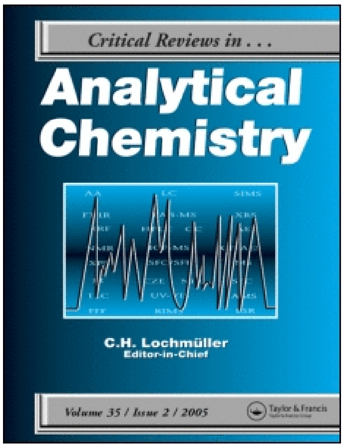

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METHODS OF ANALYSIS FOR THE NOBLE GASES

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I. INTRODUCTION

The need for an updated review of the methods of analysis for the noble gases is indicated by the continuous growth in the demands and applications for these gases. The noble gases are those elements which belong to Group VIII of the periodic table. The group consists of helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). These gases are frequently referred to as the helium group, the rare gases, and the inert gases. Since helium and argon are commercially available in large quantities, they are not appropriately labeled when called rare gases. In·1970, helium consumption in the United States was about 650 million standard cubic feet, at an estimated commercial value of $18,000,000. In the same year, the annual production of high purity argon reached 2.75 billion standard cubic feet, at an estimated commercial value of $39,000,000. Since xenon and krypton can be made to form chemical compounds, they are not truly inert gases, but more realistically remain in the rare gas category. In 1970, the total annual production of neon in the United States was estimated to be less than 3 million standard cubic feet. The annual production capacity for krypton is about 170,000 standard cubic feet, while that for xenon is approximately 12,000 standard cubic feet. At current prices, the total commercial value for all three rare gases is about $3,500,000 annually.

It is because of the extreme chemical inertness of the noble gases that methods for the qualitative and quantitative analyses of these gases are based entirely upon their physical properties and employ physical analytical techniques. Although some chemical reactions are known for the noble gases of higher molecular weight, analytical procedures based upon those reactions have not yet been developed.

Cavendish obtained the first indication of the existence of the noble gases as long ago as 1785, when he observed an inert residual volume of gas after repeatedly passing an electric discharge through air which contained excess added oxygen to react with the nitrogen. He noted that the residue, which was not nitrogen, amounted to "not more than 1/120 part of the whole" quantity of air sampled. In 1868, Janssen observed an unidentified yellow line in the solar spectrum. Lockyer concluded that this line represented a new element, which he called helium after the Greek word "helios", meaning sun. In 1891, Hillebrand obtained from uranite an inert gas which gave yellow spectral lines differing from the mapped lines of that time. By 1894, Rayleigh noted that the density of nitrogen from the atmosphere was consistently higher than the density of nitrogen from chemical sources such as ammonia, nitrous oxide, and ammonium nitrate. This difference caused him to suspect the presence of a previously unidentified element in the atmosphere. Rayleigh and Ramsay worked cooperatively on the isolation and spectroscopic characterization of this new element, which they called argon after the Greek work "argos", meaning inactive. In 1895, Ramsay showed that the gas which Hillebrand had isolated from the mineral uranite was identical with Lockyer's helium. In the same year, Kayser detected helium in the earth's atmosphere. During 1898, Ramsay and Travers discovered krypton, named after the Greek word "kryptos", meaning hidden, by spectroscopic examination and measurement of the density of the residue from a sample of liquid air. They discovered neon, named from the Greek word "neos", meaning new, as the volatile fraction of a sample of argon condensed from liquid air. A month later, they isolated xenon, named from the Greek word "xenos", meaning strange, from the residue from the evaporation of liquid air. The noble gas family was completed in 1900 when Dorn discovered radon among the radioactive decay products of radium.[1]

II. SOURCES OF NOBLE GASES

A. Natural Isotopes

The atmosphere is the only known source of all the noble gases. Argon, neon, krypton, and xenon are all available commercially as products of the fractionation of liquid air. Although helium exists in the atmosphere, commercial helium is largely obtained by extraction from certain natural gas sources. Radon is recovered in extremely small quantities as a product of the radioactive decay of radium.

The natural abundances of the noble gases in the atmosphere are summarized in Table 1.[2]

Argon, neon, krypton, and xenon are produced commercially, mainly as by-products from large-scale oxygen and nitrogen plants. The recovery of the noble gas elements from the atmosphere is based upon a complex liquefaction and rectification process[3]. In most air separation plants, the noble gases are separated as crude gases which must be further purified. A comparison of boiling points, which are presented in Table 2, shows that the most volatile fractions of air will contain nitrogen, neon, and helium, while oxygen, argon, krypton, and xenon will concentrate in the residual liquid. Further fractionation will yield an argon rich stream that is introduced into separate argon columns in which the argon is further refined by distillation. Final oxygen removal may be accomplished by passage over hot copper, by selective adsorption, or by the addition of hydrogen, followed by catalytic combustion and reliquefaction of the argon to remove the excess hydrogen. The resulting argon is 99.99% pure or better.

TABLE 1

Abundances of Noble Gases in the Atmosphere

Gas	Atmospheric concentration in dry air	
	PPM by vol	Vol %
Helium	5.24	5.24×10^{-4}
Neon	18.18	1.818×10^{-3}
Argon	9,340	0.934
Krypton	1.14	1.14×10^{-4}
Xenon	0.086	8.6×10^{-6}
Radon (a)	6×10^{-14}	6×10^{-18}

(a) Average value – concentration varies from one location to another.

The very small quantities of krypton and xenon, as well as hydrocarbons in the air, tend to accumulate in the reboiler. A liquid stream is continually withdrawn from the upper column and cycled through a rectifying column. The oxygen vapor from this krypton column is returned to the

TABLE 2

Physical Properties of the Noble Gases

	He	Ne	Ar	Kr	Xe
Atomic number	2	10	18	36	54
Atomic weight	4.0026	20.183	39.948	83.80	131.30
N.B.P., °K	4.215	27.09	87.28	119.80	165.04
Triple point					
Temperature, °K	no TP	24.54	83.81	115.77	161.38
Pressure, atm	no TP	0.4273	0.68	0.7220	0.806
Critical point					
Temperature, °K	5.199	44.40	150.86	209.4	289.74
Pressure, atm	2.261	26.19	48.34	54.3	57.64
Density, g/ml	0.0693	0.483	0.536	0.908	1.100
Density					
Gas, at S.T.P., g/l	0.17850	0.90002	1.78380	3.7493	5.8971
Liquid, at N.B.P., g/ml	0.1249	1.206	1.3936	2.415	3.057
Gas/liquid ratio (a)	700	1,340	781	644	518
Heat of vaporization at N.B.P., cal/g-mole	19.4	429	1,550	2,154	3,020
Heat of fusion at TP, cal/g-mole	no TP	80.1	283	392	548.5
Thermal conductivity, cal/(sec)(cm²)(°K/cm)					
Gas, at 1 atm, 0°C	339.0	110.1	40.5	20.9	12.1
Liquid, at N.B.P.	75	310	290	211	175
First ionization potential, eV	24.586	21.563	15.759	13.999	12.129
Min excitation energy, ev	19.818	16.618	11.548	9.915	8.315

(a) Volume of gas at 1 atm and 273.15°K (0°C) equivalent to unit volume liquid at N.B.P.

air separation column, and the krypton-xenon enriched liquid from the bottom of the krypton column is passed through a catalytic combustion unit to remove the hydrocarbons. The resulting crude mixture contains about 1% krypton-xenon, with the balance being oxygen. This crude mixture is withdrawn for further processing. The oxygen is usually removed from the crude krypton-xenon by chemical means, and the final separation of krypton from xenon is accomplished by cryogenic distillation.

Neon and helium accumulate in the condenser of the air separation column. The gas stream withdrawn from the condenser has a neon-helium content which varies from less than 1 to 12%. The nitrogen content of this stream is reduced by passing the stream through a condenser which yields a crude neon stream composition about 46% neon, 19% helium, 2% hydrogen, and 33% nitrogen. This crude neon is withdrawn from the air separation plant for further purification. In some processes, the small hydrogen content is removed by chemical oxidation followed by a drying step. The removal of nitrogen is generally accomplished by condensation from the pressurized crude gas in a liquid nitrogen cooled trap followed by adsorption on liquid nitrogen cooled charcoal. The remaining gas contains about 75% neon and 25% helium. Some of this is sold as technical grade neon. The final separation of neon from helium can be accomplished by differential adsorption. However, with the increase in the availability of very low temperature refrigeration from liquid hydrogen, the components of the crude neon are separated by condensation at temperatures near the neon boiling point.[4] This procedure is particularly advantageous when a liquefied neon product is desired.

Most of the helium produced commercially is obtained by separation from helium bearing natural gases which contain about 0.4% helium or more. The production process[5] consists basically of lowering the temperature of the natural gas until all of the components except helium and a trace of hydrogen are condensed as liquids. The resulting helium rich vapor is further purified to yield the desired quality product. Small amounts of helium can be recovered as a by-product of air separation plants or by extraction from minerals such as monazite, but these sources are not economically competitive with the natural gas source.

Radon is normally prepared at the point of use in laboratory-scale apparatus.[6] Radium salts are dissolved in water, and the evolved gas is periodically collected. The gas contains radon, hydrogen, and oxygen. This gas is cooled sufficiently to condense the radon, and the gaseous hydrogen and oxygen are pumped away.

Each member of the noble gas group is a gas at room temperature and atmospheric pressure. They are colorless, odorless, and tasteless, and their molecules are monatomic and are considered to have perfect spherical symmetry. Because of their molecular simplicity, there is much theoretical interest in their physical characteristics. With the exception of radon, the physical properties of the noble gases have been extensively studied. Some pertinent physical properties as they might pertain to the separation and determination of the noble gases are presented in Table 2. The values listed are for the naturally occurring isotopic mixtures of each gas. Table 3 presents a complete listing of the naturally occurring isotopes of each noble gas along with the relative abundance of each isotope.[7]

Chemically, the noble gases are considered to be virtually inert. A few stable chemical compounds of radon, xenon, and krypton have been prepared, but none have been reported for helium, neon, and argon. Although hydrates or clathrates of water and hydroquinone with argon and the heavier noble gases are known, most chemists do not regard these structures as chemical compounds.

Artificial Isotopic Mixtures

The common sources of noble gases which are readily available provide only the natural isotopic mixtures as presented in Table 3. However, certain special suppliers such as the Mound Laboratory can supply certain specific noble gas isotopes in essentially pure form, as well as a variety of isotopic mixtures which are not naturally occurring. These products are derived from the enrichment and separation of natural isotopic mixtures, or from the stable isotopic products of nuclear fission.

Although helium 3 exists in nature in very minute quantities, high purity helium 3 is a product of reactor technology. When lithium 6 is bombarded with neutrons, lithium 7 is formed; it disintegrates to helium 4 and tritium, and the tritium, in turn, decays to helium 3. The resultant

TABLE 3

Naturally Occurring Isotopic Abundance of the Noble Gases[7]

Element	Atomic number	Atomic weight	Isotopic mass number	Abundance, atom %
He	2	4.0026	3	0.00013
			4	99.9999
Ne	10	20.183	20	90.92
			21	0.257
			22	8.82
Ar	18	39.948	36	0.337
			38	0.063
			40	99.600
Kr	36	83.80	78	0.354
			80	2.27
			82	11.56
			83	11.55
			84	56.90
			86	17.37
Xe	54	131.30	124	0.096
			126	0.090
			128	1.92
			129	26.44
			130	4.08
			131	21.18
			132	26.89
			134	10.44
			136	8.87
Rn	86	(222)	No Stable Isotopes	

TABLE 4

Isotopic Compositions of Krypton

Isotope	78	80	82	83	84	85	86
Natural, at %	0.354	2.27	11.56	11.55	56.90	–	17.37
Fission product, at %	–	–	0.2	11	31	6	52

gas mixture is separated by thermal diffusion to yield high purity helium 3 as a commercial product.

The 3 stable isotopes of neon, neon 20, -21, and -22, are commercially available in high purity or enriched form from the separation of natural neon by thermal diffusion. The same technique is used to separate natural argon to provide high purity enrichments of argon 36, -38, and -40.

With krypton, the 6 stable isotopes which occur in nature, krypton 78, -80, -82, -83, -84, and -86, are commercially available in enriched forms, including krypton 86 in high purity. These isotopes are largely separated from natural krypton, but some isotopes are available as fission products recovered from spent nuclear fuels during reprocessing. The only krypton isotope obtained from this source and not available from natural sources is krypton 85, which is radioactive. A comparison of the isotopic compositions of krypton from natural and fission product sources, as reported by Bezella,[8] is presented in Table 4. As reported by Rohrmann,[9] the average atomic weight of fission product krypton is about 85, versus 83.8 for the natural krypton.

The 9 stable isotopes of xenon include xenon 124, -126, -128, -129, -130, -131, -132, -134, and -136. All of these occur in nature, and five are also

TABLE 5

Isotopic Compositions of Xenon

Isotope	Natural, at %	Fission product, at %
124	0.096	–
126	0.090	–
128	1.92	–
129	26.44	0.15
130	4.08	–
131	21.18	8
132	26.89	22
134	10.44	29
136	8.87	41

products of nuclear fission. The isotopic compositions of natural and fission product xenon, as reported by Bezella,[8] are compared in Table 5.

Mound Laboratory[10] is presently enriching the end isotopes from both natural and fission xenon. There are 3 end isotopes available for high enrichment: -124 from natural sources, -131 from fission sources, and -136 from both. Enriched concentrations of some intermediate isotopes are also available. The xenon 131 and -136 isotopes separated from fission source xenon contain trace quantities of krypton -85, which is radioactive and has a half-life of 10.76 years. However, techniques are available to reduce krypton 85 contamination in fission product xenon to levels in the range of 1 to 10 μCi/l of gas.

III. THE QUALITY OF NOBLE GASES AND THEIR APPLICATIONS

In reviewing the analytical methods for the noble gases, it is important to keep in perspective the major reasons why these analyses are required and performed. The analyses are necessary to meet the quality requirements set by the many uses and applications of noble gases. Their primary uses are associated with their inert characteristics. Helium and argon are used extensively in the metallurgical industry where inert atmospheres are needed. Argon, neon, krypton, and xenon are used in light sources for special applications where high intensity or longer filament life is required. Helium is used as a purge gas and pressurant gas in the missile and nuclear fields, and as a diluent in medical applications and breathing atmospheres. Helium and neon are used extensively as refrigerant fluids to establish and maintain very low temperatures in the cryogenic region for research and industrial applications. Xenon has strong anesthetic properties, but its use is limited by its high cost. In addition, all of the noble gases are used in a variety of laboratory and research applications.

The noble gases are commercially available in a variety of grades, which include a high purity grade, an ultrahigh purity grade, a zero gas or instrument grade, an ultrapure carrier grade, and a research grade. Typical purity ranges and impurity levels for commercially available noble gases are listed in Table 6.

Nearly all of the noble gases sold and used in the world today are derived from natural sources and exhibit the natural isotopic compositions. The data in Table 6 refer to noble gases with their natural isotopic compositions, since industrial processes for collection, separation, and purification of noble gases do not alter their isotopic ratios.

Most of the analytical methods reviewed in this paper deal with the determination of impurities in noble gases or with the determination of noble gases in mixtures. These procedures do not differentiate between isotopes of a given noble gas.

However, for certain special applications and advanced research studies, specific noble gas isotopes in high purity or artificial isotopic mixtures are required. A wide variety of isotopic mixtures of krypton and xenon are available. One of the promising new applications for such mixtures is in the detection and identification of nuclear fuel element leakage by isotope ratio measurements. The fuel elements are tagged with specific isotopic ratios during fabrication, and subsequent leakage during operation can be detected with indications of the identity of the leaking elements. Table 7 lists some typical noble gas isotopes which are now commercially available from the Mound Laboratory.[10]

Isotopic analyses of noble gas are performed by mass spectrometry. Specific techniques and procedures are discussed later.

IV. DETECTION AND ASSAY METHODS

A. Detection

Although the noble gas elements cannot be

TABLE 6

Typical Purity Ranges and Impurity Levels for Commercially Available Noble Gases

Impurity, ppm	Argon	Helium	Neon	Krypton	Xenon
Nitrogen	3–40	5	5	5	5
Argon	–	1	1	1	1
Helium	5	–	25–300	5	5
Neon	–	2–50	–	20	5
Krypton	–	–	–	–	25
Xenon	–	–	–	25	–
Hydrogen	1	1	1	1	1
Oxygen	1–10	1–5	1	1	5
Water	1–4	1–4	1	1	1
Methane	0.5–1	0.5	0.5	0.5	5
Acetylene	0.5	0.5	0.5	0.5	0.5
Total hydrocarbons	1–3	1	1	1	5
Carbon dioxide	0.5	0.5	0.5	0.5	0.5
Carbon monoxide	1	1	1	1	1
Nitrous oxide	0.1	0.1	0.1	0.1	0.1
Purity range, %	99.995–99.9995	99.995–99.9995	99.97–99.999	99.995	99.995

TABLE 7

Purity Ranges and Impurity Levels for Specific Noble Gas Isotopes

Isotope	Specific isotope in total noble gas, mole %	Noble gas purity, mole %
Helium3	99.98	99.5
Neon20	99.95	99.5
Neon21	90	99.5
Neon22	99.9	99.5
Argon36	99.5	99.5
Argon38	95	99.5
Argon40	99.95	99.5
Krypton78	50	99.5
Krypton82	70	99.5
Krypton83	70	99.5
Krypton84	90	99.5
Krypton86	99	99.5
Xenon124	20	99.5
Xenon129	60	99.5
Xenon131	60	99.5
Xenon136	99	99.5

identified by chemical reaction, their presence can be detected indirectly by their resistance to chemical reaction. If a gas sample is thought to contain one or more noble gases, the sample may be treated chemically to remove all components other than the noble gases. In the standard Orsat procedure for gas analysis, after removal of acidic gases, oxygen, hydrogen, hydrocarbons, and carbon monoxide, the residue is a mixture of nitrogen and noble gases. This residue can be further treated to remove the nitrogen by reaction with an active metal such as titanium, lithium, or calcium at high temperatures. Any gaseous residue after this treatment is one or more of the noble gases. Isolation and detection of the individual inert gases in the residue can be accomplished by fractional desorption from activated charcoal as described by Cady[11]. The method is very tedious and depends upon the gradual replacement of less strongly adsorbed gas by more strongly adsorbed gas. With the availability of modern instrumentation, these methods are seldom used.

Emission spectroscopy – This is a less tedious technique for the identification of individual noble gases. Each noble gas will produce a characteristic emission spectrum when subjected to an electric discharge. The radiation from the discharge tube can be introduced through a suitable slit system into a spectrograph or spectrometer. For visual observations, the light may be viewed with the help of a laboratory spectroscope which is equipped with an eyepiece. The inert gases are identified by the pattern of the emission lines or, when a visual spectroscope is used, by the color of the lines. Spectra from unknown gas samples are readily obtained by filling a discharge tube with the gas to a few torr pressure, imposing a few thousand volts AC on the electrodes, and analyzing the emitted light.

Mass spectroscopy – This is another technique that can readily be used to identify noble gases. In a mass spectrometer, the gas sample is ionized and the ions are differentiated in accordance with their ratio of mass to electronic charge (m/e). In most modern instruments, the ion current for each value of m/e is measured by a scanning device and automatically recorded. The resulting mass spectrum is examined for m/e peaks characteristic of the noble gas isotopes. The principal peaks for the inert gases can be determined from Table 3, which presents the naturally occurring isotopic abundance for the noble gases. The peak heights in natural mixtures of isotopes are in proportion to their natural abundances. For example, neon will show its most intense peak at mass number 20, a second peak at mass number 22 with about 1/10th the intensity of mass number 20, and a third peak at mass number 21 showing a very low intensity. With argon, mass number 40 will appear about 300 times as intense as mass number 36, whereas 36 will appear about 5.5 times as intense as mass number 38. The qualitative aspects of mass spectrometry as used in the detection of noble gases may be readily observed with common residual gas analyzers and unsophisticated mass spectrometers. For quantitative analysis, more sophisticated equipment and analytical technique are necessary, as will be discussed later.

Gas chromatography – This is probably the single most useful technique for the separation, detection, and identification of the noble gases. The technique involves equipment that is relatively inexpensive, easy to standardize, and easy to use. A gas mixture is separated into its pure components as it is purged through an adsorbent column by a carrier gas. As these pure components are eluted from the column with the carrier gas, their presence is detected by a suitable detector. The time required for each component to elute from the column is called the retention time and is characteristic of each specific component. The detector will produce a response in proportion to the quantity of each component eluting from the column with the carrier gas. With a strip chart recorder, a chromatogram is obtained which can be used for both qualitative and quantitative analysis. Retention times have significance only for a particular instrument and for a special set of conditions such as column packing, column temperature, gas flow, and pressure. Specific retention times are established by chromatographing the pure noble gases or mixtures of known compositions under carefully controlled conditions. Comparisons of the retention times obtained from an unknown sample with those of the pure materials permit qualitative identification. With certain columns, two or more gases can have the same retention times for a given set of conditions. Care must be taken to insure correct identification of each component.

B. Assay Methods

A variety of techniques can be used to determine the purity of noble gases. Most approaches involve measuring the total impurities and establishing the purity by difference. Since impurity levels in commercially available noble gases are quite low, modern instrumentation is generally used to determine trace concentrations of each specific contaminant. These techniques are discussed in the next section. However, assay methods are available which permit the determination of total noninert gas impurities in noble gases based on the removal of the impurities by reaction with molten lithium or titanium sponge. Two of these procedures are discussed below.

Bowman-Hartley method – This method[12] was developed for determining the total impurities in the noble gases (argon and helium) that are used in arc welding, but is also applicable to the other noble gases. The method is based upon the fact that molten lithium absorbs nitrogen, oxygen, and water vapor. The gas sample is admitted into a constant volume apparatus, where the impurities are removed by the molten lithium. The change in pressure produced by the removal of the impurities is used to determine the purity of the gas. A special apparatus is used to minimize errors due to small changes in atmospheric pressure and temperature. The apparatus is satisfactory for determining the purity of noble gases with a maximum error of about ±0.01% by volume. Since most present day commercial sources of noble gases provide a purity of 99.99% or better, this procedure finds very limited use.

Titanium absorption method – This method was developed by Dombrowski[13] for the determination of trace nitrogen impurity and total impurities in noble gases. The method involves the absorption of all impurities in the noble gas on titanium metal sponge at temperatures between 900 and 1000°C. A measured volume of the noble gas sample is passed over a preweighed quantity of titanium metal. After absorption of the impurities, the metal sponge is reweighed and analyzed by a modified macro Kjeldahl technique to determine the nitrogen content of the metal. The quantity of nitrogen absorbed by the sponge is calculated from the final weight of the titanium sponge and the difference in nitrogen analyses before and after absorption. The increase in weight of the sponge sample, the nitrogen pickup, and the volume or weight of noble gas sample permit calculation of the parts per million of total impurities in the gas sample. This technique has been used effectively for impurity levels of 10 to 200 ppm by volume. The major disadvantages are the need for very large samples when measuring low level impurities (600 STP l in the 10-ppm range) and the long time required for analysis. With the availability of instrumental techniques, this procedure is seldom used.

V. DETERMINATION OF IMPURITIES IN NOBLE GASES

The listing of impurities in Table 6 shows that nitrogen and the noble gases themselves are the major contaminants in commercial high purity noble gases. Several other contaminants such as hydrogen, oxygen, hydrocarbons, and moisture are also generally monitored. In some cases, concern may exist about minor impurities of carbon dioxide, carbon monoxide, and nitrous oxide. In general, the totals of these contaminants are present in concentrations which range from 10 to 100 ppm by volume, with concentrations of any specific contaminant ranging from 0.1 to 25 ppm. Although some chemical procedures do exist for the determination of some of these contaminants, instrumental techniques are applied almost exclusively.

A. Gas Chromatography

Gas chromatographic methods are very widely used for the determination of impurities in noble gases. Hydrogen, oxygen, nitrogen, and the noble gases are readily determined as contaminants in any specific noble gas by gas chromatographic techniques. Molecular sieve 5A is the most frequently used adsorbent for the chromatographic separation of these components, although other materials are more effective for special separations, as will be pointed out later. The selection of column packing, column size, and operating conditions as well as the carrier gas is dependent upon the bulk noble gas and the contaminants to be determined. Since each commercially available noble gas generally contains a different group of contaminants, a single gas chromatographic procedure cannot be used for the determination of impurities in all noble gases. Six different combinations of column configurations and operating conditions, as used in the Air Products and Chemicals, Inc. laboratories by Capelloni,[14] are listed in Table 8. These arrangements permit the measurement of most of the common trace impurities in the noble gases which are determinable by gas chromatographic methods.

Table 9 presents a summary of the chromatographic systems generally used to determine various contaminants in each of the noble gases. The noble gases are listed across the page in order of increasing retention time on molecular sieve. The impurities are listed vertically in order of increasing retention time on molecular sieve. The carbon dioxide is, of course, not eluted by molecular sieve under the listed conditions, and a Porapak R column is used for its determination. A brief discussion of the determination of the impurities in each of the noble gases is presented below. The procedures described provide rapid and sensitive methods for the routine analysis of the contaminant in the high purity noble gases which are commercially available. In general, the detectable limits for the contaminants discussed above range

TABLE 8

Gas Chromatographic Systems Used for the Analysis of Noble Gases[14]

	System No. →1	2	3	4	5	6
Column dimensions	(a) 12 ft × 1/4 in. OD+ (b) 12 ft × 1/4 in. OD in series	6 ft × 1/4 in. OD	12 ft × 1/4 in. OD	20 ft × 1/8 in. OD	8 ft × 1/4 in. OD	8 ft × 1/4 in. OD
Column packing	Molecular sieve 5A 30/60 mesh	Molecular sieve 5A 30/60 mesh	Molecular sieve 5A 30/60 mesh	Molecular sieve 5A 30/60 mesh	Molecular sieve 5A 30/60 mesh	Porapak R 80/100 mesh
Column temperature, °C	(a) −78 (Dry Ice) (b) +40	40	40	40	40	40
Carrier gas	Helium or Neon	Helium	Helium or Neon	Helium	Argon	Helium
Carrier gas						
Inlet pressure, psig	35	20	20	20	20	20
Flow rate, ml/min	50–60	50–60	50–60	50–60	50–60	50–60
Sample volume, ml	10	10	5	5	1 (2 atm sample pressure)	10
Filament current of the hotwire detector, mA	250	400	400	400	160	400

TABLE 9

Summary of Chromatographic Systems for Determination of Various Contaminants in the Noble Gases[a]

Impurities	He.	Ne	Ar	Kr	Xe
He	–	1	1	1[b]	1[b]
Ne	1, 3	–	1	1[b], 5	1[b], 5
H_2	1	1	1	1[b]	1[b]
O_2 + Ar	3	3[b]	–	4	2
N_2	3	3	c	4	2
Kr	3[b]	3[b]	d	–	2
Xe	3[b]	6[b]	d	6	–
Co_2	d	d	d	6	6

a. Numbers refer to chromatographic systems listed in Table 8.

b. Method not widely practiced or measurement not generally made.

c. Measurement not performed by gas chromatography for trace quantities.

d. Measurements not generally needed.

from 2 to 5 ppm, depending primarily upon the retention time and the difference between the thermal conductivity of the contaminant and the carrier gas. More sensitive techniques are available for special purposes which utilize more sensitive detector systems, such as the helium ionization detector,[15] which provides sensitivities on the order of 0.1 ppm or better for most permanent gases. The key to such analyses is the ability to make clear chromatographic separations using helium as the carrier gas. Another approach to achieving higher sensitivities is to utilize the technique of preconcentration of impurities prior to injection into the chromatograph system. Purer[16] reports a procedure for the analysis of impurities in helium in the parts per billion range with a preconcentration method. This method is reported to be satisfactory for analyses in the parts per billion range for neon, hydrogen, argon, oxygen, nitrogen, krypton, methane, and xenon in helium.

Impurities in helium – Helium is analyzed for traces of neon and hydrogen by chromatographic system No. 1 using a helium-carrier; system No. 3 is used to determine neon, the oxygen-argon composite,the unresolved peak representing the sum of oxygen and argon, and nitrogen. Krypton and xenon can also be determined with this arrangement if necessary. Figure 1 shows a typical chromatogram resulting from system No. 3 when a laboratory standard containing 900 ppm of air in 5 ml of helium was used as the sample. The trace of neon shown was an original impurity in the helium.

Impurities in neon – Neon is analyzed for

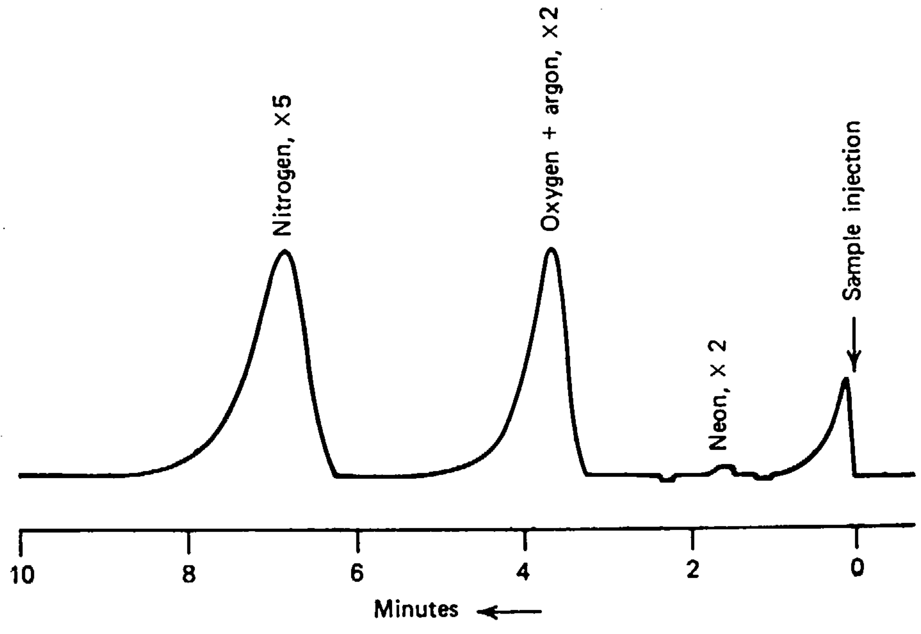

FIGURE 1. Chromatogram of 900 ppm air in 5 ml of helium. Chromatographic system No. 3 (see Table 8); carrier gas: helium. The attenuation of the recorder is indicated at the peaks.

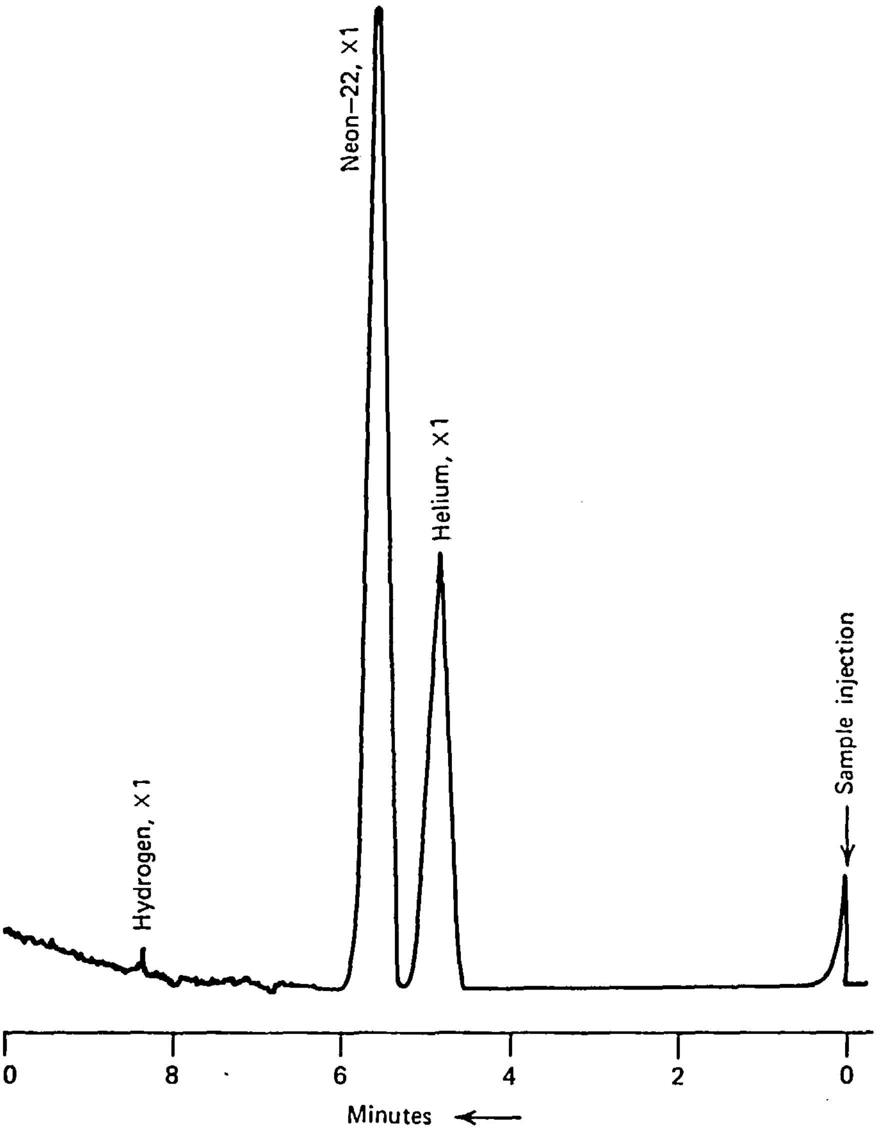

FIGURE 2. Chromatogram of impurities in a 10 ml neon sample. Chromatographic system No. 1 (see Table 8); carrier gas: neon. The attenuation of the recorder is indicated at the peaks.

traces of helium and hydrogen by chromatographic system No. 1, using neon as the carrier gas. Figure 2 shows a typical chromatogram for a commercial neon sample containing a trace amount of helium but no hydrogen. The peak immediately after the helium peak is reportedly due to ^{22}Ne, which exists in a higher concentration in the sample than in the carrier gas. The naturally occurring abundance for the isotopes of neon are shown in Table 3. During the processing of neon to obtain high purity material, several concentration and distillation steps are performed which result in changes in the isotopic ratios. In Figure 2, a significantly higher concentration of ^{22}Ne existed in the neon sample gas as compared to the noncarrier gas.

Nitrogen in neon is readily determined with system No. 3, using helium or neon as a carrier gas. With helium carrier, the large peak from the bulk neon in the sample creates a large tail that masks the oxygen-argon composite. With neon carrier, the oxygen-argon composite, nitrogen, and krypton can readily be separated; the resulting chromatogram is similar to Figure 1. Xenon in neon is readily determined with system No. 6, should such a measurement be desired. This

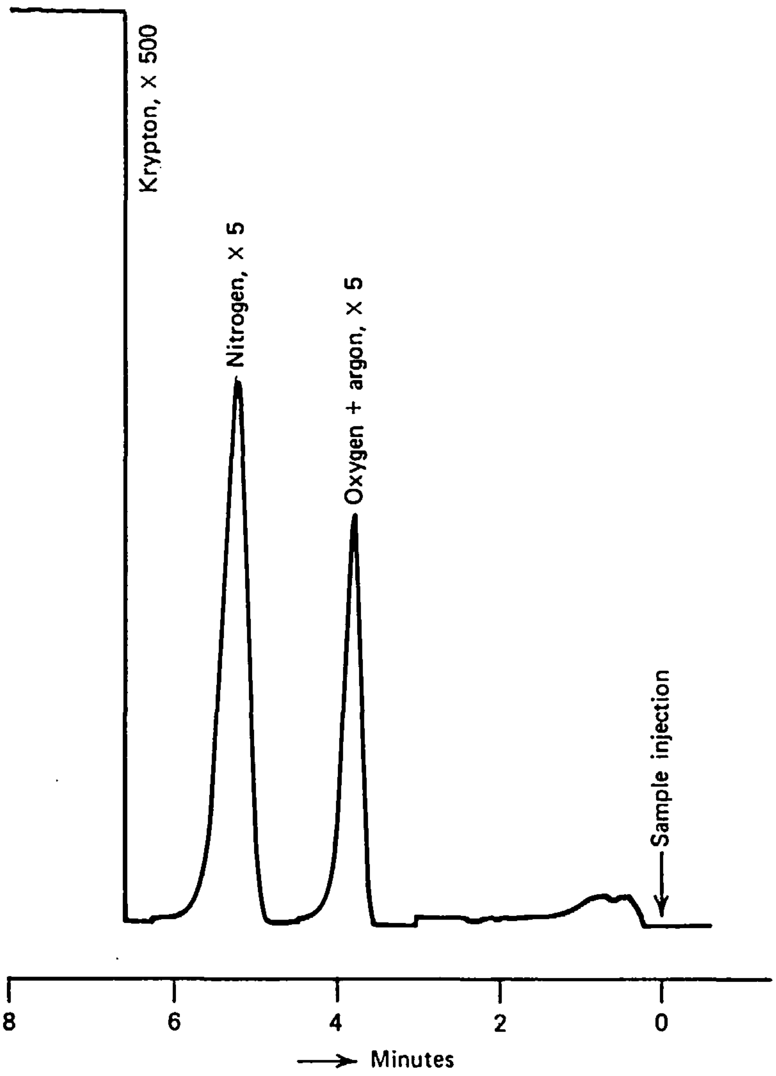

FIGURE 3. Chromatogram of impurities in a 5-ml sample of krypton. Chromatographic system No. 4 (see Table 8). The attenuation of the recorder is indicated at the peaks.

analysis is not usually performed on commercial neon, as xenon is generally not present as a contaminant.

Impurities in argon – Argon is analyzed for traces of helium, neon, and hydrogen with system No. 1, using helium or neon as a carrier gas. If argon is used as the carrier, the three contaminants can be determined by a single analysis. Trace nitrogen in argon is not determined by gas chromatography because the large tail from the bulk argon overlaps the trace nitrogen peak which follows the argon. If argon carrier is used, the nitrogen peak can be readily separated, but the sensitivity is very poor because the thermal conductivities of argon and nitrogen are so nearly equal. Special detectors that will provide increased sensitivity for nitrogen are available for use with an argon carrier, but other techniques can be used. Nitrogen in argon is usually measured by special instruments involving emission spectroscopy and ion mobility.

Impurities in krypton – Krypton is analyzed for traces of helium, neon, and hydrogen with system No. 1, or these components may be determined as a composite peak using system No. 5. The composite peak method is generally applied, since these contaminants are usually not found in commercial krypton. System No. 4 permits the separation of the argon-oxygen composite and nitrogen, which are generally present in commercial krypton. Figure 3 shows a typical chromatogram of krypton using system No. 4. The

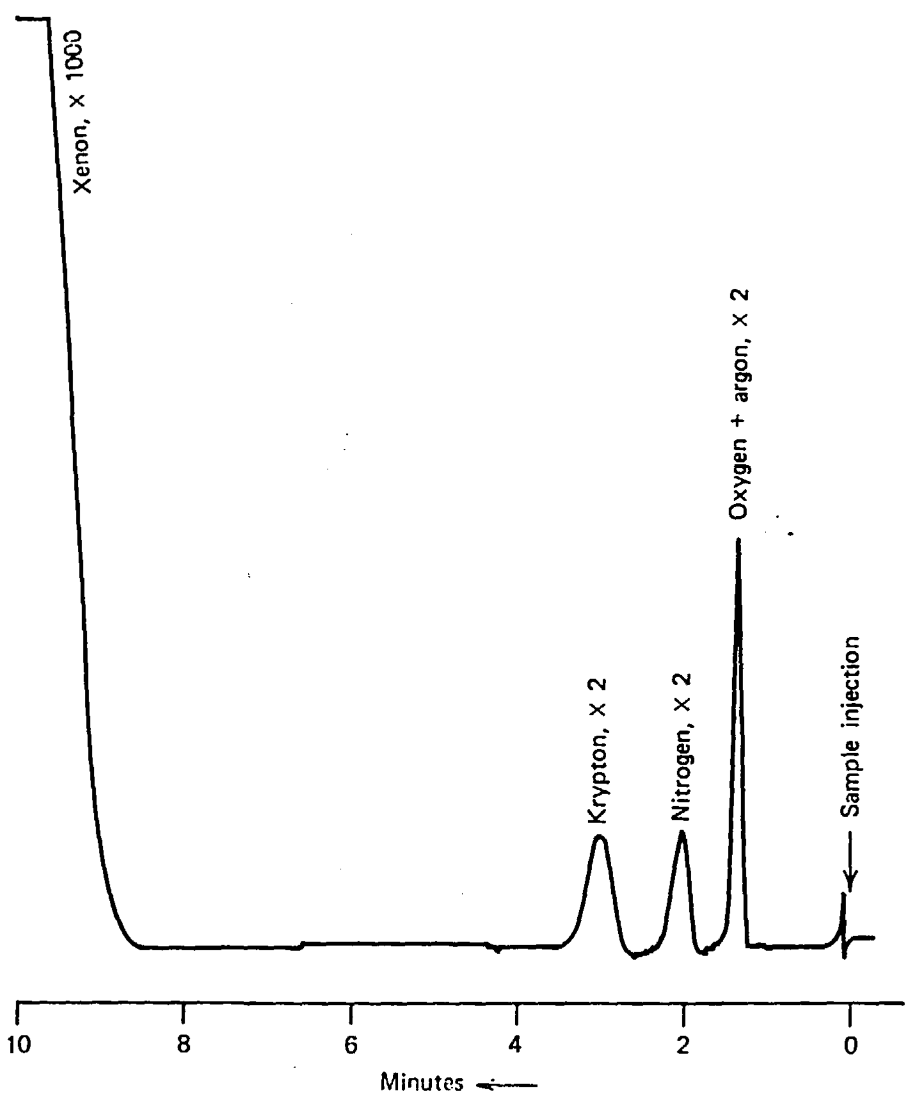

FIGURE 4. Chromatogram of impurities in a 10-ml sample of xenon. Chromatographic system No. 2 (see Table 8). The attenuation of the recorder is indicated at the peaks.

nitrogen peak is followed by the large peak due to krypton. Xenon is eluted in this system after the krypton peak, but the retention time is too long to provide high sensitivity. Xenon and carbon dioxide are generally determined in krypton with system No. 6; under these conditions, the carbon dioxide peak will elute at 4.7 min, followed by the xenon peak at about 8.0 min.

Impurities in xenon – Xenon is analyzed for trace helium, neon, and hydrogen as individual peaks with system No. 1, or more often as a composite peak with system No. 5, as is described above for krypton. The oxygen-argon composite, nitrogen, and krypton are generally determined in xenon with system No. 2 arrangement; a resulting chromatogram is shown in Figure 4. This chromatogram also shows the bulk xenon peak, which elutes well after the krypton peak and therefore provides no interference in the analysis. The carbon dioxide content of xenon is determined with system No. 6 as previously described for the carbon dioxide determination in krypton.

The chromatographic procedures described above are based upon methods applied by a major noble gas supplier.[14] Recent literature provides additional chromatographic methods for the determination of impurities in noble gases. Several of the more broadly applicable papers are summarized below.

Richardson[17] reported on the development of a continuously operating gas chromatograph for the measurement of impurities in helium used as a cover gas for a nuclear reactor. The helium was used over a heavy water bath and gas samples were withdrawn by vacuum. The D_2O was removed and the sample gas was passed through a chromatograph at a vacuum of 24 in. of Hg. Nitrogen, oxygen, deuterium, and other impurities in the helium cover gas were detected.

The determination of trace quantities of xenon in argon by gas chromatography was reported by Havlena and Hutchinson.[18] Xenon contamination in argon as a reactor cover gas was determined by passing reactor grade argon through a 2 ft X 0.25 in. copper column packed with a 1:1 mixture of 30-60 mesh charcoal and 30-60 mesh molecular sieve 5A maintained in a Dry Ice-Alcohol bath. The column was then heated to 250°C and the contents valved into a chromatograph. Argon and krypton appeared immediately, and xenon followed after 12 min. The column was 0.25 in. X 7 ft and packed with 30-60 mesh charcoal. The carrier gas was helium at 75 ml/min. Temperature programming at 13°C/min was started 10 min after sample introduction. The paper suggests that xenon in air can be determined by this same technique.

Zocchi[19] describes a method to determine methane in helium and neon in the part per billion range. The trace methane was determined by gas chromatography after concentrating the sample at -215°C on silica gel, molecular sieve 5A, or lead pellets. Preconcentration gave 100% recoveries for 8 ppb CH_4.

A gas chromatographic technique for control analysis of high purity noble gases was reported by Guerin et al.[20] Trace impurities in the part per million by volume range for O_2, N_2, H_2, CH_4, and CO were determined by direct analysis, while traces as low as a few tenths of a part per billion were detected using fractional condensation. The detectors were based on the ionization of the gases in helium or argon carrier gas by high voltage – high frequency electric discharge. The trace impurities either caused a change in the discharge current, appearing as a peak on the recorder if helium was the carrier, or produced a variation of the light intensity detected by a phototube if argon was the carrier. The paper suggests that neon, krypton, and xenon can also be analyzed by this method.

Rhodes[21] reported that traces (less than 100 ppm) of hydrogen in 99.995% pure helium were determined by automated gas chromatography on activated charcoal columns with nitrogen carrier gas and thermal conductivity detectors. The primary charcoal column was used twice in order to separate the hydrogen peak and permit venting of most of the helium which caused baseline instability. The hydrogen peak was observed on the second pass through the column. The accuracy is ±2 ppm hydrogen.

A new automatic and continuously working gas chromatograph was developed by Genkin and Shevelev[22] for the determination of trace impurities in helium down to $5 \times 10^{-6}\%$ by volume. The sample is led continuously through a bed of molecular sieve 5A which is periodically cooled to liquid nitrogen temperature, then slowly heated to 350°C. The temperature changes are programmed. The column is a vertical helix moving vertically between the lower cooling bath and the upper heating block. At the start of an analysis, the column is lowered into the cooling bath for about 3 min and the impurities are collected on the sieve. As the column is lifted with programmed velocity into the heating block, the impurities such as Ne, H_2, O_2, N_2, and Ch_4 are separated. The operation lasts from 6 to 30 min. By changing the lengths of the time intervals and the temperature of the heating block, the desired separation of impurity components is achieved. A thermal conductivity detector was employed.

Gaseous impurities in argon used to fill fluorescent lamps were separated and determined by gas chromatography with a helium detector, according to Castello and Pesente.[23] Oxygen was separated from argon on a Porapak Q column at -78°C, along with neon, hydrogen, and nitrogen. Methane and carbon dioxide were separated from argon on a Porapak Q column at 25°C. Neon, hydrogen, methane, and carbon monoxide were separated with a molecular sieve 13x column at 25°C. Sensitivities were 13, 15, 19, 10, 6, and 12 ppb for H_2, CH_4, N_2, CO, CO_2 and O_2, respectively.

A technique developed by Wallace[24] permits the determination of traces of hydrogen in bulk helium using standard equipment. A 3/16-inch I.D. by 24 ft column packed with 60 to 80 mesh charcoal was used at 40°C with a nitrogen carrier

TABLE 10

Principal Noble Gas Ions Produced in the Mass Spectrometer from Stable Isotopes

m/e	Ion	m/e	Ion
4	He$^+$	64	Xe^{2+}
18	Ar^{2+}	64 1/2	Xe^{2+}
19	Ar^{2+}	65	Xe^{2+}
20	Ne$^+$, Ar^{2+}	65 1/2	Xe^{2+}
21	Ne$^+$	66	Xe^{2+}
22	Ne$^+$	67	Xe^{2+}
28	Kr^{3+}		
36	Ar$^+$	68	Xe^{2+}
38	Ar$^+$	78	Kr$^+$
39	Kr^{2+}	80	Kr$^+$
40	Ar$^+$, Kr^{2+}	82	Kr$^+$
41	Kr^{2+}	83	Kr$^+$
41 1/2	Kr^{2+}	84	Kr$^+$
42	Kr^{2+}	86	Kr$^+$
42 2/3	Xe^{3+}	124	Xe$^+$
43	Kr^{2+}, Xe^{3+}	126	Xe$^+$
43 1/3	Xe^{3+}	128	Xe$^+$
43 2/3	Xe^{3+}	129	Xe$^+$
44	Xe^{3+}	130	Xe$^+$
44 2/3	Xe^{3+}	131	Xe$^+$
45 1/3	Xe^{3+}	132	Xe$^+$
62	Xe^{2+}	134	Xe$^+$
63	Xe^{2+}	136	Xe$^+$

gas at 10 ml/min. Retention times for helium and hydrogen were 14 and 18.4 min, respectively. With 0.5 ml of sample, essentially complete separation of the helium is obtained before the hydrogen peak appears. Sensitivities as low as 10 ppm H$_2$ are achieved.

B. Mass Spectrometry

The use of the mass spectrometer for the analysis of industrial gases has expanded rapidly with the appearance of a wide variety of residual gas analyzers and gas mass spectrometers on the market. A major advantage of the mass spectrometer for analytical work is the small quantity of sample required for complete analysis. This is of particular importance in the analysis of rare gases such as neon, krypton, xenon, and radon. For the analysis of ultrahigh purity industrial gases, the more refined, reliable, and sensitive gas mass spectrometers must be employed. However, their use has been somewhat limited by their large initial and operating costs.

A mass spectrometer can be used to determine those impurities which have different parent-ion mass numbers than those produced by the noble gases. Table 10 lists the principal noble gas ions and their mass numbers (m/e) as produced in the mass spectrometer for the stable isotopes. Table 11 lists the principal contaminants usually found in noble gases and their respective parent-ion mass numbers. As can be readily seen, only a few interfering situations exist. Traces of hydrogen in helium are obscured by the doubly ionized helium peak. Triply ionized ^{84}Kr appears at m/e 28 and can interfere with determinations of traces of nitrogen and carbon monoxide in krypton. Traces of carbon dioxide and/or nitrous oxide are obscured by the triply ionized ^{132}Xe. Traces of neon in argon are obscured by the doubly ionized ^{40}Ar, and traces of argon in krypton are masked by the doubly ionized ^{80}Kr. In addition, the analyst must recognize that two pairs of contaminant interferences also exist. These are nitrogen-carbon monoxide and carbon dioxide-nitrous oxide. If only the parent-ion peak appears in the mass spectrum for these contaminant pairs, the analyst cannot be sure whether one or the other or both

TABLE 11

Principal Contaminants in Noble Gases and Their Parent Mass Spectrometer Peaks

Contaminants	Parent-ion mass number (m/e)	Noble gas ion interference
Hydrogen	2	He^{2+}
Methane	16	None
Nitrogen	28	Kr^{3+}
Carbon monoxide	28	Kr^{3+}
Oxygen	32	None
Carbon dioxide	44	Xe^{3+}
Nitrous oxide	44	Xe^{3+}
Other noble gases		
Neon	20	Ar^{2+}
Argon	40	Kr^{2+}

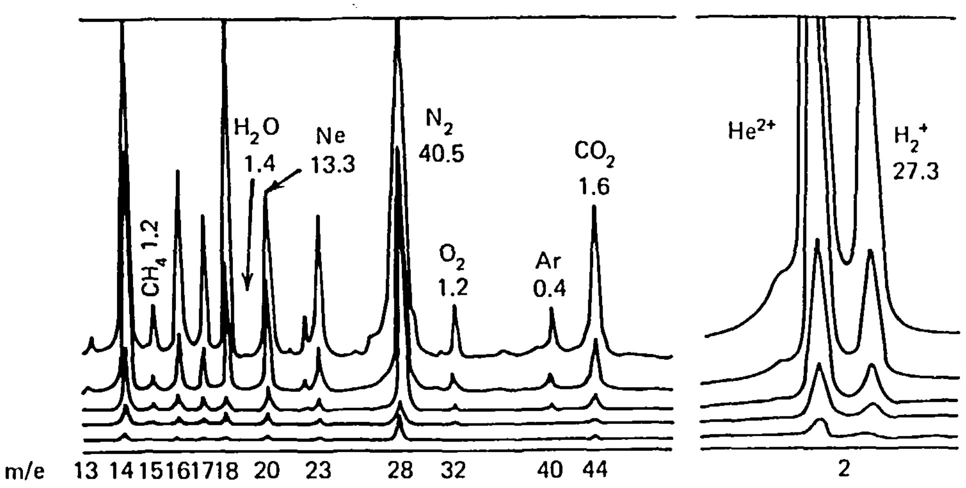

FIGURE 5. Typical high pressure, high ionizing current, mass spectrometer scan (25.0 torr, 100 μA) of impurities in helium.

are present. If contaminant concentrations are high enough that secondary ion peaks appear, more positive detection is possible. Some specific applications of mass spectrometry to the determination of impurities in noble gases are discussed below.

In 1966, Suttle, Emerson, and Burfield[25] reported on the analysis of trace impurities in helium in the part per billion range using a conventional mass spectrometer. To obtain the required sensitivity, the inlet sample pressure and the ionizing current were increased. The optimum conditions were found to be 25.0-torr inlet pressure and 100-μA ionizing current. A typical mass spectrometer scan for a sample of helium is shown in Figure 5.[25] Peaks representing specific impurities are shown along with the average concentration in parts per billion as determined by a series of analyses. Sensitivities in the range of 0.1 to 1.0 ppm were easily achieved. As shown in the scan, the hydrogen analysis was made possible because of the high resolution of the instrument, which permitted a separation of the He^{2+} and the H_2^+ peaks. Although Suttle et al.[25] reported that they had succeeded in determining water at the 1.4-ppm level, as is shown in Figure 5, many mass spectrometrists feel that water cannot be determined reliably by mass spectrometry.

This technology was extended by Weems and Emerson[26] when they combined preconcentrating techniques and high sensitivity mass spectrometry to develop a general analysis method for impurities in helium in the part per billion range. Sensitivities in the range of 0.3 to 3.0 ppb were obtained. In this analytical method, the impurities in the helium are preconcentrated using a Bureau of Mines trace impurity analyzer, as described by Kirkland et al.,[27] in which the sample is passed through a trap cooled with liquid helium. The impurity trap is first evacuated and heated to about 260°C to remove moisture and other impurities. The trap is precooled with liquid nitrogen and then immersed in liquid helium. The helium sample is passed through the trap and all impurities in the helium freeze out as solids in the trap. Essentially all of the helium passes through the trap. After 12 l of helium have passed through the trap, the inlet valve on the trap is closed, and the helium pressure in the trap reduced to 35 torr. The outlet valve is then closed, isolating the sample. When the sample has warmed to room temperature, the pressure in the trap is 50 to 60 psia. This pressure is sufficient to produce a sample pressure of 10 torr when expanded directly into the 3-l sample volume of the mass spectrometer. The sample is then analyzed using the mass spectrometer to produce a scan similar to Figure 5, but where the peaks represent considerably lower concentration levels in the original sample, since a 300-fold concentration of the impurities was accomplished by the pretreatment.

Parkinson[28] reported on the use of a dynamic sampling and calibration system with a mass spectrometer for the analysis of high purity helium. The system is capable of sampling directly from gas streams at pressures in the range of 800 torr and was satisfactorily used for the analysis of high purity helium containing less than 50 ppm by volume total impurity. The overall sensitivity is 1 ppm or better.

A mass spectrometer designed for analysis of inert gases at temperatures up to 300°C was developed by Wilson and Winkelman[29] for on-line analyses of cover gases in liquid-metal cooled nuclear reactors. The sensitivity observed for the instrument indicated that contaminant concentrations of less than 1 part in 10^8 can be detected. The quadrupole mass filter used in the mass spectrometer provides integral mass resolution for mass numbers from 1 to 500.

Talakin and Golovin et al.[30] developed a mass spectrometric method for determination of micro impurities in inert gases of high purity. A method for determination of hydrogen in neon and helium with a sensitivity of 1×10^{-4} vol % and an error of 12% is based upon the preliminary accumulation of hydrogen by adsorption on activated carbon. The method for determining nitrogen, oxygen, argon, and hydrogen in xenon, and hydrogen in krypton and argon, is based on accumulating trace impurities in the gaseous phase by condensation of the major component. The sensitivity is 2×10^{-4} % by volume with a 15% error when using a 200- to 300-ml sample of gas. Carbon dioxide and individual hydrocarbons in argon, krypton, helium, neon, and hydrogen can be determined by accumulation of trace impurities by freezing out at liquid nitrogen or oxygen temperatures. The sensitivity of this analysis with an 800-m gas sample is 3×10^{-5} vol % with a 12% error.

An improved method and apparatus for determining the impurities in helium by preconcentration and subsequent analysis by mass spectrometry are described by Emerson, Hoffman, and Weems.[31] Preconcentration of the impurities is accomplished by passing a known volume of helium at slightly above atmospheric pressure through a metal coil and trap assembly immersed in liquid helium. The concentrated impurities are then analyzed by mass spectrometry. This method can detect impurities in the range of 0.01 to 600 ppm with an accuracy of better than ±0.05 ppm at the 1-ppm level.

Another report of cryogenics applied to mass spectrometric trace gas analysis was made by Pebler and Hickam.[32] They observed that preconcentration of trace impurities in inorganic gases by applying a cryogenic freezeout technique is a convenient way to extend the sensitivity of mass spectrometric analysis into the sub-ppm range. Their method can be adapted routinely to a variety of gas systems, such as the determination of trace impurities in helium, hydrogen, and argon. The technique is also suggested as a possible method for determination of certain air pollutants. The authors claim that freezeout preconcentration can extend the sensitivity for mass spectrometric analysis by at least three orders of magnitude. With 1000 ml of the initial sample, a lower limit of 1 part in 10^8 can be attained.

C. Infrared Spectroscopy

Infrared spectroscopy provides a very sensitive and accurate method for the identification and determination of several impurities that may exist in the noble gases. Trace quantities of such contaminants as carbon dioxide, carbon monoxide, nitrous oxide, and hydrocarbons such as methane and acetylene, which all absorb strongly in the infrared, are readily determined by infrared absorption spectroscopy. Since noble gases do not absorb infrared radiation in the region between 2 and 15 µm, these contaminants can be measured with high sensitivity. The major absorption bands and minimum detectable limits of several typical gaseous contaminants that can be readily determined by infrared absorption spectroscopy, as reported by Latshaw,[33] are listed in Table 12.

Typical infrared spectra for high purity helium are shown in Figure 6. These spectra were obtained by Latshaw[33] from a Beckman IR-4 infrared spectrophotometer equipped with a Beckman high pressure, long path infrared gas cell and spectral recorder. These spectra were recorded with path lengths of 1, 5, and 10 m and a sample pressure of 10 atm. The spectra are labeled to show those contaminants that were present in the samples and to show where other contaminants would appear if they were present.

D. Emission Spectroscopy

In the days before gas chromatography and mass spectrometry, emission spectroscopy was one of the most useful methods for identifying individual noble gases and getting an indication of the gas purity. Quantitative analysis required isolation of the individual gases by tedious processes and then comparison of the emission spectrum of the isolated gases with known samples. The emission spectrum was usually obtained by causing an electric discharge through the gas at a pressure of a

TABLE 12

Major Absorption Bands and Minimum Detectable Limits for Gaseous Contaminants in Noble Gases by Infrared Spectroscopy[33]

Gas	Major bands, μm	Mimimun detectable limit, ppm[a]
CO_2	2.69, 2.76, and 4.22	0.5
CO	4.5 and 4.7	1.0
N_2O	4.45 and 4.5	0.1
CH_4	3.3, 7.65	0.5
C_2H_2	13.7	0.05
CF_4[b]	7.8	0.1
CH_2Cl_2[b]	7.95 and 13.35	1.0
SF_6[b]	10.6	1.0

a. With a 10-m cell at 10 atm sample pressure.

b. Contaminants generally found in krypton and xenon only.

few torr. The use of emission spectroscopy for examination of noble gases is now limited to such applications as a qualitative check on noble gas purity and continuous determination of a specific trace impurity such as nitrogen in argon.

Each noble gas yields a specific pattern of emission lines. The intensity of the lines varies with such factors as the pressure of the gas, the shape of the discharge tube, the voltage and frequency of the power system, the presence of impurities, the temperature, and the optics of the spectroscope. For each analytical system, careful control of conditions and comparison of unknowns with standards are required for accurate quantitative analyses. Many specific applications of emission spectroscopy to the determination of impurities in noble gases are described in the literature. Bennett[34] reports a continuous determination of nitrogen in helium down to 1 part in 10^{10} by measurement of the intensity of the first negative band head of the nitrogen molecule ion. For determining nitrogen in argon, he suggests the use of the band head in the second positive system of the neutral nitrogen molecule to obtain a similar sensitivity. Riesz and Dieke[35] described the detection of 1 part of neon in 200 million parts of helium by a special emission technique. Fay et al[36] found that nitrogen in argon could be made to emit strong band spectra by several excitation methods. The best source is a silent electric discharge, which operates satisfactorily on flowing gas streams at atmospheric pressure. The nitrogen is determined by measuring the intensity of the 3371 Å band head of the second positive system. With this method, less than 0.1 ppm of nitrogen in argon can be detected. Plant-stream analyzers for continuously recording the nitrogen content of argon have been built based upon this method. Raziunas et al.[37] describe the use of a direct current arc to determine air contamination in noble gases. A quantitative response is demonstrated for hydrogen, nitrogen, and oxygen in trace amounts in 50% argon-50% helium mixtures using a 20 A direct current arc and 1% thoricated tungsten electrodes.

Korolev and Gei[38] describe a spectral gas analyzer for measuring trace nitrogen in inert gases. The 3370 Å emission band of nitrogen is used for the measurement and provides a sensitivity for the nitrogen determination of 10^{-4}%.

A spectrographic method for determining trace impurities in neon is reported by Barabanshchikova.[39] The method is used to determine traces of nitrogen, hydrogen, and oxygen in neon with sensitivities of 5×10^{-4}, 5×10^{-4}, and 1×10^{-3}% by volume, respectively. The relative error is about 10%.

Taylor, Gibson, and Skogerboe[40] describe the use of an atmospheric pressure microwave induced discharge for the spectral determination of trace impurities in argon. Detection limits were found to lie in the fractional part per million range for carbon, oxygen, nitrogen, and hydrogen containing compounds. The method offers direct and continuous monitoring of total carbon and total nitrogen content of argon by means of inexpensive and simple instrumentation.

The determination of neon and argon in helium by atomic absorption spectrophotometry was described by Goleb.[41] The accuracies obtained for nanomoles of neon and argon were +2.1 and −1.5%, respectively. A conventional monochroma-

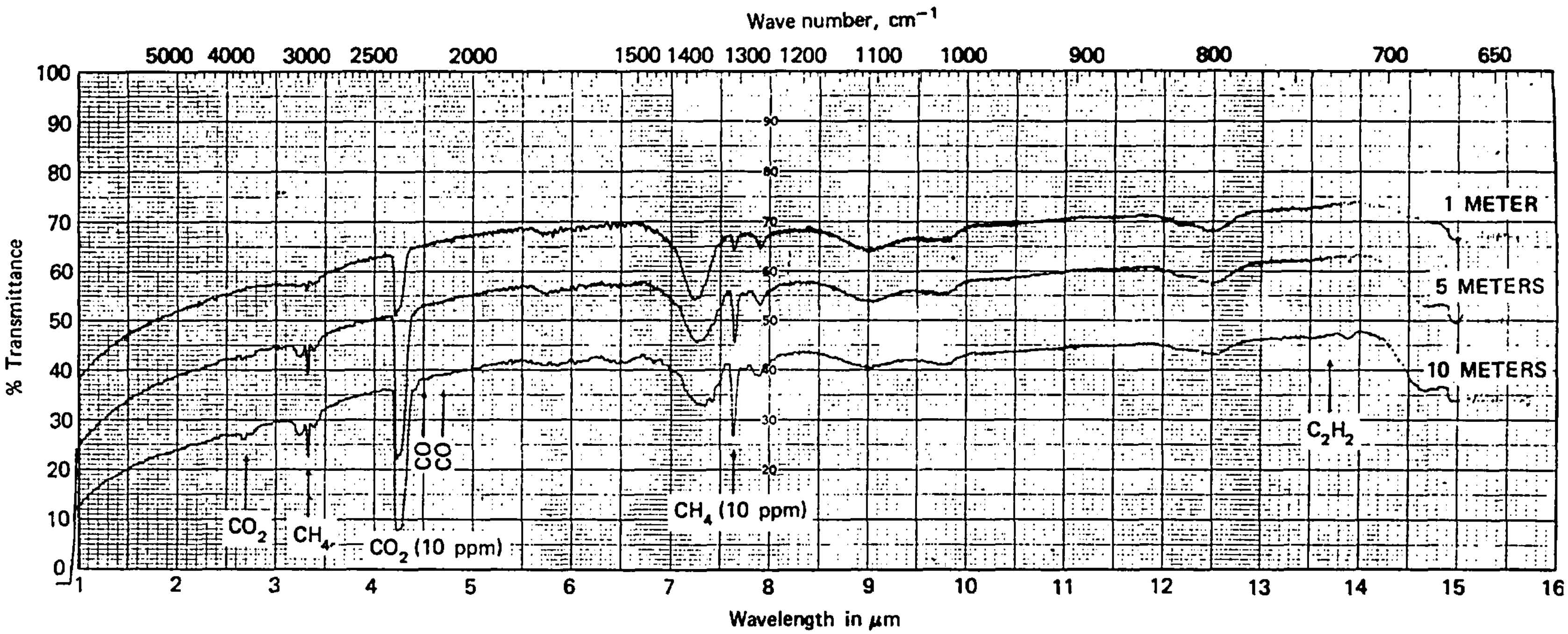

FIGURE 6. Typical infrared spectra for high purity helium.

tor was used to isolate the spectral lines for neon at 6402 Å and for argon at 8115 Å. Discharge tubes containing neon and argon were used as emission sources. This work was extended and further reported by Goleb.[42] He described the use of an alternating electromagnetic field to modulate light in an electrodeless tube for the determination of neon and argon in helium by atomic absorption. Neon and argon were determined in helium in the range of 1 to 60×10^{-9} mole.

E. Determination of Water Vapor

The water vapor contents of noble gases are generally measured by dew point determinations. The dew point temperature of a gas is that temperature at which the gas is saturated with water vapor at a particular pressure. Therefore, the partial pressure of water vapor in the gas sample is the saturation vapor pressure of water at the measured dew point. Several satisfactory dew point instruments are commercially available. An automatic dew point apparatus is reported in an article by Ilfeld,[43] which includes a table for the conversion of dew point temperature to moisture contents.

The Bureau of Mines dew point apparatus[44] or its equivalent permits the measurement of the dew point at a given pressure by cooling the gas stream to the point at which water is visually observed to condense on an illuminated mirror surface and subsequently noting the temperature. The gas is allowed to flow into the apparatus through a flow control valve and is directed through a nozzle toward the cold portion of the apparatus. The gas flows across the face of a highly polished stainless steel target, which is cooled by means of a copper cooling rod immersed in a refrigerant appropriate for the dew point being measured. Dry Ice-acetone and liquid nitrogen are frequently used for low dew points. The mirror is integral with a thermometer well which houses a calibrated mercury-in-glass thermometer that fits snugly into the well. Observation of the dew point is made through a pressure resistant transparent window. This type of dew point apparatus permits measurements with accuracies of ±0.2°F from room temperature down to 32°F and of ±0.5°F from 32 to 0°F. It is estimated that dew points can be determined with an accuracy of ±1°F from 0 to -25°F, ±2°F from -25 to -50°F, and about ±3°F from -50 to ±75°F. The lower limit for visual observation of the dew point is about -100°F. The sensitivity can be increased by measuring the dew point under increased pressure and using a photometric device to detect the formation of frost on the mirror. Table 13 provides data relating dew point temperature at a pressure of 1 atm to water vapor content.

TABLE 13

Several Dew Point Temperatures and the Corresponding Water Vapor Contents at 1 Atm

Dew point temperature		Water vapor content,[a]
°F	°C	ppm by volume
+32	0	6,000
0	-17.8	1,250
-20	-28.8	420
-40	-40	126
-60	-51.1	34
-70	-56.7	16.6
-80	-62.2	7.8
-90	-67.8	3.6
-100	-73.4	1.55

a. Values are based on the partial pressures of water vapor in equilibrium with ice at the respective temperature.

Water can also be determined with an electrolytic hygrometer employing a P_2O_5 cell. Such a device is available commercially, and in many laboratories is preferred over the dew point apparatus described above because it requires much smaller volumes of sample gas.

The water vapor content may also be determined by a gravimetric method based on the absorption of the water vapor in a weighed drying tube that is filled with an effective drying agent. This procedure is applicable to samples with reasonably high concentrations of water vapor. A discussion of the method is presented in most basic analytical textbooks. In general, the absorption technique is not applied to water concentrations below 50 ppm. Most good quality noble gases are supplied with water contents less than 1 ppm by volume.

F. Determination of Total Hydrocarbon

The total hydrocarbon content of a noble gas is generally measured with a flame ionization detector similar to that used as a detector in a gas chromatograph but without the use of a separation column and with the sample instead of the carrier gas being continuously fed into the detector. Several commercial units are available with sensitivity limits on the order of 0.5 ppm. After combustion of the hydrocarbons in a hydrogen-air flame, the increase in ion current through the flame is measured by an electrometer as an indication of the quantity of hydrocarbons entering the flame.

A sample of gas guaranteed to be hydrocarbon-free is conducted into the hydrogen-air flame, and the zero point is established on the meter or recorder. Next, a reference gas of known hydrocarbon content is passed into the flame at the same fixed flow which is controlled by the valves and regulator on the apparatus. This establishes the span or calibration point. The sample gas is then passed through the flame under the same conditions and the meter response noted. Results are generally reported in terms of total hydrocarbon content as methane equivalent, since the detector senses the number of carbon atoms passing through the flame. For example, one molecule of ethane will provide essentially twice the response as one molecule of methane. These detectors are generally used for the measurement of hydrocarbon vapor. The combustion of entrained oil droplets or solid organic particles is generally not complete and these are therefore incompletely detected.

G. USP Specifications

The *United States Pharmacopeia*[45] provides test procedures for helium that is intended for use as a diluent for medicinal gases. The USP specifications include tests for acidity or alkalinity, water vapor, oxidizing substances, and carbon monoxide. Although an assay test is not required, USP grade helium must contain not less than 95% by volume of helium, with the remainder consisting largely of nitrogen.

Acidity or alkalinity – Add 0.3 ml of methyl red Test Solution and 0.3 ml of bromothymol blue Test Solution to 400 ml of boiling water, and boil the solution for 5 min. Pour 100 ml of the boiling solution into each of 3 similar, clear glass color comparison tubes. Add 0.2 ml of 0.01 *M* hydrochloric acid to 1 tube (A) and 0.4 ml of 0.01 *M* hydrochloric acid to the second tube (B). Stopper each of the tubes, and cool them to room temperature. Pass, 2,000 ml of helium through the solution in tube A at a rate requiring about 30 min for the passage of the gas. The color of the solution in tube A should not be a deeper orange-red than that of the solution in tube B, nor a deeper yellow-green than that of the untreated solution in the third tube (C).

Water – Pass 6,000 ml of helium through a suitable water absorption tube, at least 100 mm in length, which has previously been flushed with about 100 ml of helium and weighed. Regulate the flow so as to require 15 min for passage of the gas. The gain in weight of the absorption tube should not exceed 1.0 mg.

Oxidizing substances – To a freshly prepared mixture of 1 vol of starch Test Solution and 15 vol of potassium iodide solution (1 in 200), add 1 drop of glacial acetic acid, mix, and pass 9 l of helium, at the rate of 3 l/min, through this solution. Use a glass tube having an inside diameter of about 25 mm and a height of about 250 mm to contain the solution, and use a delivery tube having a 5-mm orifice and extending to within 5 mm of the bottom of the tube. The color of the test solution should not be altered by the passage of helium, as is shown by comparison of it with another portion of the acidified starch-potassium iodide solution through which the gas has not been passed.

Carbon monoxide – Open both ends of a carbon monoxide detector tube and connect one end to the container of helium and the other end to a suitable gas flow meter. Pass 300 ml of helium through the tube at a uniform rate of about 100 ml/min. The yellow zone of the tube should show no more green color than a control tube through which 300 ml of fresh air has been passed.

H. Miscellaneous

The absolute determination of low concentrations of oxygen in inert gases by means of galvanic cells was reported by Ives, Hughes, and Taylor[46] from the National Bureau of Standards in 1968. Their method was developed for the absolute measurement of oxygen over the range from 1 to 1,000 ppm. The gas sample is passed through a series of galvanic cells similar to the type developed by Hersch. Most of the oxygen in the stream is removed in the first cell, and subsequent cells reduce the oxygen concentration to virtually zero in the effluent gas. Measurement of the increase in all cell current outputs when the gas flow rate is increased by a known increment allows calculation of the absolute oxygen concentration.

Rhodes and Tully[47] describe a high precision thermal conductivity analysis of helium-nitrogen mixtures as developed at the Bureau of Mines, Helium Research Center. The detector system consists of hot-wire elements and two fixed resistors in a Wheatstone bridge. The reference sensor is a diffusion type to reduce the effects of noise level and flow rate. The sample sensor is an active type to reduce the time constant and detector dead volumes.. Highly accurate and precise analyses of helium-nitrogen mixtures are obtained with an accuracy of ±0.01 to 0.02%

VI. DETERMINATION OF NOBLE GASES IN MIXTURES

The most popular techniques for determinations of noble gases in mixtures are gas chromatography and mass spectrometry, of which the former is the more generally applied. These methods permit determination of noble gas concentrations from levels of less than 1 ppm to levels approaching 100%.

A. Gas Chromatography

The gas chromatographic systems described in the previous section for determination of impurities in noble gases can be applied to determinations of noble gases in mixtures. For example, the system represented by Figure 2 readily permits the determination of helium or neon in almost any gas mixture. Theoretically, a single column can be set up to provide for the complete separation of the five stable noble gases, but this is not practical because of the wide range in retention times for a given set of conditions. This problem may be mitigated by the use of temperature programming, but subambient temperatures are generally required for separations of helium and neon. It is more practical to select a column and conditions for the solution of a specific problem or for the analysis of a specific gas mixture. It is unusual to encounter all five noble gases in a single sample. Several specific examples are described below[48].

Figure 7 shows a typical chromatogram obtained for the determination of krypton in the presence of air and methane. The sample consisted of 0.3% krypton and 0.6% methane in helium which also contained a trace of air as a contaminant. The column was 12 ft long and had an OD of 1/4 in., was packed with molecular sieve 13X, and was operated at 40°C. Helium carrier gas was used at 20 psig to provide a flow rate of 40 ml/min. A thermal conductivity detector was used with 300 mA filament current. A 1.5-ml sample loop was used to introduce the sample and a 0-1 mV strip chart recorder produced the chromatogram. The air component is resolved by this column into a composite argon-oxygen peak and a nitrogen peak, and these are followed by a complete separation of the krypton and methane components. This setup allows determinations of krypton, in a variety of gas mixtures, at concentrations ranging from 0.01% to essentially 100%.

Figure 8 shows three typical chromatograms of samples containing krypton, oxygen, nitrogen, and xenon. These chromatograms were obtained with a column 3 ft long and having an OD of 1/4 in., packed with molecular sieve 5A, and operated at 40°C, and with helium as carrier gas and a 1-ml sample. The detector was a thermal conductivity cell operated at a filament current of 180 mA. Chromatogram A represents a standard gas mixture containing 10.1% oxygen, 49.4% krypton, and 5.02% xenon in helium. Chromatogram B represents a sample which contains only oxygen and krypton as major components, with a trace of nitrogen. Chromatogram C represents a sample which contains oxygen, nitrogen, krypton, and xenon. The integrated peak area and peak attenuation are recorded for each peak. Using the known percentage values from A as a standard, the concentration of the components in B and C can be calculated.

Recent literature describes many additional chromatographic techniques for the determination of noble gases in mixtures. Several of the more pertinent methods are reviewed below.

Overfield and Winefordner[49] describe the measurement of permanent gases by a flame emission gas chromatographic detector. The detector is sensitive to permanent gases such as oxygen, nitrogen, carbon dioxide, argon, and helium when used in a negative mode. The sample gases are introduced into the hydrogen carrier gas, and the flame background emission of the hydroxyl band is then monitored by using a monchromator-photomultiplier-amplifier-electrometer-recorder system. The response is linearly dependent on the amount introduced over 4 decades, and the detection limits are about 10^{-6} g/sec for the gases listed.

An improved method for chromatographic determination of helium in "conservation" gas streams was reported by Seitz and Churchwell.[50] Helium in a mixture with nitrogen, hydrogen, and methane was determined on a molecular sieve 5A column at 38°C with a thermistor detector and

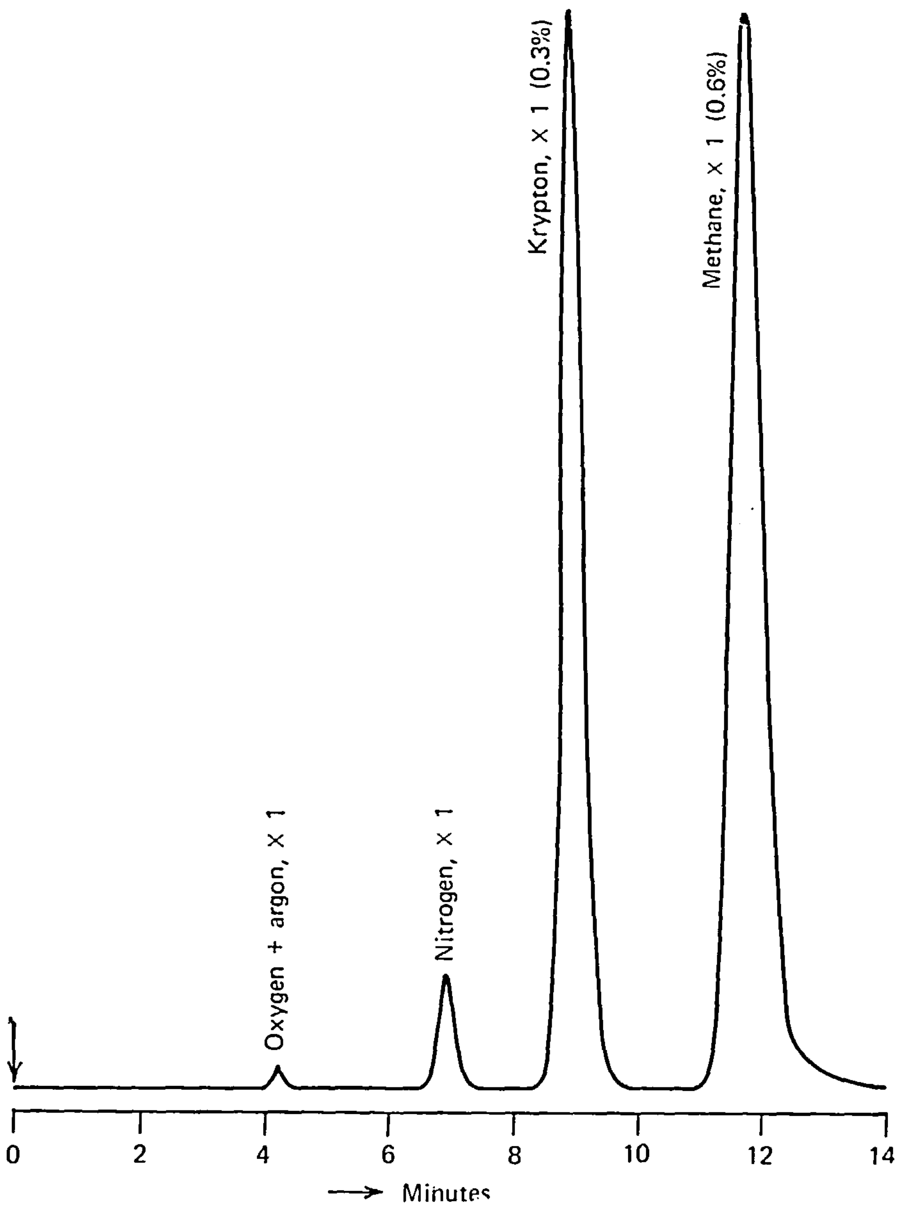

FIGURE 7. Typical chromatogram of krypton and methane in 1.5 ml of helium with traces of air present. The attenuation of the recorder is given at the peaks. For conditions, see the text.

argon carrier gas using a 0.25-cm^3 atm sample. A standard deviation of 0.04% helium and an accuracy of 0.1% helium were obtained in both the 46 to 56 and 90 to 100% helium ranges.

Ikels and Neville[51] described an improved multigas analyzer for respiration gases. The gas chromatographic system uses an electrochemical oxygen sensor to detect and measure helium, neon, argon, nitrogen, nitrous oxide, and carbon dioxide in oxygen carrier gas. A Porapak Q column separated carbon dioxide, nitrous oxide, sulfur hexafluoride, and water vapor, while a molecular sieve 5A column separated helium-neon, argon, and nitrogen.

The separation of helium 3, neon, and hydrogen in helium 4 was evaluated using a Porapak Q column at cryogenic temperatures by Weems, Hoffman, and Howard[52] at the Helium Research Center. The separation was effected by using a 4.9-m by 0.47-cm, ID column filled with 80/100

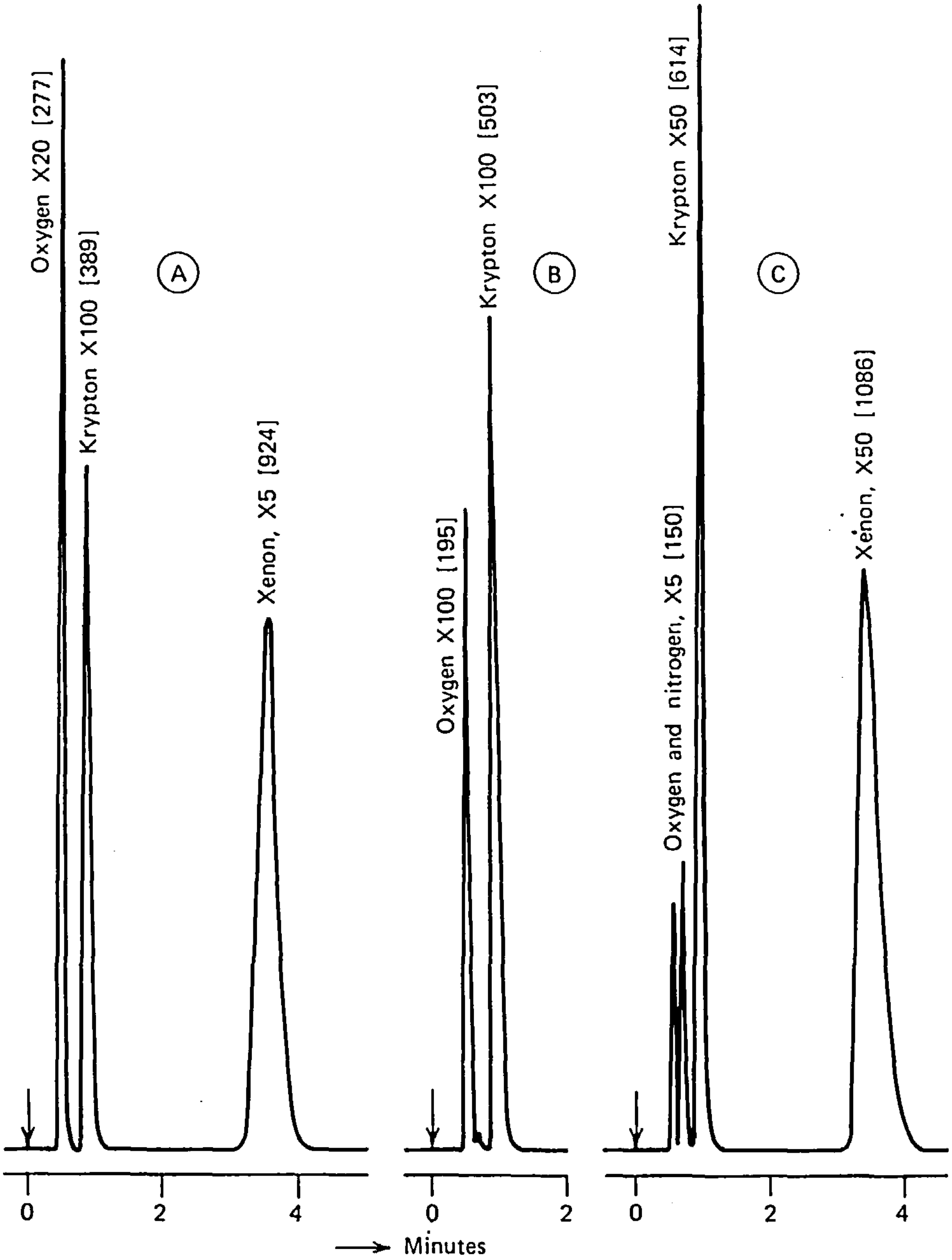

FIGURE 8. Series of chromatograms showing typical quantitative analysis of krypton and xenon. The attenuation of the recorder is given at the peaks. Numbers in parentheses represent peak area in counts (arbitrary units). For conditions, see the text.

mesh Porapak Q at 76°K using helium 4 as carrier gas. A chromatographic method of analysis was devised using this separation technique approach.

Lovelock et al.[53] reported on the analysis of rare gases in the atmosphere by gas chromatography using a small volume thermal conductivity detector and a palladium transmodulator. The analysis was performed directly on a 10-ml sample of air by using a single column operated at room temperature. A gain in sensitivity of 10^3 is obtained by the use of the palladium transmodulator, which effects concentration of the eluted components in the hydrogen carrier after the column but prior to the detector. The system was developed for the analysis of planetary atmospheres, but is of general use where high sensitivity gas analysis is required.

The gas chromatographic measurement of

hydrogen, methane, and neon in air is described by Heidt and Ehhalt.[54] The method uses a 5A molecular sieve column and a radiofrequency discharge glow detector to detect 0.003 ppm H_2, 0.02 ppm CH_4, and 0.4 ppm Ne in a 5-ml sample of air. With repeated comparison to a standard, the error for natural concentrations of these gases in the troposphere is ±3%.

Thombs[55] reported that pulses of noble gases injected into the nitrogen carrier gas in a gas chromatograph produce response from a flame ionization detector. The responses are caused by a dual perturbation of the blank signal resulting from the trace components in the nitrogen carrier. One type of perturbation is explicable from the theory of vacancy chromatography, while the other results from the influence of the noble gas on the net rate of production of charge carriers in the flame.

B. Mass Spectrometry

By examining the data on the naturally occurring isotopic abundance of the noble gases, as listed in Table 3, and the principal noble gas ions produced in a mass spectrometer for these isotopes, as listed in Table 10, the typical mass spectra for natural mixtures of these isotopes with some indication of relative peak heights could be predicted. However, actual mass spectra that were obtained by running pure samples of the various noble gas are reported in the literature. Figures 9, 10, 11, and 12 show the mass spectra for neon, argon, krypton, and xenon, as reported by Cook.[56] The peaks are labeled with the appropriate m/e values, and the attenuation factors are shown above the peaks where they apply. Examination of these mass spectra and Table 10 reveals that overlapping of peaks for the natural and stable isotopes occurs in only three cases. These occur at m/e values of 20, 40, and 43 for the Ne^{+}-Ar^{2+}, Ar^{+}-Kr^{2+}, and Kr^{2+}-Xe^{3+} ion pairs. When looking for characteristic isotope patterns for the noble gases, these situations must be borne in mind. For example, the quantitative estimation of the amount of neon in a mixture containing argon could not be based on the intensity of mass peak 20 unless the contribution of Ar^{2+} to that mass peak were subtracted. This can be done by estimating the argon concentration from mass peak 40, and calculating the contribution of Ar^{2+} to mass peak 20 from a knowledge of the mass spectrometer response and the assumption that the argon isotopic distribution is the same as for the naturally occurring element. A more direct approach is to use the peak at m/e 22 for the estimation of neon when the presence of argon

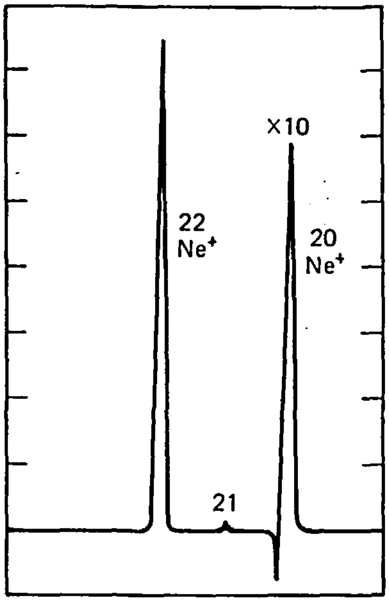

FIGURE 9. Mass spectrum of atmospheric neon.

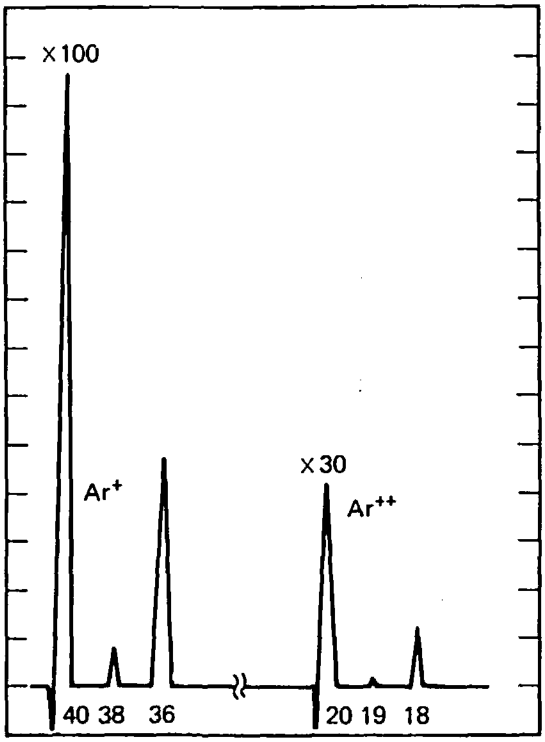

FIGURE 10. Mass spectrum of atmospheric argon.

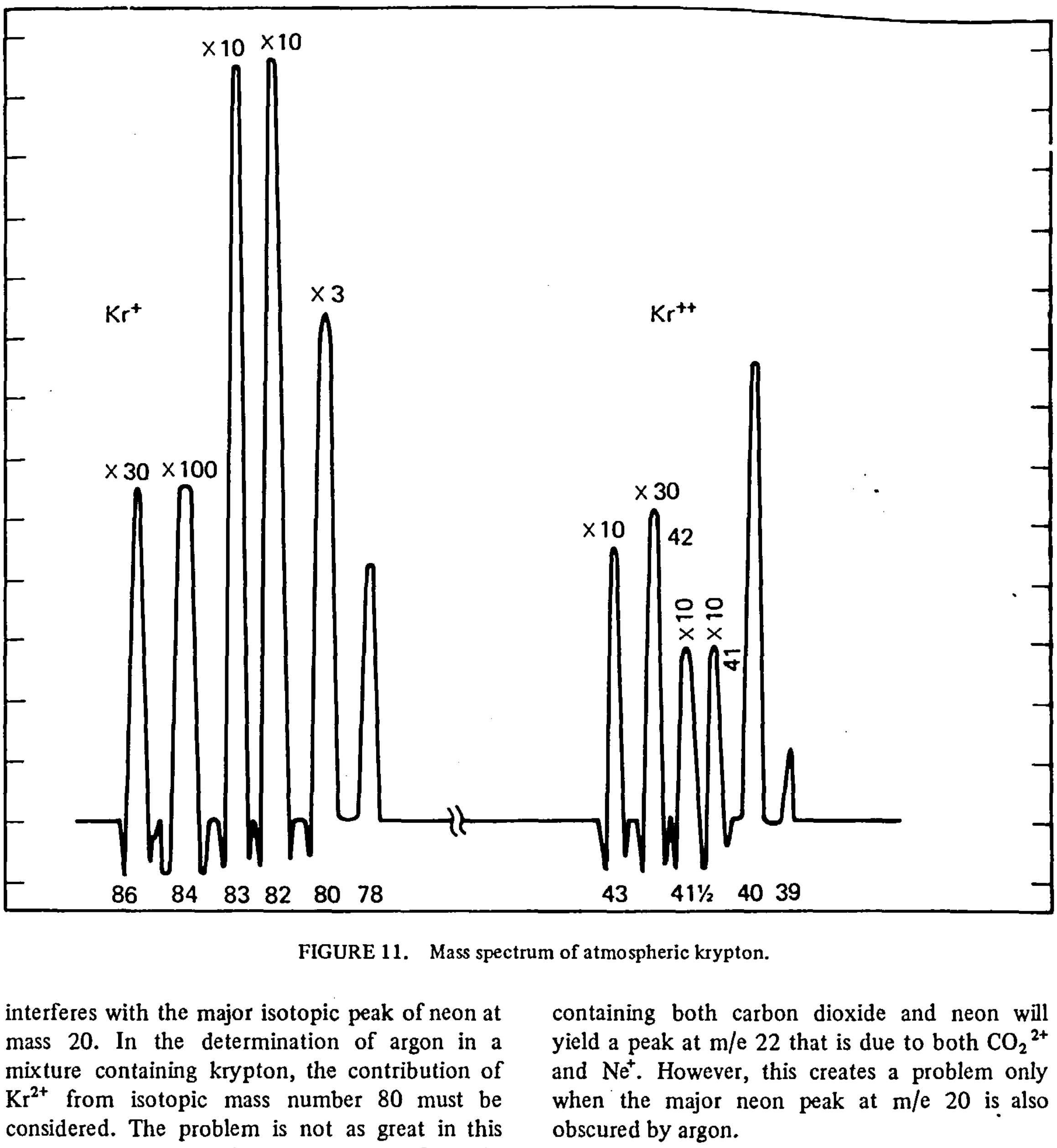

FIGURE 11. Mass spectrum of atmospheric krypton.

interferes with the major isotopic peak of neon at mass 20. In the determination of argon in a mixture containing krypton, the contribution of Kr^{2+} from isotopic mass number 80 must be considered. The problem is not as great in this case, since mass number 80 accounts for only 2.27% of the isotopic abundance for krypton. This indicates that the contribution of doubly ionized Kr^{2+} to the peak at m/e 40 is not very significant in comparison to the singly ionized Ar^+ with an isotopic abundance of 99.6%, unless, of course, the sample contains very much more krypton than argon. The correction can be avoided by using the Ar^+ peak at mass number 36, but this entails a significant loss of sensitivity, since the isotopic abundance of ^{36}Ar is only 0.337%.

Mass peak overlapping occurs with gases other than the noble gases. For example, a sample containing both carbon dioxide and neon will yield a peak at m/e 22 that is due to both $CO_2{}^{2+}$ and Ne^+. However, this creates a problem only when the major neon peak at m/e 20 is also obscured by argon.

In general, the concentration of any gas in a gas mixture may be calculated from the height of a clear peak that is compared with the height of the corresponding peak in a calibration run in which the gas pressure and other conditions are suitably controlled. A clear peak is one which is not partly due to some other gas. In the calibration run, either a sample of the pure gas or a mixture of known composition containing the desired gas may be used. If a clear peak is not available, a peak due mostly to the desired gas must be identified. If the concentrations of the impurity contributions can be obtained from other peaks, suitable allow-

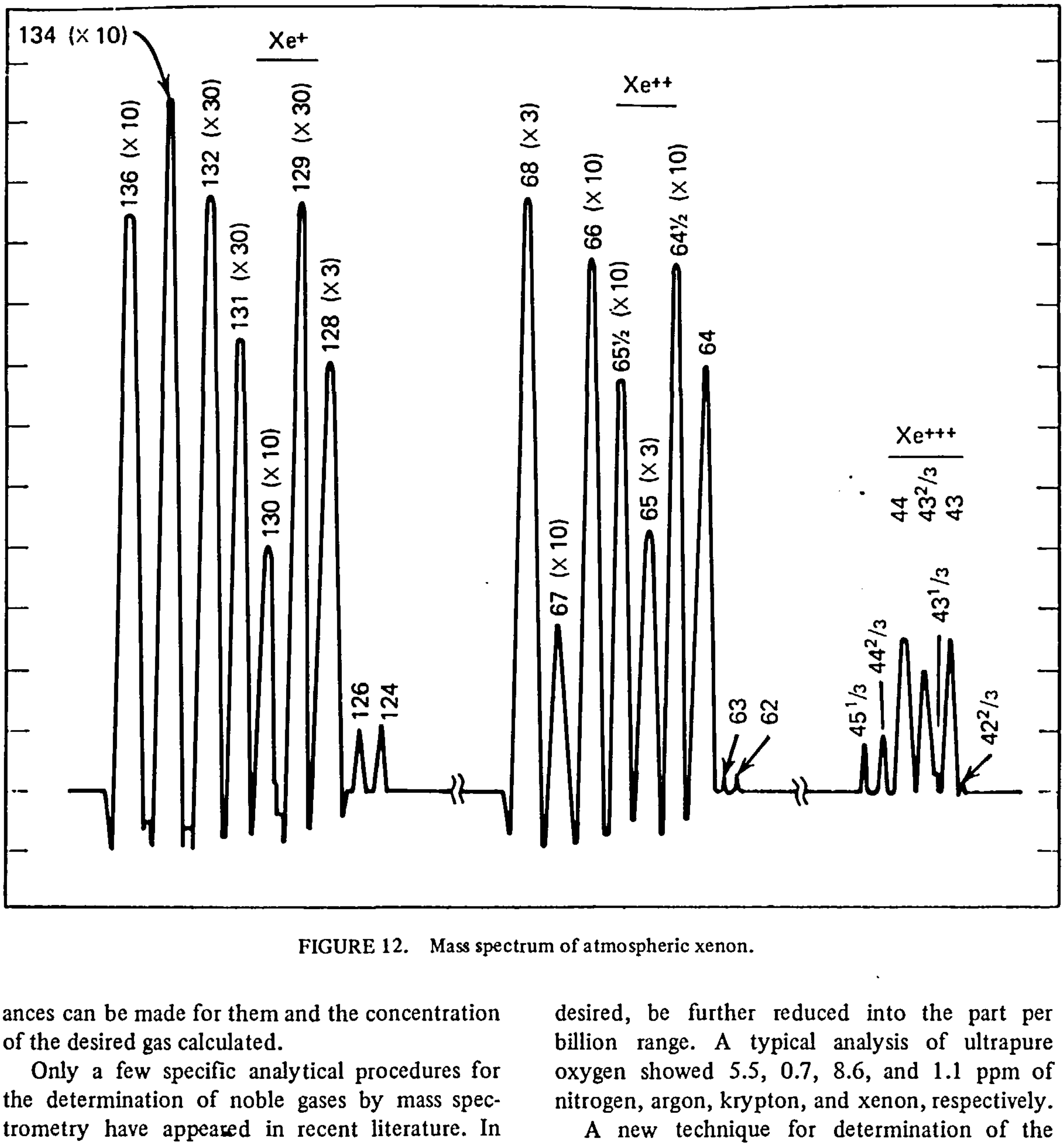

FIGURE 12. Mass spectrum of atmospheric xenon.

ances can be made for them and the concentration of the desired gas calculated.

Only a few specific analytical procedures for the determination of noble gases by mass spectrometry have appeared in recent literature. In 1967, Roboz[57] reported on a mass spectrometric determination of trace noble gas impurities in oxygen. The method employs a sodium-potassium alloy (NaK) for quantitative removal of the oxygen from the gas phase with a 100% retention of the inert impurity content of the sample. An impurity enrichment factor of the order of 10^6 is obtained, and the adverse effects of oxygen on the ion source are eliminated. The residual impurities, which include nitrogen, argon, krypton, and xenon, are determined by any mass spectrometer without modification. The author reports threshold limits in the range of 0.1 ppm which can, if desired, be further reduced into the part per billion range. A typical analysis of ultrapure oxygen showed 5.5, 0.7, 8.6, and 1.1 ppm of nitrogen, argon, krypton, and xenon, respectively.

A new technique for determination of the concentration of noble gases in films was developed by Winters and Kay.[58] It utilizes laser induced flash evaporation followed by mass spectrometric analysis of the released gas. The technique can be used for determination of noble gases and nitrogen in most thin-film materials on a wide variety of substrates. Under ideal conditions, gas concentrations of a few parts per billion can be detected.

Stump and Walter[59] describe a technique for determining inert gases in conjunction with a mass spectrometer. They developed a method for the determination of helium 3 in hydrogen which contained tritium, which complicates the mass 3 peak. Their method involves the removal of all hydrogen isotopes by using a titanium sublimation pump and measuring the sample pressure before and after the removal. The quantity of helium 3 can then be measured without interference. Accurate determinations of low concentrations of helium 3 in tritium (±5% relative error in the 1% helium 3 range) were obtained.

C. Miscellaneous Methods

A variety of unique methods for the determination of noble gases in mixture are reported in the recent literature. Several of these are summarized below to broaden the scope of this review.

A method and apparatus are described by Emerson and Kaplan[60] for the determination of the helium content of gaseous mixtures. The work was done so that the Bureau of Mines could more accurately and economically analyze helium-containing natural gas, crude helium, and helium in gases used in research. Activated coconut charcoal is utilized at liquid nitrogen temperature to absorb components other than helium in the sample. The resulting helium pressure is measured and compared to the resulting pressure from the sampling of high purity helium under the same conditions. A transducer is used to measure the helium pressure. Twenty or more analyses with a standard deviation of ±0.04% can be made in an 8 hr day.

Penchev et al.[61] describe a sensitive spectroanalytical method for the determination of neon in natural gases. They analyzed mixtures containing from 1×10^{-3} to 100% neon in helium, as well as gas mixtures isolated from natural gases, by adsorbing other gases on activated charcoal at $-195°C$. The best results were obtained by measuring the intensity of the Ne I line at 585.85 nm. With a gas mixture containing 2.09% Ne, the standard deviation of replicate measurements was ±0.12% and the relative error of the mean was 5%.

Helium in natural gases and air was determined by using a commercially available leak detector as reported by Schwarz-Bergkampf and Franschitz.[62] The apparatus was calibrated by correlating the detector response with the logarithm of the helium concentration over the range from 2×10^{-4} to 10%.

Crawford, Frazer, and Holt[63] describe an apparatus for the automatic determination of the rate of release of helium from various solids as a function of temperature. Samples are maintained in a vacuum or in a gas other than a noble gas and held at temperatures from 200 to 1,400°C. Helium evolved from the sample is periodically removed. A quantitative determination and standardization for helium are automatically performed. If a gas atmosphere is used, this is removed from the helium by use of a titanium sublimation pump. The helium that remains is then measured with a low resolution, high sensitivity, residual gas analyzer (partial pressure gage). The system is capable of measuring at least 10^{-10} cm^3 (STP) helium.

In 1970, Gilbert[64] prepared a review of the detection and determination of various elements including the noble gases by direct emission flame spectroscopy. This review should be consulted by those interested in the subject.

The analysis of gaseous inclusions in glass using a quadrupole mass spectrometer is reported by Fowkes and Parkinson.[65] Gases such as hydrogen, carbon dioxide, carbon monoxide, oxygen, argon, and nitrogen have been detected in bubbles from a variety of sources. The performance was verified by runs made with synthetic gas bubbles made from standard gas mixtures.

Since the advent of nuclear fission, there has been increasing concern over the accumulation and measurement of radioactive species in the atmosphere. Several radioactive noble gases are among those species. Several pertinent articles from the literature are reviewed to give the reader a brief exposure to the methods and techniques used for detection and measurement of radioactive noble gases. Sax, Denny, and Reeves[66] describe a modified scintillation counting technique for routine atmospheric ^{85}Kr determinations using plastic-scintillation shavings in a gas-tight vial which can be filled with gas containing krypton and counted by scintillation spectrometry. The counting efficiency was 94.4% and the average deviation was less than 0.7%. Precise determinations can be made on less than 0.5 ml of nearly pure krypton, which is equivalent to the krypton present in about 17 ft^3 of air. Methane interferes and must be removed by combustion with oxygen. The detection limit for ^{85}Kr was 1 pCi/m^3 of air.

An on-line monitor of natural gas lines for tritium and ^{85}Kr is reported by Brundage, Motes, and Gant.[67] The system monitors beta activity using a proportional counter with four separate cathode frameworks. The threshold for detection was 2×10^{-3} pCi/cm^3. Prevo and Santomassimo[68] also describe instrumentation for monitoring of krypton 85 and tritium in natural gas. The system uses $CaF_2(Eu)$ crystals to monitor the activity and provides sensitivities of 1.3×10^{-7} μCi/cm^3 for ^{85}Kr and 2×10^{-5} μCi/cm^3 for ^3H.

The detection of argon 39 in atmospheric argon is reported by Loosli and Oeschger.[69] With an extremely sensitive proportional gas counting technique, the argon 39 activity of atmospheric argon was measured for the first time by comparison of recent atmospheric argon with argon originating from ^{40}K decay in well gas. Measurements ranging from 0.084 to 0.121 disintegrations/min/l of argon were obtained. Comparisons of argon collected in 1940 with samples from 1967 suggest that the bomb test contribution to the atmospheric ^{39}Ar activity is less than 0.005 dpm/l of argon.

Dalu et al.[70] describe an automatic counter for direct measurement of radon concentration in air. The apparatus consists of a brass chamber into which air samples flow at 4 l/min, with a ZnS(Ag) scintillator coated with gold within the chamber. The detector is optically coupled with a photomultiplier which provides a minimum detectable concentration of radon of 0.7×10^2 atoms/l or 4×10^{-15} Ci/l. Samples containing 4×10^5 atoms/l can be measured with a standard error of 0.5%.

An instrumental procedure for the determination of the quantity and the radioactivity of argon, krypton, and xenon was developed by Vespalec, Pietrik, and Moravek[71] and an automatic analyzer was designed. A sample was taken from the residual gases remaining after absorption in a solution of KOH. After the catalytic combustion of oxygen and conversion of CO to CH_4 in a stream of H_2, gas chromatography was employed to separate argon, krypton, and xenon. The radioactivity of the pure components was measured with a flow-type proportional counter. The system can be adapted to determine these components in the coolants of nuclear power plants.

VII. DETERMINATION OF ISOTOPIC ABUNDANCE OF NOBLE GASES

The mass spectrometer is the most widely used tool for the determination of the isotopic distribution in natural and enriched noble gases. For pure samples and for samples of a single noble gas with no impurity that will interfere with the noble gas mass spectrum, the isotopic distribution can be determined by comparing the height or intensity of each isotopic peak with the sum of all the peaks for that particular noble gas. This assumes that the peak height response is linear over the entire range measured and that each isotope exhibits the same sensitivity factor. For most measurements, this approach is acceptable. Each isotopic peak could be calibrated if the appropriate isotopes were available in pure forms.

For natural or enriched noble gas isotopic mixtures, a similar approach can be taken if the interfering ion pairs discussed in a previous section are taken into account and if the nonnoble gas impurities do not interfere. Analytical services for isotopic analysis are provided by the Mound Laboratory and several private analytical service laboratories.[72,73]

Several pertinent articles from the recent literature are reviewed to illustrate specific isotopic ratio measurement procedures. Megrue[74] reported an isotopic analysis of rare gases with a laser microprobe coupled with a high sensitivity mass spectrometer. The system is used to determine isotopic abundances of rare gases from microgram samples of polished meteorites. The technique was demonstrated by determination of primordial helium and neon in meteorites.

Eleven different abundance ratios of the nine stable isotopes of xenon were measured by Bruchhausen, Gebauer, and Zahn.[75] Since no standard isotope of xenon is available for such measurements, a secondary standard, Xe^{128}/Xe^{136}, is used and a correction factor applied, which is the mass discriminating factor D. By assuming D=1, an error of 1% is observed in the measurement of the intensity ratio of the two isotopes. As a result of the measurements, the atomic weight of xenon was calculated to be 131.288 ± 0.002. Though the values are within the limits of error, there is a deviation from the standard value (131.30) that could not be explained.

Emerson, Suttle, and Hoffman[76] describe an improved method for the separation of neon from natural gases and the atmosphere and the subsequent measurement of the isotopic abundances of neon samples with improved precision. Neon is concentrated directly from high helium content natural gases or from the atmosphere by using two adsorption traps of activated coconut charcoal at 30 and 77°K. With this method, a survey was made of the isotopic composition of neon in natural gases. The results confirmed the presence of excess ^{21}Ne and supported the belief that neon is produced in the earth's crust in the course of extensive nuclear processes. A redetermination of the isotopic composition of atmospheric neon gave percentage abundances of ^{20}Ne, 90.61 ± 0.03; ^{21}Ne, 0.264 ± 0.003; and ^{22} Ne, 9.13 ± 0.03, which are reasonably close to the accepted figures.

The isotopic abundances of atmospheric neon, argon, and krypton were determined directly without the use of an instrument correction factor by Melton, Massey, and Abels.[77] The results for neon and argon are almost identical to those previously reported. The krypton values are ^{78}Kr 0.355, ^{80}Kr 2.256, ^{82}Kr 11.553, ^{83}Kr 11.536, ^{84}Kr 56.982, and ^{86}Kr 17.318, with an atomic weight of 83.8005 amu based on ^{12}C = 12.0000.

A magnetic resonance mass spectrometer for studying the isotopic composition of helium was described by Mamyrin et al.[78] The parameters of a mass spectrometer system are described for measuring the absolute and relative contents of ^{3}He and ^{4}He isotopes in solid and gaseous specimens of varying origin down to ^{3}He/^{4}He = 10^{-10}. The maximum sensitivity of a mass analyzer with respect to ^{3}He was 5×10^5 atoms.

In 1972, Currie[79] discussed the measurement of the environmental levels of rare gas nuclides and the treatment of very low level counting data. He described the measurement and interpretation of very low level activities of ^{37}Ar, ^{39}Ar, ^{81}Kr, and ^{85}Kr in the atmosphere as planned by the Natural Bureau of Standards. In 1973, Currie[80] reports on the development of a measurement system to determine the cosmic ray production rate and the natural levels of the 35.1-day half-life ^{37}Ar in the atmosphere. The measurement process will permit the quantitative determination of as little as 10^{-3} disintegrations/min of Ar 37 per liter of argon sample. The sample is treated by quantitative separation of the noble gases from about 1 m^3 of air using a CaC_2 reactor, gas chromatographic separation of the argon fraction, isotopic enrichment of the purified argon by a factor of about 70, use of special low level gas proportional counters together with massive shielding and anticoincidence meson cancellation, and the application of pulse discrimination based upon both amplitude and rise time. The information on ^{37}Ar is to be used to derive information about atmospheric mixing.

VIII. SUMMARY

The importance of the noble gases in science and technology cannot be emphasized too much. It is said that man would never have gotten to the moon without helium. Perhaps that is an overstatement, but the noble gases are becoming a more vital part of our society as time passes. With the advent of modern analytical instrumentation, analyses of noble gases have become highly precise and rapid. Techniques and methods have been developed for most analytical requirements in science and industry. Pioneering work continues to be done in those areas associated with low level radioactive noble gases formed in nature and fission product noble gas, both stable and radioactive. With the current emphasis on ecology, environmental protection, and nuclear power, significant further advancements can be anticipated in the detection and identification of trace radioactive noble gas species and in the measurement of their properties, activities, and concentrations.

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