detector or the analytical system quantitatively. In work with ammonia, acidic gases should be carefully eliminated; otherwise, no other detectable interferences were observed with ammonia.

Tubes containing hydrogen sulfide must be calibrated under nitrogen and stored in nitrogen when not in use. Because permeation is a two-way process, the inside of the tube contains 0.2 atmosphere of oxygen when in equilibrium with air. As oxygen permeating into the tube reacts with H_2S, elemental sulfur is deposited within the Teflon wall and an unknown fraction of the escaping H_2S is consumed. Any sulfur deposited inside the walls of the tube alters the permeation rate; both effects render previous calibration invalid.

Calibration curves of some permeation tubes containing NO_2 exhibited a slight curvature during the period of apparent steady state. This phenomenon could not be explained with existing data. The curvature was slight, so that if the calibration of the tube was continued to include the period of use, the error would be minimal.

Exposure of permeation tubes containing nitrogen dioxide to excessive moisture reduced its concentration in the standard air sample. The amount of NO_2 found, see Figure 7, was inversely proportional to the relative humidity. Apparently, NO_2 emerging from the tube reacts with ambient moisture $(2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3)$. In work with this gas, an initial dilution should be made with dry cylinder air; further dilution to the desired concentration can then be made with purified air to conserve the use of cylinder air, since the reaction occurs to a significant extent only on the surface of the Teflon tube where NO_2 concentration is high. Once the NO_2 was diluted and in the gas phase, moisture had no effect on the concentration of NO_2. The best operating temperature for NO_2 permeation tubes is 25 °C or above.

No interferences have been observed with tubes containing hydrocarbons. Some interferences are seen with tubes containing the more reactive gases, but these usually are negligible if the tubes are handled properly and reasonable precautions are taken.

Table I shows typical permeation rates of various devices

Table I. Precision of Permeation Rates

Compound	Permeation rate, μg/min	Rel dev, %
Butane	0.992 ± 0.0138	1.39
NO_2 (triple-walled)	0.567 ± 0.007	1.23
SO_2 (thick-walled)	0.286 ± 0.002	0.70
NH_3	0.687 ± 0.0008	0.12

and their relative deviations. In general, the lower the output, the greater is the relative deviation from the mean.

Precision, Accuracy, and Stability. Precision and accuracy of the rate of permeation from the tube for any particular gas depend upon the precision and accuracy of the balance used and on the degree of temperature control. With a permeation rate of 1 μg/min or higher, accuracy is greater than 99%. A temperature change of 0.1 °C gives an error of approximately 1%.

Accuracy of a standard concentration generated from a permeation tube depends on the flowmeter, which can be calibrated to an accuracy of 1 to 2%. For greater accuracy a dry test meter, calibrated with a spirometer can be used. The overall accuracy of the system is of the order of 1 to 2%, assuming no interfering reactions or conditions.

Tubes are normally stable for a period of 3 months after steady state is reached. The lifetime of the tube is function of the capacity of the tube (internal volume) and the thickness of the wall, and may be extended by changes in these parameters. (When not in use for an extended period, tubes may be stored in a refrigerator in a sealed vessel containing a suitable absorbent and drier.) With other permeation devices, such as double-walled tubes, triple-walled tubes, drilled rods, and microbottles, stability and lifetime can be extended to years (5,7).

Determination of Trace Impurities in Argon by Microwave Induced Excitation

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An atmospheric pressure microwave induced discharge has been used to spectroanalytically determine trace molecular impurities in argon. Detection limits have been determined for carbon, oxygen, nitrogen, and hydrogen containing compounds. These typically fall in the fractional parts per million range and the precision observed is generally better than ±10%. To demonstrate the sensitivity of the technique, an analysis of 99.9995% pure argon has been carried out indicating the total impurity level to be 30 ppm. The method described offers the opportunity of directly and continuously monitoring the total carbon and total nitrogen content of argon using relatively low cost and operationally simple instrumentation.

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RECENTLY ATMOSPHERIC PRESSURE INERT gas plasmas have begun to emerge as spectroanalytical excitation sources. Several studies have been concerned with the use of high power radiofrequency generated plasmas (1-4) and plasma arcs (5, 6). At the opposite extreme, Cooke and associates (7)

(1) E. H. Sirois, ANAL. CHEM., **36**, 2389 (1964).
(2) R. H. Wendt and V. A. Fassel, *ibid.*, **37**, 1920 (1965).
(3) *Ibid.*, **38**, 337 (1966).
(4) C. D. West and C. N. Hume, *ibid.*, **36**, 412 (1964).
(5) R. J. Heemstra and N. G. Foster, *ibid.*, **38**, 492 (1966).
(6) R. Mavrodineanu and R. C. Hughes, *Spectrochim. Acta.*, **19**, 1309 (1963).
(7) A. J. McCormick, C. S. Tong, and W. D. Cooke, ANAL. CHEM., **37**, 1470 (1965).
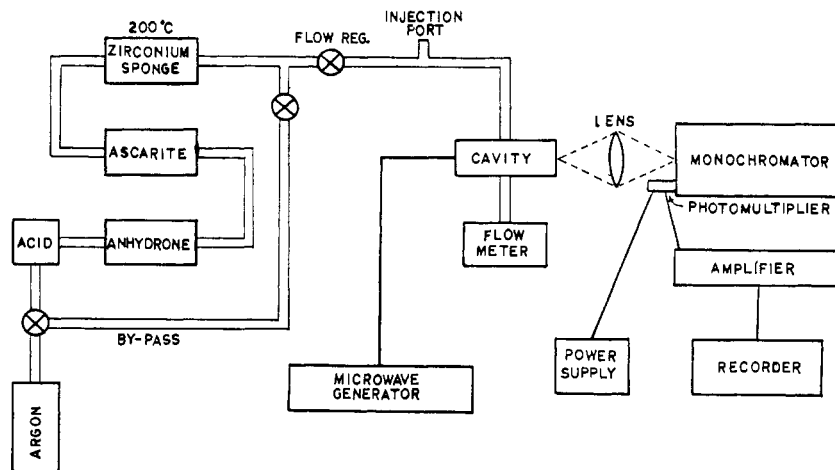
Figure 1. Block diagram of apparatus

and Bache and Lisk (8–10) have successfully used the low power microwave induced discharge as a spectrometric detector for gas chromatography. Molecular compounds containing atoms such as nitrogen, sulfur, phosphorus, and the halogens were determined by using atomic line or molecular band spectra characteristic of the hetero species. By observing the atomic emission of carbon, Cooke (7) has estimated that as little as 10^{-16} gram can be detected. More recently Runnels and Gibson (11) have utilized a thermal evaporation technique to introduce metallic species into the microwave plasma at atmospheric pressure. A solution sample, evaporated onto a wire filament, was vaporized into the excitation medium by resistance heating. This simple expedient permitted the detection of several metallic elements at the 10^{-10} to 10^{-12} gram level (11).

In extending the application of this system to the spectroanalytical determination of other metals, it has been determined that background interferences originating from the excitation of molecular impurities in the argon seriously limit the detection capabilities for a number of elements. Subsequent use of higher purity argon and inclusion of a gas purification train in the system drastically improved but failed to eliminate the problem entirely. Accordingly, it was decided to investigate the microwave excitation technique for the determination of molecular impurities in argon.

The use of emission spectrometric techniques to determine contaminants in inert gases has been limited (12). In general, static discharge tubes of both the dc and high frequency Geissler type have been employed (13–18). The detection limits reported depend on the contaminant and typically fall in the 10^{-3} to 10^{-5} weight percent range.

(8) C. A. Bache and D. J. Lisk, ANAL. CHEM., 37, 1477 (1965).
(9) Ibid., 38, 783 (1966).
(10) Ibid., 39, 786 (1967).
(11) J. H. Runnels and J. H. Gibson, ibid., p 1398.
(12) O. P. Bochkova and E. Ya Shreyder in "Spectroscopic Analysis of Gas Mixtures," Chap. 5, Academic Press, New York, 1965.
(13) O. P. Bochkova, L. P. Rozomuvskaya, and S. E. Frisch, Opt. Spektrosk., 5, 91 (1958).
(14) O. P. Brochdova and I. J. Schreider, Zavod. Lab., 21, 311 (1955).
(15) V. L. Dianov-Klokov, ibid., 22, 444 (1956).
(16) O. S. Duffendock and R. A. Wolfe, Proc. Sixth Summer Conf. Spectrosc., Boston, Mass., 1939, p 66.
(17) S. E. Frisch and V. A. Konovalov, Zh. Tekh. Fiz., 4, 523 (1934).
(18) A. Monfils and P. Posen, Rev. Universelle. Mines Net. Nec., 6, 79 (1950).

A recent review by Roboz (19) discusses the capabilities of several popularly used mass spectrometric methods for determining impurities in permanent gases. In several instances, preconcentration techniques are required to achieve adequate sensitivity. Hickam (20), for example, developed a freeze-out preconcentration process to permit the determination of fractional parts per million concentrations and Roboz (21) employed a sodium–potassium alloy to concentrate impurities in a number of gases. While preconcentration techniques are frequently required and, therefore, widely accepted; a method sufficiently sensitive to preclude the necessity for utilizing such techniques would simplify the analysis procedure and improve the overall analytical definity through a reduction in the number of steps required for the analysis.

The present report deals with the development of the microwave discharge for the direct and continuous emission spectrometric determination of molecular impurities in argon. The parameters of this instrumental system have been optimized, analytical curves have been developed, and evaluative analyses have been carried out. The method developed provides a relatively simple, sensitive, and selective means for determining carbon, nitrogen, hydrogen, and oxygen containing species at concentration levels below 1 part per million.

EXPERIMENTAL

Instrumentation. The instrumentation employed was that described by Runnels and Gibson (11) modified to permit convenient handling of, and calibration for, gas analysis. The gas flow system is shown in Figure 1. Passage of the argon through sulfuric acid, anhydrone, ascarite, and hot zirconium sponge effectively removes the major portion of the organic, water, carbon dioxide, and oxygen and nitrogen impurities, respectively. A Harvard Instrument Co. model 906 infusion pump was used with gas syringes to dope the argon stream with known amounts of the respective impurities through the silicone rubber septum shown in greater detail in Figure 2. Borosilicate glass and stainless steel tubing was used throughout to minimize the blank problem discussed below. A quartz discharge tube, 1 mm i.d. and 3 mm o.d. by 20 cm, inserted into a stainless steel Swagelok fitting

(19) J. Roboz, in "Trace Analysis: Physical Methods," G. H. Morrison, Ed., Interscience, New York, 1965, p 464.
(20) W. M. Hickam, 9th Ann. Conf. Mass Spectrometry, ASTM Committee E-14, Philadelphia, 1961, p 346.
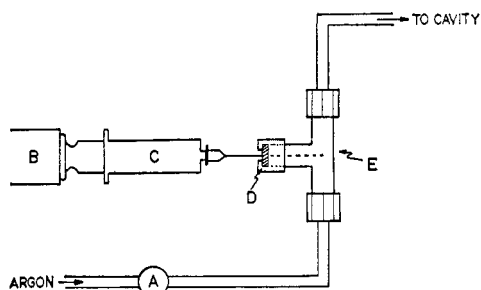(21) J. Roboz, ANAL. CHEM., 39, 175 (1967).

Figure 2. Diagram of injection port

A. Nupro Model "S" metering valve
B. Infusion pump
C. 2-cubic centimeter syringe
D. Silicone rubber septum
E. ¹/₄-inch Swagelok stainless tee fitting

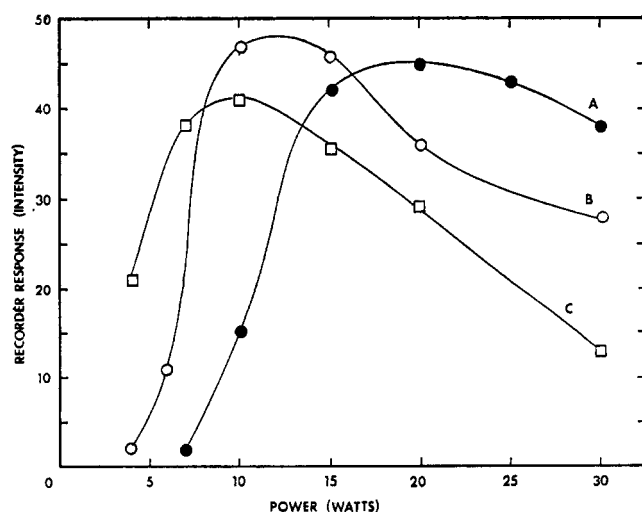**Figure 3. Intensity vs. microwave power**

A. Carbon—2478.6 Å
B. OH—3067.2 Å
C. Hydrogen—4861.3 Å

Figure 4. Intensity vs. vertical position in discharge

Zero indicates leading edge of discharge

A. Carbon—2478.6 Å
B. OH—3067.2 Å
C. Hydrogen—4861.3 Å

Figure 5. Effect of argon flow rate on emission intensity of hydrogen

through a silicone rubber septum was utilized throughout the investigation.

Analytical Procedure. The flow rate of argon was maintained constant at 300 cm³/min for all determinations by a precision adjust metering valve (A in Figure 2). The microwave power maximizing the emission intensity was set for each analytical species and the cavity tuned to zero reflected power. All measurements were made at atmospheric pressure. The monochromator was set at the appropriate wavelength, the background level determined while passing purified argon, and the impurity line or band intensities were measured with the argon by-passing the purification train.

Calibration curves for the various species were obtained by controlled feed rate injection of suitable reagent grade gases into the purified argon stream at the injection port. The use of the infusion pump permitted continuous variation of the injection rate. Accordingly, the impurity concentration for each injection rate could be determined from the flow rate of the argon and the relative densities of the two gases. The choice of gases for calibration is discussed below.

RESULTS AND DISCUSSION

Selection of Analysis Conditions. To assess the analytical characteristics of the microwave plasma for the present application, the effects of the various excitation parameters were
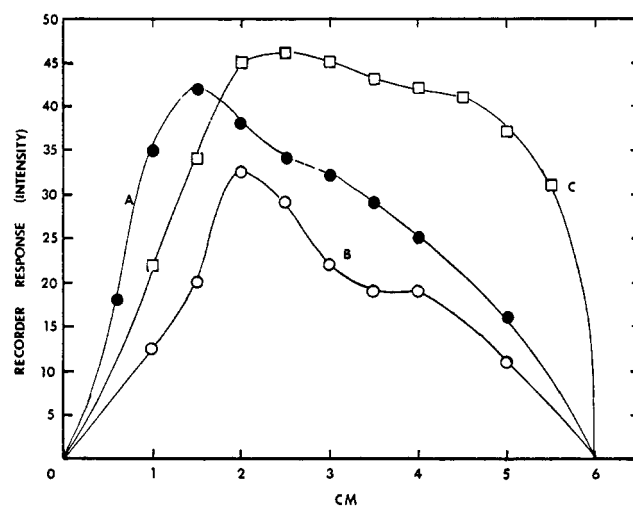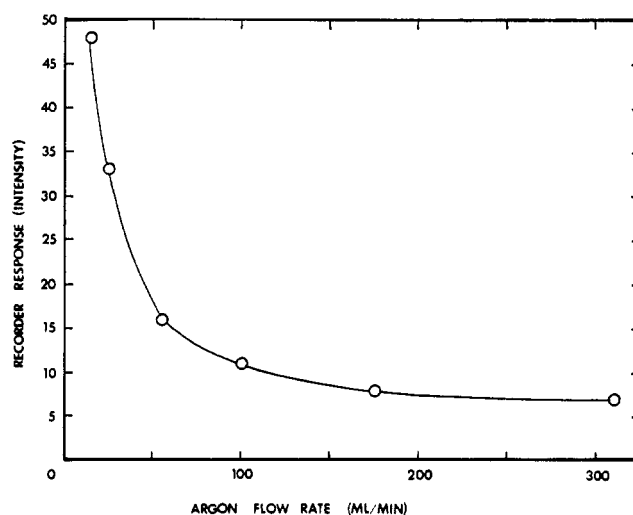
investigated. Figure 3 indicates the effect of microwave power on the measured intensities for the carbon and hydrogen lines and the OH band as examples. Curves for all species studied are of the same general shape and a compromise power setting of approximately 12-15 watts could be utilized for all species without major losses in sensitivity.

In determining the region of greatest emission in the discharge, positional discrimination was increased by masking the slit of the monochromator to permit sampling of light from only a 2-mm portion of the plasma. Figure 4 presents positional intensity profiles for three example species. These profiles are essentially the same in character as that observed for CH by Runnels and Gibson (11) and, again, a compromise setting approximately 2 cm from the leading edge of the plasma could be selected for all species examined.

The argon flow rate affects the emission intensities of all impurities in the manner illustrated for a constant concentration of hydrogen in Figure 5. Although intensity losses are realized by utilizing higher flow rates, it is to be noted that a tenfold decrease in the flow rate would not produce a

Table I. Detection Limits for Impurities in Argon

Impurity gas	Species observed	Wavelength, Å	Detection limit, ppm[a]
CH₄	C	2478.6	0.05
CH₄	C₂	5165.2	0.1
CH₄	CH	4314.2	0.2
CH₄	CN	3883.4	0.05
CO₂	CO⁺	2189.8	2.1
H₂	H	4861.3	1.8
He	He	. . .	N.D.[b]
Kr	Kr	5870.9	1.2
N₂	N₂	3371.3	0.7[c]
NH₃	NH	3360.0	0.03[c]
O₂	O	. . .	N.D.
H₂O	OH	3067.2	0.1
CH₄	Total carbon in all forms	Composite	0.05
C₂H₆	Total carbon in all forms	Composite	0.05
CH₃OH	Total carbon in all forms	Composite	0.05
N₂	Total nitrogen in all forms	Composite	0.07[c]
NH₃	Total nitrogen in all forms	Composite	0.07[c]

[a] By weight.
[b] Not detectable below 40% by weight.
[c] Limited by residual N₂ level in purified argon.

Figure 6. Analytical curves for carbon species in parts per million carbon by weight using methane as calibration gas

A. CH—4314.2 Å
B. C₂—5165.2 Å
C. CN—3883.4 Å
D. C—2478.6 Å

Figure 7. Analytical curves for carbon species in parts per million carbon by weight using ethane as calibrating gas

A. CH—4314.2 Å
B. C₂—5165.2 Å
C. CN—3883.4 Å
D. C—2478.6 Å

like increase in the emission intensity. Consequently, the net gain in the relative detection capability of the technique that can be realized by going to lower flow rates is generally less than a factor of 5. Moreover, at flow rates above 200 ml/min, the discharge is more stable and the measurement precision is considerably improved. Thus, 300 ml/min was chosen for the investigation reported herein.

The blank problem experienced in the early stages of the investigation has been mentioned. Purification of the argon is of major assistance but it is further necessary to utilize glass and/or metal construction of the gas transport system insofar as possible. The use of polypropylene or Teflon (Du Pont) tubing, for example, contributes appreciably to the blank for a number of molecular impurities on a long term basis. The same is true for glass or metal but these materials can be easily degassed by moderate heating with a torch while passing argon through the system. After degassing, the blank may be held at a generally insignificant level by maintaining a slight positive pressure on the system at all times.

Analytical Sensitivity. Table I presents the detection limits observed for the atomic and the fragment wavelengths listed. The values given are for the listed impurities with the following exceptions. The total carbon and total nitrogen estimates were obtained from composite analytical curves. The concentrations for atomic and diatomic species were redefined in terms of the element in common for these species and the measured intensities for the species involved were summed accordingly. For example, the total carbon detection limit represents total elemental carbin in all forms: C, C₂, CH, and CN (See Figures 6 and 7). The detection limits were defined as outlined by Skogerboe *et al.* (*22*). The measurement reproducibility and the curve slopes used in these definitions were determined within a factor of two–three of the detection limit levels by five successive measurements. The *t* statistic was subsequently applied for the number of degrees of freedom in-
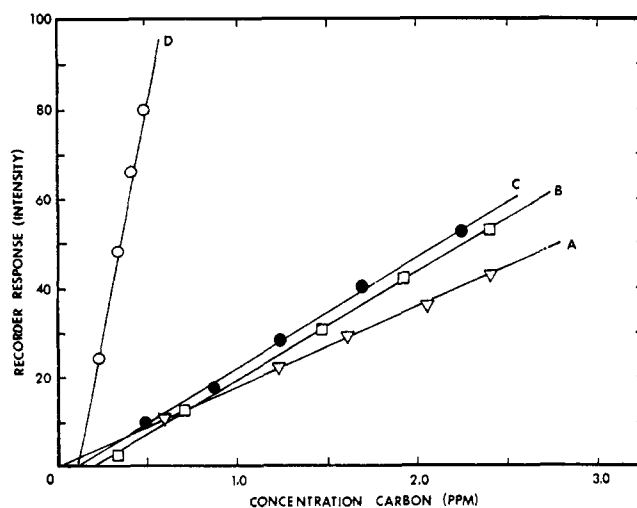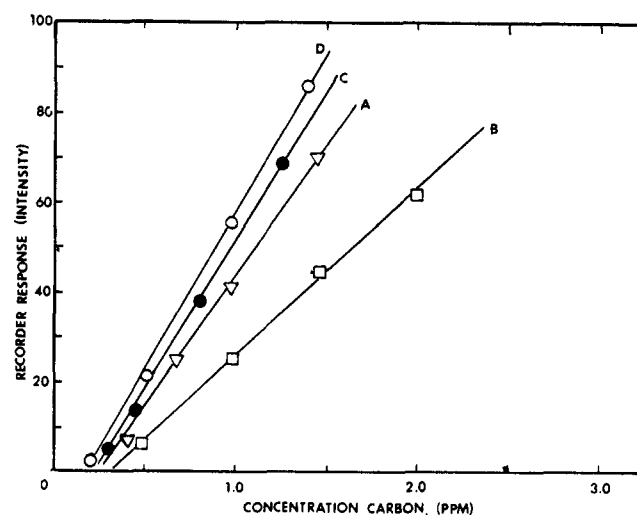
volved at the 95 percent confidence level. This approach produces a reasonably conservative estimate of the detection limit.

Data for the determination of the impurity, krypton, are also presented because of interest in this element as a decay product in radiochemical applications utilizing high purity argon. It must also be noted that attempts to determine helium were unsuccessful at levels below 40% by weight. In view of the fact that Runnels (*23*) found that metallic species were excited when introduced downstream from the discharge, one might conclude that collision with the 11.6 eV metastable state of argon is a prominent cause of excitation in the microwave plasma. The inability to excite helium with an excitation potential of 21.2 eV lends credence to this possibility.

(22) R. K. Skogerboe, A. T. Heybey, and G. H. Morrison, ANAL. CHEM., **38**, 1821 (1966).

(23) J. H. Runnels, Ph.D. Dissertation, Colorado State University, 1968, Chap. 10.

Table II. Dependence of Impurity Emission on Calibrating Gas

| Species	Calibrating Gas								
	H_2O	CH_4	C_2H_6	CH_3OH	H_2	N_2	NH_3	CO_2	O_2
C	No	Yes	Yes	Yes	No	No	No	No	No
C_2	No	Yes	Yes	Yes	No	No	No	No	No
CH	No	Yes	Yes	Yes	No[a]	No	No	No	No
CN	No	Yes[b]	Yes[b]	Yes[b]	No	No	No	No	No
CO^+	No	No	No	No	No	No	No	Yes	No
H	No[a]	No[a]	No[a]	No[a]	Yes	No	No[a]	No	No
N	No	No	No	No	No	No	No	No	No
N_2	No	No	No	No	No	Yes	Yes	No	No
NH	No	No	No	No	No[a]	No	Yes	No	No
O	No	No	No	No	No	No	No	No	No
O_2	No	No	No	No	No	No	No	No	No
OH	Yes	No	No	Yes	No	No	No	No	No

[a] Appears at concn ratios of 500:1.
[b] Due to combination of free carbon with residual nitrogen in purified argon.
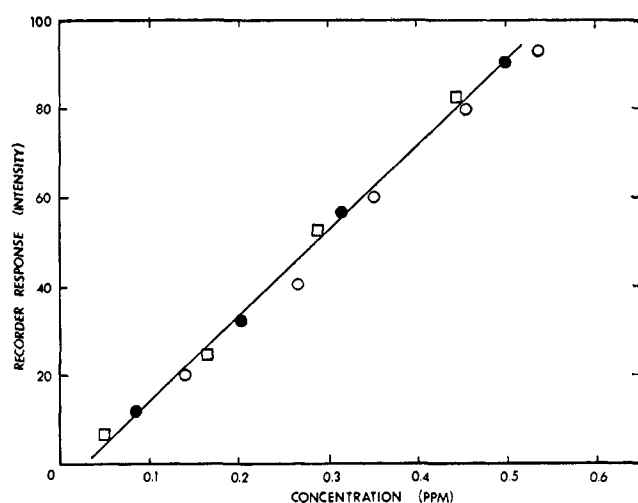
Figure 8. Analytical curve for total carbon

● Methane
○ Methanol
□ Ethane

Analytical Selectivity. Most analysis reports furnished by gas producers state the impurity levels in terms of total carbon, total nitrogen, etc. One might logically expect that, for the emission spectrometric method, the intensity observed for any particular emitting species would be dependent on the identity of the entity from which the emitting species is derived. Moreover, emission is observed for several diatomic species which may originate from fragmentation of molecules containing both constituents or from the combination of the separated constituents. These factors, then, relate to the problem of analytical calibration. There may also be instances for which a more specific statement regarding the actual identity of the impurities in the argon is required. Consequently, consideration of the analytical selectivity of the microwave plasma method is appropriate.

Runnels (23) reported that the introduction of organic compounds into the plasma resulted in total fragmentation of the compound into atomic and diatomic species and this has been supported by our subsequent investigations. The question that relates to selectivity, then, is actually twofold. Does the population of fragments produced depend on the physical (structural) characteristics of the parent molecule? and how prominent are recombination processes in the energetic plasma medium? In essence, if the answers to these questions are

negative, the emission spectrometric method would be adequate only for the specification of concentrations on a gross identity basis, i.e., total carbon, total organic, etc. In the converse, a greater degree of specificity would be possible.

In an attempt to answer these questions, a variety of gases was used to develop calibration curves for the various emitting species as indicated in Table II. The Table indicates the additive gases for which an emission line or band characteristic of the analytical species could be observed. Atomic emission from carbon, for example, was observed only when carbon-containing gases were introduced into the plasma. The CH band was observed only when compounds containing carbon and hydrogen were introduced. In addition, by holding the carbon-hydrogen compound concentration constant and introducing excess hydrogen, it was determined that the CH emission did not increase until the hydrogen-to-organic compound concentration ratio exceeded 500 to 1. Hence, recombination of separate entities to form diatomic fragments does not appear to be a problem at the nominally low concentrations characteristic of the more pure grades of argon. In the same type of experiment, it was found that atomic emission from hydrogen occurred only when hydrogen gas was introduced and the hydrogen line was enhanced by the addition of carbon-hydrogen compounds when the C-H compound to hydrogen concentration ratio exceeded 500 to 1. Even at these higher concentration ratios, the increase in the hydrogen line intensity (for example) due to the C-H compound is not as great as it would be if hydrogen alone were added in an equivalent amount. In general, the 500 to 1 concentration ratio interference effect on the measured intensities held for all the competing additive-analytical species combinations indicated by superscript a in the Table. This leaves the question regarding the possible relationship between the structural characteristics of the additive (impurity) compound and the line and band intensities. Inferences related to this question were obtained by comparing the data obtained from the addition of methane, ethane, and gaseous methanol to the argon stream.

The results presented in Figures 6 and 7 for methane and ethane distinctly indicate that the population of fragments produced depends on the physical characteristics of the parent molecule. When the intensities of the carbon fragment wavelengths are added, however, the cumulative curves obtained from methane, ethane, and methanol are identical within experimental error, Figure 8. Similar results were obtained for nitrogen species. In view of these observations and those presented in Table II, it appears that an analysis based on the

cumulative total carbon or nitrogen data may be reasonably used as an indication of the total hydrocarbon or nitrogen compound impurity level in argon.

Analytical Application. A typical analysis was carried out on 2 cylinders of argon; welding grade and research grade. The analysis for the latter, provided by the manufacturer, specified "no detectable impurities" (99.9995% pure by volume) but the analysis method utilized to determine this was not stated. The analysis results are presented in Table III indicating total detectable impurity levels of 226 and 30 ppm for the welding grade and research grade argon, respectively. The relative standard deviation values presented in the last column of Table III were determined for the welding grade analysis by five consecutive measurements for each species reported.

Conclusions. The data presented above imply that the microwave plasma can be satisfactorily used for reproducibly determining hydrocarbon and nitrogen containing compounds in argon without the necessity of a preconcentration step.

The detection limits that can be realized range from the low to the fractional parts per million level, calibration is relatively simple, and the system offers the possibility of continuous nondestructive monitoring for individual impurities. In view of these factors, the relatively low cost of the instrumentation required, and the comparative operational simplicity, the plasma technique may well be the method of choice for determining impurities in argon.

Finally, the fact that the plasma apparently reduces the molecular impurities to potentially reactive fragments suggests that it might be used as an intermediary process for reducing the impurity levels in argon.

Palladium–Hydrogen System

Efficient Interface for Gas Chromatography–Mass Spectrometry

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The property of palladium–silver (25%) tubing to selectively diffuse hydrogen has been used to develop a new type of interface for gas chromatography–mass spectrometry. Optimum efficiency can be maintained at temperatures in excess of 200 °C when the separator is placed in an oxidizing atmosphere such as laboratory air. Catalytic reduction which was anticipated to be a potential handicap of the palladium–silver interface has been investigated and found to be specific for compounds with conjugated unsaturation such as dienes, α,β-unsaturated aldehydes, ketones, and nitriles. The palladium–silver separator was developed for a gas chromatograph–mass spectrometer instrument specifically intended for spaceflight experiments. However, its advantages of possessing a simple and rugged construction, near 100% efficiency, and a quantitative delivery of most sample substances make it attractive for more general use.

THE CONSIDERABLE IMPROVEMENT in analytical capability which may be derived from the combination of gas chromatography and mass spectrometry (GC–MS) has encouraged the development of various interface devices, or as they are more commonly called, molecular separators. These serve primarily as pressure reduction systems by selectively diminishing the total mass flow of carrier gas which enters the mass spectrometer to a level consistent with the maintenance of an adequate vacuum. The different types of separator and their performance characteristics have been reviewed by Rees (1). A recent article by Watson (2) discusses the advantages of combined GC–MS, and also includes a description of the various types of interface. All of the presently available separators, with the exception of the Ryhage jet-orifice type (3), rely on a membrane device through which carrier gas (usually hydrogen or helium) and sample components are separated because of a difference in their rates of effusion or permeation. The separator is generally enclosed in a vacuum chamber which must be continuously pumped to ensure efficient removal of the separated carrier gas. One limitation common to all of these devices is the loss of some of the sample which invariably accompanies removal of the carrier gas.

In normal laboratory practice there are no special limitations on the size, weight, and power required for effective

(1) D. I. Rees, *Talanta*, **16**, 903 (1969).
(2) J. T. Watson, in "Ancillary Techniques in Gas Chromatography," L. S. Ettre and W. H. McFadden, Eds, Interscience, New York, N. Y., 1969, p 158.
(3) R. Ryhage, *Ark. Kemi*, **26**, 305 (1967).