Effect of doping gases on microwave-induced emissive spectrometric detectors for gas chromatography

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In contrast to the above situation, just the opposite trend is noted in the abundance of ions produced by the corresponding electrophilic addition reaction in CI(CH$_4$) spectra (4). Here, ions such as the (M + 1)$^+$ (Equation 1) and (C$_n$H$_{2n+1}$)$^+$ (Equation 6) fragments decrease in abundance from 70 to 40% as the chain length is increased from 6 to 20 carbon atoms. Alkenyl ions (C$_n$H$_{2n-1}$)$^+$ resulting from attack of reagent ions on the saturated hydrocarbon chain (Equations 2-5) show a corresponding increase in abundance from 24 to 48%. Field suggests that these results reflect the relative directing ability of a double bond and saturated alkane moieties on the course of ion molecule reactions involving electrophilic reagent ions (4). A single double bond was shown to exert about the same influence as 14 methylene units in a hydrocarbon chain. In an earlier study, we found that reactions of NO$^+$ with straight chain alkanes (alkyl and/or hydride abstraction and subsequent β-fission) are either endothermic or slightly exothermic (10). Accordingly, it is not surprising that the double bond plays such an influential role in the ion-molecule chemistry of NO$^+$ and olefins.

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Effect of Doping Gases on Microwave-Induced Emissive Spectrometric Detectors for Gas Chromatography

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The effect of doping gases on a reduced pressure (1 Torr) microwave-induced helium plasma has been studied. The results show that the quantity of oxygen added as a doping gas is critical in maximizing the selectivity and sensitivity of the microwave-induced emissive spectrometric detector for the determination of chromium. The addition of approximately 3% O$_2$ maximizes emission from atomic chromium and simultaneously quenches molecular emissions. Possible mechanisms of fragmentation and excitation are given.

The development of the microwave-induced emissive spectrometric detector (MIESD) (1) for gas chromatography has been followed by its application for sensitive and selective organic analyses (2-12). Compounds analyzed have usually contained a heteroatom (such as sulfur, phosphorus, or a halogen) and it is the atomic emission from these atoms which can be monitored selectively. Alternatively, this detector can be operated in the nonselective mode, usually with an increase in sensitivity, by monitoring the atomic carbon emission (1). Also, methods have been

developed for determining interelement ratios (12, 13) using atomic emissions, while molecular emissions have been used to determine the extent of deuterium labeling in hydrocarbons (14).

Recently, the MIESD has been employed for the selective determination of inorganics. Bache and Lisk (15) used a reduced pressure helium plasma for the analysis of organomercury compounds recovered from fish. Dagnall et al. (16) employed an atmospheric pressure argon plasma for the determination of a number of metal chelates. Talmi and Andren (17) determined selenium in environmental samples, also using an atmospheric argon plasma.

Recent work in our laboratories (18) involving the use of a reduced pressure helium plasma for the selective detection of chromium β-diketonates has shown that the presence of trace quantities of oxygen (10) is important in obtaining atomic chromium emission instead of molecular emission. The results of this work indicate a need for an understanding of the mechanism of fragmentation and excitation in microwave discharges in order to have a basis for optimizing the MIESD. For this reason, the effect of oxygen, nitrogen, argon, and hydrogen on the spectral characteristics of a reduced pressure helium plasma has been studied.

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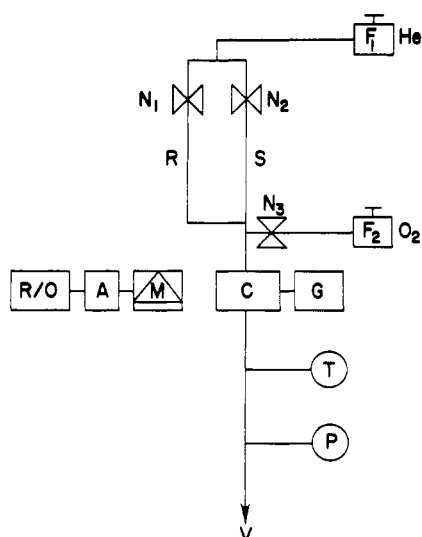
Figure 1. Flow system

F_1, F_2 = flow controllers and flow meters; N_1, N_2, N_3 = fine control needle valves; R = reference container; S = sample container packed with 3% OV-7 on Chromosorb W-HP (100–120 mesh); G = microwave generator; C = ¼-wave Evenson cavity; M = monochromator; A = photomultiplier tube, power supply, and amplifier; R/O = strip chart recorder; T = McLeod gauge; P = absolute pressure gauge; V = to vacuum

EXPERIMENTAL

Chelate Preparation. Chromium trifluoroacetylacetonate [$Cr(tfa)_3$] was prepared by the method which has been previously described (19), and was characterized by its melting point and infrared spectrum.

Gases. Helium (99.99+% pure) was obtained from the cryogenics laboratory of The Pennsylvania State University, and oxygen (99.5% pure), argon (99.5% pure), nitrogen (99.5% pure), and hydrogen (99.5% pure) were obtained from Phillip Wolf and Sons, Lewistown, Pa.

Apparatus. The flow system was similar to that used previously (18) except that oxygen was added through a side-arm on the plasma cell slightly above the discharge region, as shown in Figure 1. The plasma was maintained in a length of silica tubing (2-mm i.d., 6-mm o.d.) placed inside a ¼-wave Evenson cavity (Opthos Instrument Co.). Power was supplied with a microwave generator operating at 2450 MHz (Scintillonics HV-15A), and pressures were measured with a McLeod gauge (The Virtis Company, Inc.) and an absolute pressure gauge (Model 61-050, Wallace and Tiernan). The emission spectrum was monitored with an atomic absorption spectrometer with flame emission chopper (for ac amplification) and wavelength scanning accessories (Varian AA-4), and a permanent record was obtained on a strip-chart recorder (Hewlett-Packard). The instrumental response was calibrated with a standard Tungsten Lamp (General Electric).

The gas chromatographic system was the same as that described previously (18). When two doping gases were used simultaneously, both gases were added through the side-arm on the discharge tube.

Procedure. The spectral characteristics of the reduced pressure microwave-induced helium plasma were examined as a function of pressure and as a function of added oxygen. The vacuum system was first pumped down to less than 10^{-3} Torr (zero on the McLeod gauge) and then flushed with the gas of interest for half an hour at a pressure at least twice that to be used in the subsequent experiments. The gas was then brought to the desired pressure (measured with the pressure gauge), and the plasma was initiated and allowed to stabilize before the emission spectrum was recorded. After each subsequent change in pressure, this procedure was repeated. Spectra were recorded from 6800 to 2000 Å at a scan rate of 100 Å/minute.

The effect of oxygen on the emission spectrum obtained when $Cr(tfa)_3$ was passed into the helium plasma was also studied. The chelate was sublimed into the discharge by placing the solid sample in the sample column and supplying heat with a heating coil which was controlled by a variac. The temperature was measured with a thermocouple wrapped inside the heating coil, which in turn was wrapped with glass insulating tape. The entrance of the che-
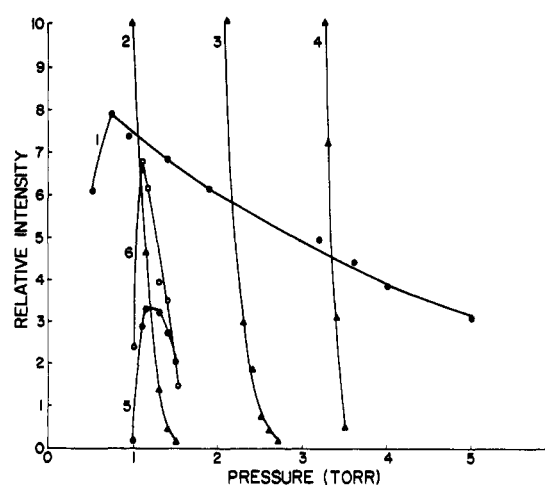
Figure 2. Relative intensity of emission vs. total pressure

(1) He(I) 6678 Å as a function of added He. (2) He(I) 6678 Å, P_{He} = 1.0 Torr; function of added O_2. (3) He(I) 6678 Å, P_{He} = 2.1 Torr; function of added O_2. (4) He(I) 6678 Å, P_{He} = 3.1 Torr; function of added O_2. (5) O(I) 4368 Å, P_{He} = 1.0 Torr; function of added O_2. (6) OH 3082 Å, P_{He} = 1.0 Torr; function of added O_2

late into the plasma is accompanied by a striking color change from light pink to deep blue. The chelate was introduced into the plasma at a rate of approximately 1 µg/sec. To ensure that the chelate was entering the plasma at a constant rate, a number of chromium lines were scanned repetitively after the temperature had reached a constant value. The reproducibility of the emission intensity of the chromium lines was approximately 7% (10 scans). Spectra were recorded from 5300 to 3800 Å at a scan rate of 100 Å/min.

RESULTS AND DISCUSSION

The emission spectra of the helium plasma, the helium with trace oxygen plasma, and the $Cr(tfa)_3$ in a helium with trace oxygen plasma have been shown previously (18). Figure 2 shows the variation of emission intensity for a number of lines as a function of pressure, and curve 1 shows the emission intensity of the atomic helium line at 6678 Å as a function of total helium pressure. This line is representative of the entire helium spectrum, since the same general trend is observed for all other helium lines in the 2800 to 6800-Å region.

In addition to collisional deactivation, reactions which may explain this gradual decrease in intensity with an increase in pressure are as follows (20):

(a) excited pair ionization (21–23)

$$He^* + He^* \rightarrow He^+ + He + e \qquad (1)$$
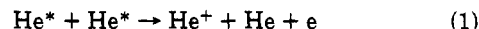
(b) Homonuclear associative ionization (also called the "Hornbeck–Molnar" reaction) (24–36)

$$He^* + He \rightarrow He_2^+ + e \qquad (2)$$
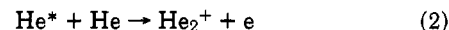
where He^* refers to an excited electronic state of helium. The second reaction has been shown to involve only those excited states which lie above the metastable states of helium (26, 27). Both of the preceding reactions reduce the population of the excited states, and the cross section should be expected to increase with an increase in pressure. The rapid drop in intensity at pressures below 0.75 Torr results from the difficulty in maintaining a stable discharge below this pressure with the present equipment.

Curves 2 through 4 (Figure 2) show the effect of maintaining the helium pressure (P_{He}) constant and adding small amounts of oxygen. The other helium lines show the same trend and, in these cases, we see a relatively rapid decrease in helium emission with an increase in oxygen par-
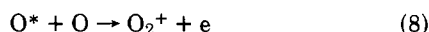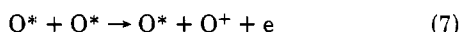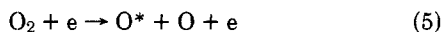
tial pressure (P_{O_2}). This can be explained on the basis of Penning ionization (37–41):

$$He^* + O_2 \rightarrow O_2^+ + He + e \qquad (3)$$

Penning ionization occurs with those species whose ionization potential is lower than the energy of the helium excited state (20, 42). Although the reaction normally occurs with the long-lived metastable states of helium (38), other excited states may also be involved (20). Penning ionization may also lead to dissociation (20):

$$He^* + O_2 \rightarrow O^+ + O + He + e \qquad (4)$$

Curve 5 (Figure 2) shows the variation of an oxygen atomic emission (4368 Å) in a plasma where P_{He} is constant and oxygen is added. Although, to our knowledge, reactions of the type shown in Equations 1 and 2 have not been reported for oxygen, the following analogous reactions seem feasible:

$$O_2 + e \rightarrow O^* + O + e \qquad (5)$$

$$O + e \rightarrow O^* + e \qquad (6)$$

$$O^* + O^* \rightarrow O^* + O^+ + e \qquad (7)$$

$$O^* + O \rightarrow O_2^+ + e \qquad (8)$$

Reactions 5 and 6 could explain the increase in emission intensity with increasing pressure, while reactions 7 and 8 could explain the subsequent decrease, although reaction 7 probably has a very small cross section under these conditions. These reactions are only speculative and do not explain the occurrence of a maximum at a specific pressure.

Although not shown in the diagram, the emission intensity of an OH band system around 3000 Å increases slowly with an increase in P_{He}. However, if P_{He} is kept constant and O_2 is added to increase the total pressure, curve 6 (Figure 2) is obtained. In this instance, there is a relatively rapid increase in intensity followed by a rapid decrease. The OH comes initially from water vapor (43) introduced as an impurity in the gases and/or leaks in the system. Therefore, the OH emission is expected to increase with P_{He}, provided that no reactions to remove the OH* occur to any appreciable extent and that collisional deactivation is not important. Conversely, when P_{O_2} is increased at constant P_{He}, OH emission goes through a maximum. It seems likely, therefore, that this decrease results from reactions of OH*, one or more of which may be with O* since oxygen emission intensity reaches a maximum at approximately the same total pressure. This would be an additional mechanism for the reduction of oxygen emission intensity.

Figure 3 shows the effect of adding oxygen to Cr(tfa)₃ in a helium plasma. This diagram shows the variation in emission intensity of the Cr(I) 3984-Å line (Curve 1), the He(I) 4713-Å line (Curve 2), and the O(I) 4368-Å line (Curve 3). It should be noted that no chromium atomic emissions are observed in a pure helium plasma. The emission spectrum contains only molecular emissions from the chelate, fragments, and, without oxygen, the discharge tube clogs readily and it is difficult to obtain an emission spectrum. With the addition of as little as 0.01 Torr of oxygen, there is a dramatic decrease in molecular emission, and the chromium atomic lines appear. As many as 200 Cr(I) are observed in the 5300–3800-Å region. In addition, there was no problem of clogging of the discharge tube.

On comparing Figures 2 and 3, it can be seen that the He and O spectra are very similar in both cases.

Determination of Excitation Temperatures. The temperature of a radiating atomic vapor can be determined using the emission intensities of a number of lines in the emission spectrum of the vapor (44), according to the fol-
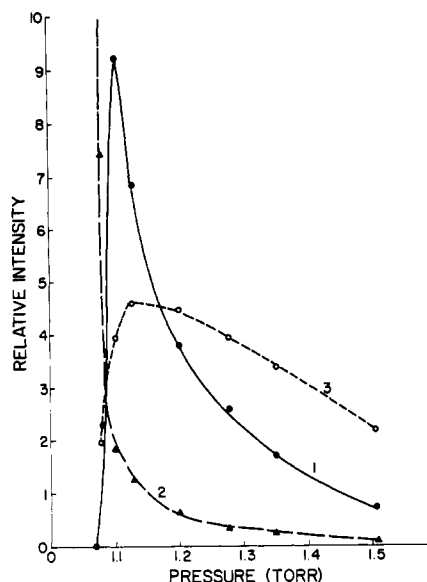

Figure 3. Relative intensity of emission vs. total pressure

P_{He} = 1.07 Torr, function of added O_2. (1) Cr(I) 3984 Å, (2) He(I) 4713 Å, (3) O(I) 4368 Å

lowing equation, which assumes the existence of local thermodynamic equilibrium:

$$\log \frac{I_{mn}\lambda_{mn}}{g_m A_{mn}} = \text{constant} - \frac{E_m}{2.303\,kT} \qquad (9)$$

where I_{mn} is the intensity of the emission at wavelength λ_{mn} originating in state m and terminating in state n, g_m is the statistical weight of the upper state $(q = 2J + 1)$. A_{mn} is the Einstein coefficient of spontaneous emission ("transition probability"), E_m is the energy of the upper state, k is the Boltzmann constant, and T is the absolute temperature.

Equation 9 shows that if $\log (I\lambda/gA)$ for a number of lines is plotted vs. the energy of the upper state (in ergs) the slope is equal to $-1/2\cdot303\,kT$. Transition probabilities and values of g_m and E_m were taken from Wiese, Smith, and Glennon (45), and Corliss and Bozmann (46). The emission intensities were corrected for instrumental response by calibration vs. a standard tungsten lamp. The output of the tungsten lamp is low in the ultraviolet, which leads to a large uncertainty in the instrumental response in this region of the spectrum. Therefore, no atomic lines below 3800 Å were used for the determination of temperatures.

Figure 4 shows a typical plot of $\log (I\lambda/gA)$ vs. E_m for the determination of the Cr excitation temperature. A total of 29 lines were used, and a straight line was fitted to the data using a linear least squares method. A temperature of 5490 K was calculated from the slope. Figure 5 shows the chromium excitation temperature as a function of P_{O_2}. The error bars of each point represent the uncertainty in the temperature calculated using the standard deviation of the least squares slope. In determining the temperature for different pressures, the same 29 lines were used in each case, and it can be seen that, except for the first point, the temperature is essentially constant within experimental error. The first temperature is significantly different, but this is probably due to the fact that, at such a low oxygen partial pressure, there is still some molecular emission which is not apparent in the other spectra. This molecular emission made it difficult to locate the chromium atomic lines.

Other results are shown in Tables I and II. The helium excitation temperature is on the order of 2200 K and remains constant, within experimental error, upon the addi-
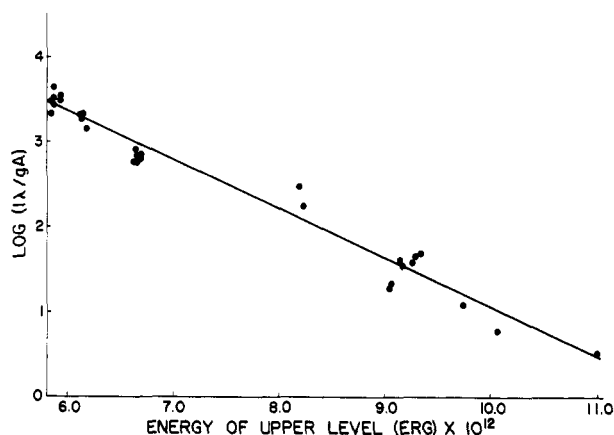
Figure 4. Determination of Cr excitation temperature

P_{He} = 1.07 Torr, P_{O_2} = 0.44 Torr

Table I. Helium Excitation Temperature as a Function of P_{He}^a

P_{He} (torr)	No. of lines	T (K)	T_{max} (K)	T_{min} (K)
0.75	5	2170	2350	2020
0.95	7	2160	2390	1970
1.4	7	2190	2420	1990
1.9	7	2220	2460	2020
3.2	7	2270	2620	1990
3.6	7	2280	2720	1970
4.0	7	2350	2790	2020
5.0	7	2370	2920	1990

a See legend to Figure 5.

Figure 5. Excitation temperature vs P_{O_2}

(1) Cr; P_{He} = 1.07 Torr. (2) He; P_{He} = 1.0 Torr. T = −3.15 × $10^{15}/m$, where m = slope of least squares line fitted to log ($I\lambda/gA$) vs. E_m; T_{max} = −3.15 × $10^{15}/(m - s)$, where s = standard deviation of least squares slope; T_{min} = −3.15 × $10^{15}/(m + s)$

Table II. Helium Excitation Temperature as a Function of $P_{O_2}^a$

P_{O_2} (Torr)	No. of lines	T (K)	T_{max} (K)	T_{min} (K)
0.0	6	2300	2600	2060
0.1	7	2170	2440	1960
0.2	7	2270	2720	1940
0.3	7	2300	3060	1840
0.4	6	2350	3420	1810

a See legend to Figure 5.

tion of either helium or oxygen. The uncertainty in the helium temperature (approximately ±500 K) is larger than that in the chromium temperature since fewer helium lines are available. Again, to compare trends in temperature with pressure, only those lines which were present in all spectra were used. As a result, the trend in temperature may be more meaningful than the actual temperature.

An interesting result was obtained by attempting to determine the helium temperature in the experiments with Cr(tfa)₃: the uncertainty in the slopes was found to be on the order of 50–70% and, in one case, nearly 100%. Since the relative spectral intensities are proportional to the relative population of the excited states, and the relative population is determined by the temperature, a large uncertainty in the temperature determined by this approach may indicate that a Boltzmann distribution no longer exists. This suggests that the excited states of the helium may enter into the fragmentation/excitation reactions, and that they do so with considerably different cross sections. Since the helium temperature was essentially constant in the experiments where oxygen was added to a constant P_{He} plasma, and since the uncertainty was smaller, each excited state of He above the metastable states must have very nearly the same cross section for reactions of the Penning ionization types.

Possible Mechanisms. The fact that there is no chromium atomic emission observed in a pure helium plasma is puzzling. Since the ionization potential of helium is 24.6 eV, there should be sufficient energy available for fragmentation of the chelate and excitation of chromium. With the addition of trace amounts of oxygen, the chromium atomic lines are observed. Two possible mechanisms are as follows: (a) Formation of species such as CO reduces Cr^{3+} to Cr. Atomic chromium is then excited by collision with either an electron or He*. (b) The addition of oxygen increases the concentration of electrons, which provides a more high-
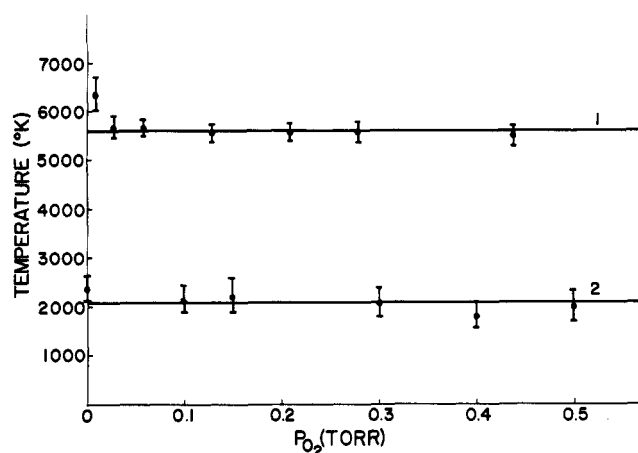
ly reducing environment through three-body collisions. In addition, collisions with high energy electrons increase the fragmentation.

To test the first mechanism, N₂ or H₂ was used as a doping gas in place of O₂. Nitrogen reacts with organic compounds in electrical discharges to form CN, which is known to be a strong reducing agent in flames. Although CN emission was apparent when N₂ was used as the doping gas and H(I) emission was observed when H₂ was added, no chromium emission was observed. These results suggest that the first mechanism does not explain the results completely.

The addition of N₂ or H₂ to a helium plasma should also increase the concentration of electrons through Penning ionization. This seems to indicate that the second mechanism may not be correct either. Other results indicate that the mechanism may involve a combination of the two. In any case, the fragmentation/excitation of Cr(tfa)₃ is peculiar to oxygen.

Preliminary investigations of the MIESD have been made using argon and oxygen mixtures as the doping gases. These studies have shown the following results: 1) The response of the MIESD to Cr at constant P_{He} (0.41 Torr) and P_{O_2} (0.07 Torr) increased relative to the response of the flame ionization detector (FID) with added argon until P_{Ar} reached 0.09 Torr when the response decreased. 2) If Ar was used as the sole doping gas, the plama was quickly extinguished and the plasma cell blocked upon the elution of 0.5 μl of solvent (split 15:2 between the FID and MIESD, respectively). This result should be compared with the capacity of the He + O₂ MIESD reported previously (18), namely, that 11 μl of solvent could be introduced directly into the MIESD without experiencing extinguishing or clogging. In addition, the response of the MIESD to Cr was reduced when Ar was used as the sole doping gas.

These results lend support to the second mechanism,

since the ionization potential of Ar is lower than the energies of the two metastable states of He. However, there seems to be more involved than simply an increase in electron concentration since the presence of O_2 is necessary to prevent the deposition of carbonaceous material. Presumably, carbon is removed as CO and CO_2.

Analytical Implications. An inspection of Figure 3 reveals that, while the presence of oxygen is necessary to observe chromium atomic emission, there is an optimum P_{O_2} due to the quenching properties of oxygen. The advantages of adding oxygen are as follows: 1) The addition of oxygen increases the atomic Cr emission. This, of course, improves sensitivity for the chromium chelate. 2) The addition of oxygen reduces molecular emissions from species such as N_2 and N_2^+, introduced through leaks in the system. This means a reduction in background, and is especially important if the 3579-Å chromium line is used for analysis, since there is a very intense N_2 band in this region. 3) The addition of oxygen quenches molecular emissions from species such as CH and CN, which are the result of fragmentation. This is important in improving selectivity.

The following disadvantages are the result of adding oxygen: 1) The chromium emission reaches a maximum and then decreases rather quickly with the addition of oxygen. Curve 1 in Figure 3 shows the importance of maintaining the flow of oxygen constant to maximize precision. 2) Curve 6 in Figure 2 shows that the background in the 3100- to 3000-Å region is high due to the formation of OH. This precludes the use of this region for sensitive analysis unless water can be rigorously excluded.

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Determination of Alkylarsenic Acids in Pesticide and Environmental Samples by Gas Chromatography with a Microwave Emission Spectrometric Detection System

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The applicability of a gas chromatograph with a microwave emission spectrometric detector (GC-MES) to the determination of alkylarsenic acids in commercial pesticides and in environmental samples is described. The analytical procedure involves $NaBH_4$ reduction of the arsenic acids to the corresponding arsines, followed by either extraction of these arsines or their flushing from the sample solution and collection in cold toluene at -5 °C. In either case, the arsines are separated on a GC column and determined by a MES detector by measuring the emission intensity of the As 228.8-nm spectral line. Various parameters affecting the production and collection of the arsines, such as the reduction conditions, sample volume, losses due to volatilization, and arsine rearrangement side reactions are discussed along with instrumentation parameters such as column operation and microwave power. The various alkylarsines separated on the GC column were positively identified by a mass spectrometer. Since the MES detector is highly selective to arsenic ($>10^4$), the absolute sensitivity (20 pg of arsenic) is very little dependent on the molecular structure of the arsines. The relative sensitivity for water samples is at least 0.25 µg/l.