear calibration curves can virtually always be obtained for nitrogen in argon concentrations ranging from 0.001-0.01, 0.01-0.1, and 0.1-1%. This is done by selecting a discharge tube of proper diameter, and adjusting its pressure level. The curves can be plotted in terms of either absolute values of photocurrent $a$, or of the relative values $\alpha / \alpha_0$. Relative measurements can be made with the aid of a fixed calibration graph which remains constant over a long time. In absolute measurements, however, the calibration curves may undergo a parallel shift, due to instability of the unit. If the relative analysis uses a single photomultiplier, two readings must be taken—one with the filter, the other without—for determining $\alpha / \alpha_0$. An alternative, more convenient method is to obtain the $\alpha / \alpha_0$ ratio directly with the aid of a ratiometer circuit.

Various modifications of the photoelectric circuit for indicating the ratio of two luminous fluxes were discussed in Section 14.

Nitrogen determinations in argon may be seriously distorted by the presence of other gaseous impurities such as oxygen or carbon dioxide. Oxygen concentrations of the order of 0.1% do not affect the analysis of pure and technical-grade argon. At oxygen concentration of the order of 1%, a parallel shift of the curves is noted, producing results which are too low. In view of this, the unit has facilities (see Fig. 19) for scrubbing the sample free of oxygen. This is a trap with copper filings placed in a furnace at 350-400°C. In low concentrations carbon dioxide also does not affect nitrogen determination and is, furthermore, easily removed from argon.

Borok and Aleksandrov [358] separated the desired radiation by means of filters and designed an automatic gas analyzer for continuous nitrogen analysis in argon. They used two filters:
Table 2  Basic data yielded by simplified analysis

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>Component determined</th>
<th>Concentration range, %</th>
<th>Excitation conditions</th>
<th>Filters</th>
<th>Radiation detector</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + N₂ + CO₂ + O₂ + hydrocarbons</td>
<td>N₂</td>
<td>10⁻³-10⁻², 10⁻²-10⁻¹, 10⁻¹-1</td>
<td>r-f discharge f = 6 Mc, d = 1 mm, p = 50-100 mm Hg, gas stream</td>
<td>UFS-3, UFS-4</td>
<td>Photomultiplier FEU-17, Photomultiplier FEU-19</td>
<td>O₂ and CO₂ in concentrations lower than 0.1% do not affect the nitrogen analysis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-20</td>
<td>r-f discharge f = 6 Mc, d = 1 mm, p = 2-5 mm Hg, no gas stream</td>
<td>λₘ = 366 millimicrons</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1-1, 0.01-0.1</td>
<td>r-f discharge f = 30 Mc, d = 5 mm, p = 0.3 mm Hg</td>
<td>S36-11, PS-11</td>
<td>STsB-3, STsB-6</td>
<td>[353]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10⁻²-10⁻¹</td>
<td>AC current f = 50 cps, V = 2000 V, d = 2 mm, p = 10 mm Hg</td>
<td>λₘ = 390 millimicrons</td>
<td>ZhS-11</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10⁻⁴ and higher</td>
<td>r-f discharge f = 2450 Mc, p = 20 mm Hg, r-f discharge f = 2450 Mc</td>
<td>λₘ = 400 millimicrons, λₘ = 399.9 millimicrons</td>
<td>Photocell</td>
<td>[312] [417]</td>
</tr>
<tr>
<td>Total hydrocarbon content</td>
<td></td>
<td>10⁻³-10⁻²</td>
<td>r-f discharge f = 6 Mc, d = 1 mm, p = 200 mm Hg</td>
<td>λₘ = 516.8 millimicrons</td>
<td>Photomultiplier FEU-19</td>
<td></td>
</tr>
</tbody>
</table>
| He + H₂ + N₂  | N₂     | 10⁻³-10⁻² 10⁻²-10⁻¹ | r-f discharge \( f = 6 \text{ Mc} \)  
\( d = 2 \text{ mm} \)  
\( p = 40-60 \text{ mm Hg} \)  
gas stream | \( \lambda_m = 420 \) millimicrons | Photomultiplier FEU-17 | N₂ and H₂ are determined independently over the same 10:1 (upper to lower limit) concentration range |
| H₂     | 10⁻³-10⁻² 10⁻²-10⁻¹ | r-f discharge \( f = 6 \text{ Mc} \)  
\( d = 2 \text{ Mc} \)  
\( p = 40-60 \text{ mm Hg} \) | \( \lambda_m = 507 \) millimicrons  
\( \lambda_m = 486 \) millimicrons | Photomultiplier FEU-17  
Photomultiplier FEU-19 |
| He + Ne | Ne     | 10⁻³-1 | r-f discharge \( f = 6 \text{ Mc} \)  
\( d = 1 \text{ mm} \)  
\( p = 100 \text{ mm Hg} \) | \( \lambda_m = 640 \) millimicrons  
red filter | Photomultiplier FEU-19  
Photomultiplier FEU-22  
with amplifier |
| He + Ne in air | Ne     | 20-35 | r-f discharge \( f = 6 \text{ Mc} \)  
\( d = 0.5 \text{ mm} \)  
\( p = 2 \text{ mm Hg} \) | \( \lambda_m = 640 \) millimicrons  
\( \lambda_m = 588 \) millimicrons | Photomultiplier FEU-22  
Photomultiplier FEU-19  
with amplifier |
| He     | 5-10 | r-f discharge \( f = 6 \text{ Mc} \)  
\( d = 0.5 \text{ mm} \)  
\( p = 2 \text{ mm Hg} \) | \( \lambda_m = 588 \) millimicrons  
\( \lambda_m = 447 \) millimicrons | Photomultiplier FEU-19  
with amplifier |
the first isolates primarily the 4000-5500 Å spectral region, which abounds in argon lines, while the transmission peak of the second filter coincides with the nitrogen bands 3600 Å. The use of a loop-shaped discharge tube (5 mm I.D.) allowed the use of photocells for indication. The effect of pressure on the shape of calibration curves was tested in special experiments. A working pressure of 0.3 mm Hg was selected on the basis of general considerations regarding the gas consumption, as well as the normal operating conditions of the oil diffusion pump producing the gas stream. The pressure is adjusted automatically. A detailed description of this gas analyzer and of its operation was given in Section 14.

Dianov-Klokov and Saltykova [359] used a filter with $\lambda_m 3990$ Å, $\Delta \lambda 150$ Å to separate the nitrogen radiation, plus a special filter for argon. The nitrogen in argon was again determined by the gas flow technique. The glow was excited in a discharge tube provided with internal electrodes (capillary 2 mm, I.D., pressure about 10 mm Hg). An original system operating with a single photomultiplier and a ratiometer (see Section 14) was used to indicate the intensity ratio of the two fluxes.

All these techniques, while embodying somewhat different designs, are based on the same principle of using light fluxes of high intensity. This allows considerable simplification of both the analytical procedure and the equipment. The general method is no less accurate than the more complex spectroscopic techniques, and at the same time it enables the analyst to carry out a determination within 2-3 min. It can be used to determine nitrogen in other inert gases, as well as hydrogen in helium, neon in helium, and a neon-helium mixture in nitrogen. All that is necessary is the selection of filters suitable to each analytical problem.

The results of the simplified methods are summarized in Table 2.
GAS MIXTURE ANALYSIS IN GAS DISCHARGE TUBE

As was shown in the case of analysis of hydrogen in helium, the use of wideband filters reduces the relative sensitivity of the analysis.

27. GAS MIXTURE ANALYSIS IN GAS DISCHARGE TUBES

Pure inert gases, their mixtures, and hydrogen are used in industry to fill various types of gas-discharge devices (gas rectifiers, thyratrons, voltage stabilizers). The performance of such equipment, as well as its useful life, depends to a large extent on the composition of the filling gas, as well as maintenance of its purity during service. The filling gas cannot be sampled for spectroscopy while the equipment is in operation. The composition of the gas can only be checked either before the final assembly of the device, or when it is no longer in service.

In many cases, however, the composition and purity of the filling gases can be tested in the gas discharge device itself, during its normal operation. While the data on this are, so far, quite scarce, they are of great interest, inasmuch as they broaden the scope of procedures of emission analysis.

In one study [293] neon admixtures (10^{-3}-1%) in helium were analyzed directly in a TG-1P tube (filament voltage, 6.3 V; plate current, 35 mA; working gas pressure, 2 mm Hg) by the three-standard method. An arc discharge occurs in this tube during normal operation. The glow was observed through 1 mm diameter apertures in the tube plate. These perforations did not affect the tube characteristics. The reference tubes were filled with the reference mixtures in a separate installation. Direct analysis in TG-1P tubes yielded results which showed good agreement with those obtained by the use of a high frequency discharge. No changes in the gas composition were noted at the end of the service life of
the tubes. The same tubes, according to the authors of [293], can be used as light source in analyzing helium purity.

Kotlik and Lomonosova [294] recommend using a glow discharge produced in pilot lamp SN-1 for testing the composition of argon-helium and argon-neon mixtures. The lamp operated on an AC line current. The argon in helium analysis was based on the line pair Arλ 4159 Å—Heλ 4471 Å. In the argon concentration range of 0.5-2.0%, the operating pressure in the lamp was 30 mm Hg. In the argon in neon analysis, the pressure was 30 mm Hg for the 0.1-1% argon range and 20 mm Hg for the 2-8% argon range, whereby the line pair used was Arλ 4191 Å—Neλ 5341 Å. The spectra were recorded photographically. Photoelectric indication was the alternative method in argon-helium determinations. A λ 4200 Å interference filter was employed to separate the radiation due to argon lines.

Musson-Genon and Deschamps [434] determined the water vapor in tubes such as those used in radar installations while the tubes were in operation. They did this by monitoring changes in intensity of the OHλ 3064 Å band. The discharge was excited by means of a pulse high frequency oscillator at a tube pressure ranging from 1 to 20 mm Hg. The tube filling consisted of carbon dioxide (as the principal component), hydrogen and water vapor. The calibration curve, plotted prior to the operation on the basis of known water vapor concentrations (the water vapor pressure varied from 0.5 to 16 mm Hg), served to follow changes in these concentrations while the tubes were operating. The method is not without faults, since other factors, besides water vapor, may cause the appearance of OH bands in a spectrum.

It is still more difficult to make emission-spectroscopical analyses of residual gases as well as gases liberated during the normal operation of vacuum equipment. Such analytical tasks are generally carried out by use of mass spectrometer techniques.
A mass spectrometer of special design, devised for analyzing gases released during the manufacture and normal operation of electronic tubes, was described by Morrison [435]. The tubes are opened under vacuum, by means of a special device. The gases are collected in a measuring pipet with the aid of a small Töpler pump, and are then analyzed in the mass spectrometer. It was shown experimentally that the bulk of the gas consists of carbon monoxide and evolves from the plate and its supporting structure. Gases collected in this manner can also be analyzed by microspectroscopical microtechniques.

Residual gases can also be analyzed with the aid of standard resonance mass spectrometers of the omegatron type [436], at pressures as low as $10^{-11}$ mm Hg.

28. ANALYSIS OF GAS MIXTURES IN MEDICINE

The first experiments on determination of nitrogen in exhaled gases date back to 1944, when Lilly and Anderson [437] developed a simple gas analyzer. A tube operating on a stabilized direct current (2-5 mA) was the light source, and the glow of the positive column was analyzed. A filter and photocell were used to separate the wavelength range of 3100-4800 Å. It was established by special tests that the photocell failed to detect the radiation emitted by the $\text{O}_2$, $\text{CO}_2$ and water vapor impurities, hence it indicated changes in the nitrogen concentration. This gas analyzer was further improved [438] and could be used for nitrogen determinations in the concentration range of 0.5 to 80%. The analysis was of the flow type.

White et al. [439-443] carried out a series of studies on the analysis of exhaled gases. Tubes of the type used by Lilly and Anderson, as well as tubes using external electrodes, were the light sources. The oscillator frequency was varied between $3 \cdot 10^3$ to $6 \cdot 10^3$ cycles. A modified Beckmann spectrophotometer, operating
as monochromator, indicated the radiation. Photographic measurements were taken simultaneously. Pressure in the discharge tube was varied from a few tenths to several mm Hg. Analytical procedures were developed for CO\textsubscript{2}, N\textsubscript{2} and O\textsubscript{2}. In the early experiments, the CO\textsubscript{2} analysis was based on the band CO\textsubscript{2}λ 4815 Å, and in later studies, on CO\textsubscript{2} bands in the λ 2883-2896 Å region. Calibration curves were plotted for CO\textsubscript{2} determination in the concentration range 3-10%. Nitrogen analysis, for concentrations ranging from 25-80%, was based on the λ 2372 Å band. A triplet line λ 7774 Å and a singlet line λ 8446 Å were used to analyze oxygen in concentrations of 0.25-100%. The analysis was continuous, its total time not exceeding 0.1 sec.

Reviews of the studies on emission spectral analysis of exhaled gases were presented by White and Lovelage [438, 439].

Comparing the results obtained by mass spectrometric and spectroscopic nitrogen determinations, White [439] came to the conclusion that while spectroscopic analysis is less accurate than mass spectrometry, it is both more sensitive and less time-consuming.

Determination of changes in nitrogen content in medical research with the aid of a low frequency discharge was discussed by Nakagawa [444]. The analysis of a mixture of N\textsubscript{2}, CO\textsubscript{2}, H\textsubscript{2}O and O\textsubscript{2} at rapidly changing oxygen content, based on the oxygen band absorption in the Schumann region, is described in Section 33.

29. SPECTRAL ANALYSIS OF ISOTOPES

Both atomic and molecular spectra can be used for determining the isotopic composition of a mixture.* Atoms of the same element that differ in weight (isotopes) have differing energy levels.

*The fundamentals and more important results of spectral analysis of isotopes are discussed in [209, 445 and 446].
This shift in levels leads to differences in the transition frequencies between levels, which in turn manifest themselves in altered wavelengths.

Two factors are responsible for isotopic shifts: 1) the nuclear mass is finite (it is not infinitely large with respect to the mass of an electron); 2) the nuclear volume is finite [19]. Differences between the masses of nuclei lead to changes in the Rydberg constant. The following equation holds for a single electron system:

\[
\frac{\Delta \lambda}{\lambda} = \frac{m}{M} \left( \frac{1}{A_1} - \frac{1}{A_2} \right) = \frac{m}{M} \frac{(A_2 - A_1)}{A_1 A_2},
\]

where \( m \) is the electron mass, \( M \) is the proton mass, \( A_1 \) and \( A_2 \) denote the atomic weights of the two isotopes. It follows from (5.1) that the isotope shift is approximately inversely proportional to the square of the average atomic weight. In the case of light nuclei, the isotope shift which is caused by a change in the mass of the nucleus can be detected without using high resolution equipment. For a hydrogen-tritium mixture, the shift of the first few terms in the Balmer series is of the order of two angstroms (2.37 Å for \( H_3 \) and 1.78 Å for \( H_2 \)). A far less pronounced isotope shift is noted for helium lines, and a still smaller one for carbon and nitrogen lines. The elements from the middle of the periodic system are characterized by very small isotope shifts. In the case of the heavy elements the shift increases, as the volume effect becomes the primary factor. The nucleus can no longer be treated as a point, so that its dimensions must be taken into consideration [19].

Because of the low isotope shift values obtained for the atomic lines of nearly all elements, the determination must be based on molecular spectra, where the isotope shifts are generally considerably more pronounced. Such molecular shifts result from differences in the frequency of natural vibrations of the isotopic molecules, as well as from differences in their moments of inertia.
The energy of a molecule can be expressed as the sum of electronic \( E_e \), vibrational \( E_v \) and rotational \( E_r \) energies:

\[
E = E_e + E_v + E_r. \tag{5.2}
\]

The isotope mass has little effect on the electronic energy of a molecule, and hence the shift of energy levels, caused by shifts in the electronic levels, is neglected.

The isotope shifts will now be calculated for the vibrational levels. The vibrational energy is determined from the equation

\[
E_v = \hbar \omega \left( \nu + \frac{1}{2} \right) - \hbar x \omega \left( \nu + \frac{1}{2} \right)^2 + \ldots, \tag{5.3}
\]

where \( \hbar \) is Planck's constant divided by \( 2\pi \), \( \omega \) is the angular vibrational frequency, \( \nu \) is the vibrational quantum number, and \( x \) is the anharmonicity constant.

Neglecting the anharmonicity, we shall calculate the vibration frequency \( \nu_v \) corresponding to a transition between two vibrational levels:

\[
\nu_v = \omega \left( \nu' - \nu'' \right). \tag{5.4}
\]

The angular vibrational frequency \( \omega \) can be found from the equation

\[
\omega = \sqrt{\frac{k}{\mu}}, \tag{5.5}
\]

where \( k \) is the quasielastic modulus** and \( \mu \) is reduced mass. For a diatomic molecule, we have

\[
\mu = \frac{m_1 m_2}{m_1 + m_2}, \tag{5.6}
\]

where \( m_1 \) and \( m_2 \) are the respective masses of the two nuclei \( \alpha \) and \( \beta \).

We thus obtain for the isotopic shift \( \Delta \nu_v \)

\[
\nu_{v_1} - \nu_{v_2} = \Delta \nu_v = \frac{1}{2\pi} \left( \omega_2 - \omega_1 \right) \left( \nu' - \nu'' \right). \tag{5.7}
\]

The values \( \omega_1 \) and \( \omega_2 \) will now be expressed in terms of the reduced

---

*Equation (5.2) is approximate, since to some extent these energies are interdependent.*

**\( k \) is more commonly referred to as the force constant (Editor's note).
masses of the two isotope molecules:

\[ \nu_v - \nu_v = \frac{\omega_1}{2\pi}(\rho - 1)(v' - v'') \]  

(5.8)

where \( \rho = \sqrt{\frac{\mu_2}{\mu_1}} \). Hence

\[ \frac{\Delta \nu}{\nu_v} = \rho - 1. \]  

(5.9)

Superimposed upon the vibrational isotopic effect is a rotational isotopic effect, which produces an additional shift of rotational lines [16]. The rotational energy \( E_T \) of a diatomic molecule is determined with the aid of the equation

\[ E_T = hB_0/(J + 1), \]  

(5.10)

where \( h \) is the Planck constant, \( J \) is the rotational quantum number, \( B_0 \) is a constant whose value depends on the moment of inertia of the molecule, \( I_0 = \mu r_0^2 \), and \( r_0 \) is the distance between the nuclei:

\[ B_0 = \frac{h}{8\pi^2 r_0}. \]  

(5.11)

The expression for the vibration frequency corresponding to a transition between two rotational terms \( (J-1 \rightarrow J) \) can be written in the form

\[ \nu_r = 2B_0J. \]  

(5.12)

where \( J \) is the rotational quantum number of the upper state. Remembering equations (5.10), (5.11) and (5.12), we calculate \( \Delta \nu_T/\nu_T \) for the two isotope molecules:

\[ \frac{\Delta \nu_T}{\nu_T} = \rho^2 - 1. \]  

(5.13)

The overall isotopic shift \( \Delta \nu \) arising from the shift in both the vibrational and the rotational terms is given by the approximate expression

\[ \Delta \nu = (\rho - 1) \nu_v + (\rho^2 - 1) \nu_r. \]  

(5.14)
Since \( v_v \gg v_r \), it follows that the isotope shift is determined largely by the shift of the vibrational levels.

We now turn to the discussion of the methods of isotope analysis, and the more important results obtained therefrom.

Thus far, analytical procedures have been developed for the gaseous mixtures of hydrogen isotopes [209, 290, 447-455], helium isotopes [209, 456, 457], carbon isotopes [209, 458, 459], and nitrogen isotopes [209, 460-464].

Spectroscopic studies of isotopic mixtures involve certain difficulties. Equipment of high resolving power is required for the resolution of spectral lines which differ in wavelength by only a few tenths of an angstrom, and for the quantitative measurement of the ratio of their intensities. Such high resolution equipment must be even more efficient in cases where the concentration ratio of one isotope to the other is very high, since the intensity measurement then involves a weak line located next to a very strong line. For this reason, procedures for the spectral analysis of isotopes use either diffraction grating spectrographs or Fabry-Perot standard interference filters in conjunction with a spectrograph or an appropriate light filter.

The analysis of isotopic mixtures, on the other hand, does not involve some difficulties encountered in analysis of ordinary gas mixtures which can be of an arbitrary composition. The requirements are not nearly as high with respect to the stability of the light source or the constancy of pressure in the discharge tube. Nor is it necessary to create discharge conditions especially favorable for the excitation of a particular component of the mixture. Any changes in discharge parameters should have the same effect on the lines of both isotopes, since the excitation potentials of isotopic spectral lines are very nearly the same, as are the effective cross sections of atomic excitations and the transition probabilities.
A basic problem in developing methods for analysis of isotopic mixtures concerns the feasibility of devising an analytical procedure which uses no reference standards. To start with, it is essential to check whether the changes in the ratio of isotopes in the mixture manifest themselves in changes in the ratio of the intensities of their spectral lines. If such a relationship does exist, there is no need for standards, and the intensity ratio of the isotopes can be taken as a measure of relative concentration. This intensity ratio is influenced by many factors. The most important of these, it would seem, is the separation of isotopes in the narrow capillaries of the input system, and of the discharge tube proper. It follows that analysis without standards requires conditions under which such separation does not occur [209]. The elimination of standards considerably simplifies and reduces the duration of the analytical procedure.

Let us now review in some detail the analyses of various isotopic mixtures.

**Determining the isotopic composition of hydrogen**

Most of the experimental work on isotope analysis was devoted to this problem. The early studies were aimed at evaluating the hydrogen enrichment with deuterium [401, 465]. The deuterium determination procedure was refined by Van Tiggelen [447], who carried out the analysis in a sealed discharge tube, using photographic recording of spectra. The earlier methods for analyzing mixtures of hydrogen isotopes were substantially modified by Broida et al. [448-450]. The analysis was of the flow type, with photoelectric indication of the spectra.

Broida and Moyer [448] showed that the ratio of line intensities of hydrogen and deuterium (which is the measure of the deuterium concentration) depends on the discharge tube diameter, the pressure in the tube, the current density, and the rate of gas flow.
through the discharge tube. The relative line intensities may also be affected by the presence of impurities. Figure 85 shows a schematic diagram of the Broida apparatus for determination of deuterium in hydrogen (deuterium concentration ranges from 76 to 95%). The hydrogen and deuterium were obtained electrolytically, and deuterium was freed of hydrogen by diffusion through a heated palladium capillary. Reference mixtures were prepared in a 3 liter vessel at a pressure of the order of 600 mm Hg. The analysis was of the flow type, to eliminate hydrogen adsorption on and its evolution from the discharge tube walls. The gas flow rate was regulated by using capillaries of various diameters. The mixture was excited in a 10 cm long, 4-8 mm I.D. discharge tube, connected to a 400 W high frequency oscillator. To achieve a more stable glow, the tube was cooled with running water. A diffraction grating monochromator (D = 10.4 Å/mm) coupled to a photomultiplier indicated the output radiation.

The hydrogen:deuterium line intensity ratio varies with the pressure in the tube. To maintain a steady pressure, a 500 cm³
vessel was connected to the tube. In addition, a Töpler pump was provided which made it possible to vary the pressure, increasing it approximately fourfold without changing the composition of the mixture. The authors of [448] point out that when one of the isotopes predominates in the mixture, the intensity of each line need not be measured with an accuracy of 0.5% in order to determine the concentration with this accuracy. The error in determining the ratio of concentrations of deuterium and hydrogen \( \delta(D/H) \) is determined from the equation
\[
\delta \left( \frac{D}{H} \right) \leq 0.005 \left( \frac{D}{H} \right)^2.
\] (5.15)

This means that in the particular case where \( D/H = 9 \), an error amounting to about 0.4 or 4% can be allowed in \( D/H \) determination to obtain a 0.5% error in the deuterium concentration [448].

A method for analyzing a ternary hydrogen-deuterium-air mixture in an arrangement of the type shown in Fig. 85 is described by Broida and Morgan [449]. The air has no effect on the relative intensities of the hydrogen and deuterium lines. The \( D/H + D \) ratio remains constant to within 0.07% upon addition of 4.8% air, and constant to within 0.1% if the amount of added air is 50%. Figure 86 shows the calibration curves of Broida and Morgan for determination of air in a hydrogen-air-deuterium mixture. The accuracy of analysis with the aid of these curves is about 0.1%, with the limit of detection for air being 0.01%. The curves were plotted for air concentrations below 6%, and deuterium concentrations above 90%, but the range can be extended considerably for both components.
It was found that the ratio of line intensities is not the same as the ratio of concentrations of hydrogen and deuterium in the mixture. The analysis was therefore based on calibration curves plotted for specified discharge conditions.

Zaydel' et al. [453] investigated the possible causes of discrepancies between the line intensity and isotope concentration ratios. They tested the effects of self-absorption, degree of dissociation, separation of mixture components, light scattering, overlapping of component lines, etc. They concluded that isotope separation in the capillaries was the major factor involved. By selecting the right pressure and flow rates, they were able to obtain line intensity ratios which were equal to ratios of isotope concentrations. This enabled them to develop a procedure for hydrogen determination in deuterium employing no standards. This procedure is valid within the concentration range of 2 to 90%. The apparatus and analytical results are described in [209, 290, 453].

Borgest and Zaydel' [209, 455] suggested the use of an interference polarization filter for determining traces of deuterium in hydrogen. The filter attenuated the stronger $\text{H}_2$ line so that the edge of the line no longer interfered with determination of deuterium concentrations of the order of 0.01%. This analysis uses calibration curves.

Ostrovskaya and Zaydel' [454] proposed reducing the pressure in the discharge tube to 1-2 mm Hg in order to improve the resolution of hydrogen and deuterium lines. This led to a narrowing of the line shapes for both gases, since these shapes resulted from collision broadening. According to these authors, analysis without standards can be employed at concentrations down to 0.1%. The determination of lower concentrations requires standards. For deuterium concentrations close to the natural content in hydrogen
(0.015%) the error reaches 25%, but it decreases at higher concentrations. A visual method based on the use of a polarization deuterometer was developed for determining large deuterium concentrations in hydrogen.

Oganov and Striganov [451, 452] used standards to analyze ternary mixtures of hydrogen, deuterium and tritium.

The analysis of isotopic hydrogen-deuterium mixtures is also used to determine hydrogen in metals via the method of isotopic equilibration [290].

**Determining the isotopic composition of helium**

Such a method was developed by Artaud, Blaise and Gerstenkorn [457]. The isotope shift of the He $\lambda$ 6678 Å line amounted to 0.5 Å. Therefore, high dispersion equipment was necessary (Fig. 87). Special techniques were used to obtain narrow spectral lines. The glow was studied inside a hollow cathode cooled with liquid air. The discharge tube current uses a few milliamperes. The analysis was conducted without the use of standards. The ratio of concentrations of the helium isotopes was assumed equal to the ratio of areas under the spectral peaks. Special tests demonstrated that the instrument does not distort the intensity distribution, and that the line contours are subject to the Doppler effect. The Doppler
broadening is inversely proportional to the square root of the atomic mass, and hence the ratio of concentrations of the helium isotopes is given by the expression

$$\frac{C_{He^3}}{C_{He^4}} = \frac{h_3}{h_4} \sqrt{\frac{m_{He^3}}{m_{He^4}}} = 1.15 \frac{h_3}{h_4},$$

(5.16)

where $h_3$ and $h_4$ are the peak heights in the recordings and $m_{He^3}$ and $m_{He^4}$ are the masses of the helium isotopes.

**Determining the isotopic composition of carbon**

This analysis is based on molecular spectra, in which the isotope shifts may amount to several angstroms. Broida and Fergusson [458] converted carbon to acetylene and excited the glow in an acetylene flame. Acetylene analysis was based on heads of bands $C^{12}C^{12} (\lambda 4737 \text{ Å})$ and $C^{12}C^{13} (\lambda 4744 \text{ Å})$. The spectra were detected by the photoelectric method, and calibration curves were plotted on the basis of standard mixtures. The analytical results were distorted by the presence of carbon dioxide in the air. In addition to carbon-containing samples, the isotopic composition of acetylene can be analyzed by this method.

An alternative method was developed by Zaydel' and Ostrovskaya [209, 459], using the arrangement for analyzing mixtures of hydrogen isotopes [453]. Carbon analysis was based on the CO $\lambda 4124$ Å band excited in a methane-oxygen mixture, and calibration curves based on the standards were used. It was necessary to take into account the overlap of the band $N_2\lambda 4142$ Å. The method is suitable for working with concentrations ranging from 1 to 60%. The analytical accuracy is 5–7% at low concentrations (1–5%), and improves to 2–3% in the 10–60% concentration range. The amount of gas consumed in a single determination varies from 0.1 to 0.2 cm$^3$. Analysis time is 10–15 min.
Determining the isotopic composition of nitrogen

The early determinations of isotopic composition of nitrogen were qualitative, and were designed to assist in regulation of isotope separation. Hoch and Weisser [460] were the first to develop a quantitative analysis. They compared the heads of molecular bands whose intensities were determined from photographs obtained at different exposures. They also determined the Schwarzschild constant. The analytical pairs used were $\lambda$ 3159 and $\lambda$ 3577 Å for $N^{14}N^{14}$, $\lambda$ 3162 and $\lambda$ 3573 Å for $N^{14}N^{15}$. An h-f oscillator provided the source of light. The concentration range was 0.38-99%, and the accuracy was about 2%. An analogous procedure was proposed by Zahn [463]. The mixture was analyzed in a high frequency discharge excited by an oscillator generating a frequency of 7 Mc. The discharge tube capillary was 1 mm I.D., and the gas pressure in the tube was about 2 mm Hg.

A photographic method for analyzing mixtures of nitrogen isotopes was developed by Gorbunov and Zagorets [461]. Over the concentration range of 0.38 to 8.5%, their analysis used an r-f oscillator and a quartz discharge tube with external electrodes. The nitrogen pressure was varied from 0.05 to 2.5 mm Hg. The results were accurate within 2-3%. A photoelectric method for determining nitrogen isotopes was used in [462, 464]. In [462] an r-f oscillator generating 2450 Mc was used, with the pressure maintained at 1 mm Hg. The detection was achieved by means of a monochromator with a resolution of 0.1 Å, and scanning rate of 5 Å/min. The analysis was either of the flow type or proceeded in a sealed tube. While the accuracy was higher in the first case, the quantity of gas required was also considerably greater (20 cm³ at $p = 1.5$ mm Hg). The analysis time was 10 min. The analysis was based on the lines of the rotational structure of the 1.0 and 0.1 bands in the second positive system. Within the
0.38–90% concentration range, the analysis required calibration curves.

Zaydel' and Ostrovskaya [464] described a method for nitrogen isotopes useful over the 0.38–15% range, and employing no standards. The spectra were excited in a high frequency discharge at a frequency of 6 Mc. The heads of band 2.0 of the second positive system were used as the basis of analysis. An accuracy of about 5% was attained at concentrations close to the natural one (0.038%).

This completes the list of gaseous mixtures that can now be analyzed by spectroscopic methods. The range will doubtless be extended. The composition of any isotopic mixture can probably be determined by spectroscopic means. It is interesting to note that deuterium, the heavy isotope of hydrogen, was discovered by studying hydrogen spectra [465], and many other isotopes were discovered in the same manner.