

Detection of Argon by Penning Ionization and Competitive Absorption Using a Sensitized Photoionization Detector

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A novel application of a commercial photoionization detector for the quantification of argon is described and applied to the headspace analysis of water. Using an argon lamp as the excitation source, argon is measured indirectly by its effect on an ionizable gas present in the detection cell. Nitric oxide is added to the effluent of a gas chromatography column, resulting in an elevated background ion current in a photoionization detector. By varying the amount of nitric oxide added to the detection cell, two modes of operation were demonstrated: a competitive absorbance mode in which a high background of nitric oxide photoionization was reduced in response to the presence of argon and a Penning ionization mode in which a relatively lower background of nitric oxide photoionization was enhanced in response to the presence of argon. Optimized Penning ionization detection with a nitric oxide concentration at ~940 ppmv was used to analyze air and the headspace of water samples. The limit of detection was determined to be 14 pmol of Ar s⁻¹.

Argon is a stable element constituting 0.934% of the Earth's atmosphere by volume. It is extremely well mixed and unreactive, making it an ideal tracer for past exposure of a subset of the hydrosphere or biosphere to air. Thus, argon has been employed as a tracer in biological systems,¹ and nitrogen/argon and oxygen/argon ratios have been used to gain a historical perspective of the atmospheres of Earth² and Mars.³ We are especially interested in the measurement of nitrogen/argon ratios in natural waters as an indicator of denitrification.^{4,5} Since the atmosphere has a constant composition of both argon and nitrogen, in the absence of biota, natural waters exposed to and equilibrated with the atmosphere will have a constant ratio of these two dissolved

gases at a given temperature. Variations in this ratio can be related to biological activity.

The permanent gases have been separated by gas chromatography using a variety of column types and detected by thermal conductivity,^{6,7} mass spectrometry,^{1,5,8} and the helium ionization detector.^{6,9} Thermal conductivity is relatively insensitive, mass spectrometry is highly sensitive but expensive and difficult to deploy in the field, and the helium ionization detector is not commercially available. Therefore, we have developed a new approach to argon detection based on sensitization of a commercially available photoionization detector (PID).

The PID has been described in the literature.^{10–12} In normal operation of the PID, compounds with an ionization potential less than the energy of the selected radiation source are photoionized, and the resulting ions are collected as a current at polarized electrodes. The method described here utilizes a commercial PID, equipped with an argon lamp (11.7 eV), in gas chromatography to detect argon indirectly by the effect it has on an ionizable dopant gas. Nitric oxide (ionization potential 9.25 eV) was added to the system postcolumn, resulting in an increased background current. Over the concentration range used for these experiments (0–0.5% NO), two distinctly different regions were observed. At NO concentrations above ~0.15%, the photoionization current was reduced in response to argon. Operated in this way, the response of the detector is based on atomic absorbance; argon selectively absorbs the radiation and decreases the light intensity available for the direct photoionization of NO. This process is hereafter referred to as competitive absorbance. At NO concentrations lower than ~0.15%, an enhancement of the background photoionization was observed in the presence of argon. We attribute the latter result to Penning ionization.

Penning ionization is the process by which a molecule becomes ionized through collision with an electronically excited metastable species; e.g., when Ar and NO are both present in the photoionization detector the Penning ionization process consists of the following steps:

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Here, M is any gas molecule, principally He in our detection system. The quantum yield for Penning ionization is determined by the competition for deactivation of metastable Ar* by reactions R2 and R3 and is given by

$$\phi_{\text{PI}} = k_2[\text{NO}] / (k_2[\text{NO}] + k_3[\text{M}]) \quad (\text{E1})$$

where k_2 and k_3 are the second-order rate coefficients for reactions R2 and R3, respectively. First proposed by Penning in 1926,¹³ this form of ionization has been utilized in such applications as Penning ionization electron spectroscopy,¹⁴ the argon ionization detector for gas chromatography,¹⁵ and the helium ionization detector.⁹

EXPERIMENTAL SECTION

The experiments described here were carried out using a Hewlett-Packard 5730A gas chromatograph equipped with a CTR III concentric packed column (Alltech) specifically designed for the separation of permanent gases at ambient temperature. A concentric column is one in which a narrow-diameter column is placed through the center of a wider column, allowing the gas stream to be split into two portions onto two different stationary phases. The stationary phases have sufficiently different flow-restricting characteristics to prevent the two portions from coeluting, resulting in two sets of peaks per injection. Since oxygen and argon are difficult to separate at ambient temperatures,⁷ the CTR III uses an oxysorbent stationary phase in the inner column to remove oxygen. In normal analyses, oxygen is quantified by difference. Figure 1 shows a chromatogram resulting from a series of three injections of argon.

The HNU PI-52 photoionization detector was equipped with an argon lamp (11.7 eV) as the ionization source. A new lamp was installed for these experiments. Ultrahigh-purity helium, prepurified argon, and a 1.5% NO/He mixture used for this work were obtained from US Welding (Denver, CO). The helium carrier gas flow rate was controlled by use of a Tylan FC 260 mass flow controller. NO was introduced into the system as a dilute mixture in helium in order to better control its flow rate and ultimate concentration. The NO/He flow rate was controlled with a needle valve and monitored with a Tylan FM 380 mass flowmeter. Calibration standards were prepared by dynamic dilution of argon in helium using Tylan mass flow controllers, and injections were made with a gas injection valve (Valco Instrument Co., Inc.). The entire apparatus was placed inside a fume hood to prevent exposure to the toxic gas NO. Data were collected with a DOS-based computer and analyzed using the Peaksimple Data System for Chromatography (SRI Instruments).

To achieve the best performance, it was observed that the detection system often required a stabilization time of 1 h or more.

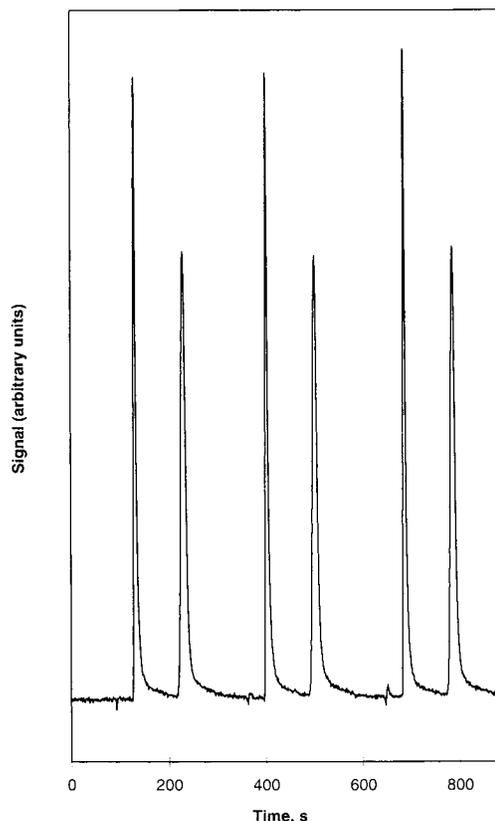


Figure 1. Chromatogram showing three consecutive injections of 9×10^{-9} mol of argon. Sample splitting by the concentric column results in two peaks per injection. NO concentration 323 ppmv; carrier gas flow rate 93 sccm.

Since the response of the detector to argon was either enhanced or reduced NO photoionization, depending on the amount of NO present, optimization of the NO concentration was critical to the performance of the detection system. The optimum NO concentration was determined by making injections of argon while varying the amount of NO added to the detection cell. A plot of Ar peak height vs NO concentration is shown in Figure 2. With no NO present in the detection cell, injections of argon gave no response. As the NO mixing ratio was increased from 142 to ~ 940 ppmv, the height of the chromatographic peak above the background photoionization increased. Above ~ 940 ppmv, the peak height decreased with increasing NO mixing ratio, and NO mixing ratios greater than 0.15% yielded argon peaks that were negative relative to the baseline. The region of NO concentration where the net signal changes from negative to positive is not analytically useful, as neither Penning ionization nor competitive absorbance dominates. Figure 3 shows an actual and a simulated chromatographic peak resulting from an injection of argon in this transition region.

Detection Mechanism. While the observed signal from the PID is a function of processes secondary to the absorption of light (e.g., quantum yield for photoionization and ion collection efficiency), absorption is the primary process leading to the observed ion current. As such, the PID is a type of absorbance detector. Over the linear range of the PID with respect to background NO photoionization, the NO present in the cell is optically thin; i.e., only a small fraction of the available light is being absorbed by NO. Under these conditions, adding argon to

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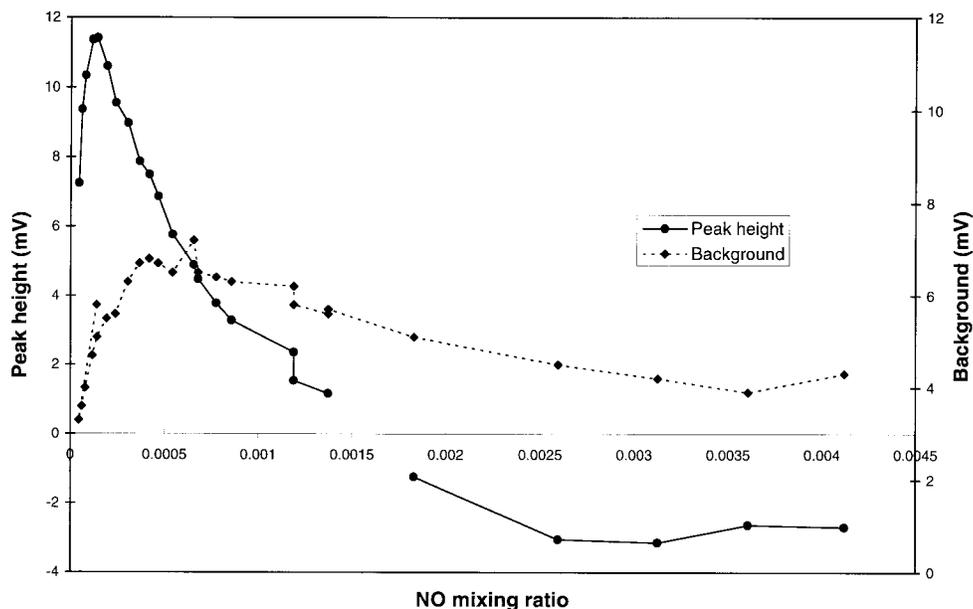


Figure 2. Background signal and peak height relative to background as a function of NO concentration for injections of 1.64×10^{-6} mol of argon.

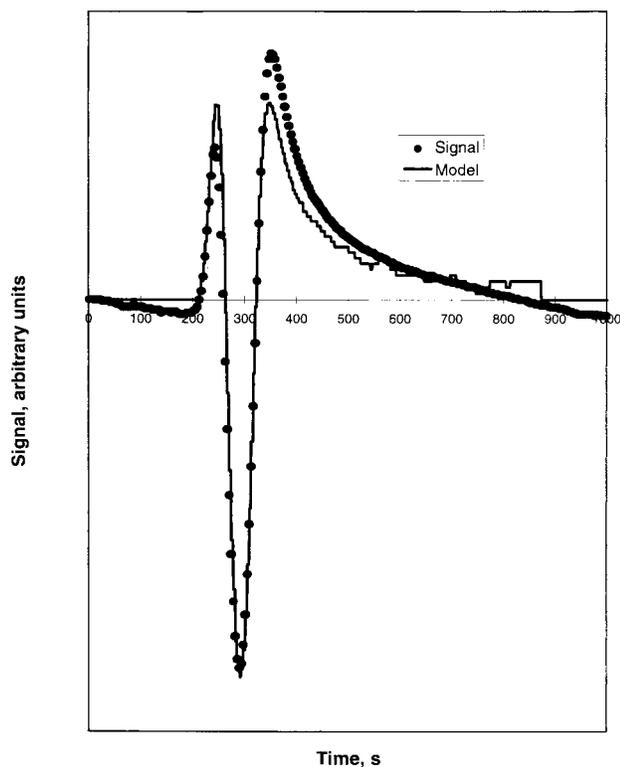


Figure 3. Comparison of the observed detector response to an injection of 9.56×10^{-8} mol of Ar (after correction for column split) for an NO concentration of 3.62×10^{16} molecules cm^{-3} with a simulated response using eq E2. Simulation parameters are $\epsilon_{\text{Ar}}^{\text{I}} = 1.76 \times 10^{-16}$ $\text{cm}^3 \text{ molecule}^{-1}$, $\epsilon_{\text{NO}}^{\text{I}} = 1.11 \times 10^{-18}$ $\text{cm}^3 \text{ molecule}^{-1}$, $\phi_{\text{NO}} = 1.0$, $\phi_{\text{PI}} = 0.02084$, and $l_0 = 2.50 \times 10^8$ arbitrary units.

the detection cell serves to increase the effective photon capture cross section in the cell simply by increasing the number of photon-absorbing molecules. The light captured by argon can ionize additional NO molecules indirectly by the process of Penning ionization, resulting in an increase in ionization above the background.

As with a fluorescence detector, the response to direct NO photoionization becomes nonlinear when the NO present in the detection cell becomes optically thick and most of the available light is absorbed. Under these conditions, the presence of argon will reduce the number of photons directly absorbed by NO, and if the quantum yield for ionization by the Penning process is less than the quantum yield for direct photoionization of NO, the signal will decrease with increasing Ar concentration, as is observed. As a result, under conditions that are optically thin in NO, the detector provides a positive response to Ar due to Penning ionization, but under optically thick conditions, a negative response is obtained.

Based on the Beer–Lambert law, a general equation can be derived to describe the signal (defined here as rate of ion pair formation) relative to the baseline (no Ar) for competitive absorption of light by Ar and NO with both direct photoionization of NO and Penning ionization:

$$S = \frac{I_0 \epsilon_{\text{NO}} C_{\text{NO}} \Phi_{\text{NO}} + I_0 \epsilon_{\text{Ar}} C_{\text{Ar}} \Phi_{\text{PI}} (1 - e^{-(\epsilon_{\text{NO}} C_{\text{NO}} + \epsilon_{\text{Ar}} C_{\text{Ar}})l})}{\epsilon_{\text{NO}} C_{\text{NO}} + \epsilon_{\text{Ar}} C_{\text{Ar}}} - I_0 \Phi_{\text{NO}} (1 - e^{-\epsilon_{\text{NO}} C_{\text{NO}} l}) \quad (\text{E2})$$

where I_0 is the incident lamp intensity, ϵ_{NO} and ϵ_{Ar} are the extinction coefficients for NO and Ar, respectively, C_{NO} and C_{Ar} are the concentrations of NO and Ar respectively, Φ_{NO} is the quantum yield for direct photoionization of NO, Φ_{PI} is the quantum yield for Penning ionization, and l is the effective absorption path length. Under conditions of low NO and Ar concentrations (optically thin), the approximation $(1 - e^{-x}) \approx x$ for small x may be applied to eq E2 to give the result

$$S \approx I_{\text{Ar}} \epsilon_{\text{Ar}} C_{\text{Ar}} \Phi_{\text{PI}} \quad (\text{E3})$$

and the signal is predicted to increase linearly with Ar concentra-

tion. The effect of NO concentration on the signal arises through its effect on the quantum yield for Penning ionization, given in eq E1. The effect is predicted to be a linear dependence of the signal on [NO] for $k_3[M] \gg k_2[NO]$ and to become independent of NO concentration at higher [NO] such that $k_2[NO] \gg k_3[M]$.

For conditions of very high NO concentration (optically thick), $(1 - e^{-x}) \approx 1$, eq E2 simplifies to

$$S \approx I_0 \frac{\epsilon_{Ar} C_{Ar}}{\epsilon_{NO} C_{NO} + \epsilon_{Ar} C_{Ar}} (\Phi_{PI} - \Phi_{NO}) \quad (E4)$$

and for $\epsilon_{NO} C_{NO} \gg \epsilon_{Ar} C_{Ar}$ we have

$$S \approx I_0 \frac{\epsilon_{Ar} C_{Ar}}{\epsilon_{NO} C_{NO}} (\Phi_{PI} - \Phi_{NO}) \quad (E5)$$

Thus, the signal is negative with respect to the baseline if Φ_{NO} is greater than Φ_{PI} and its magnitude increases linearly with Ar concentration when the detector is optically thick with respect to NO. The effect of NO concentration on the signal is again complicated by the effect of NO on the quantum yield for Penning ionization. Increasing NO concentration causes the signal to become negative due to competitive absorption, but the magnitude of this negative peak decreases as the NO concentration increases as a result of an increased quantum yield for Penning ionization with increasing NO concentration (eqs E1 and E5). The effect agrees qualitatively with the results of Figure 2.

Figure 3 compares the simulated response with the experimental result for an injection of 9.56×10^{-8} mol of Ar in the presence of a nitric oxide concentration of 3.62×10^{16} molecules cm^{-3} . To simulate the chromatographic response, the profile of Ar concentration vs time was first determined by measuring the response to an injection of Ar using a low NO concentration where the signal is linear in Ar concentration. The area of the profile was then normalized to the number of moles of Ar injected in order to obtain the absolute Ar concentration profile. This profile served as input to eq E2 to calculate the profiles for other NO concentrations. For the simulation shown in Figure 3, both Penning ionization and competitive absorption contribute significantly to the signal, and the profile shape is sensitive to all parameters of eq E2. The fit given in Figure 3 is not a unique solution but illustrates that eq E2 can describe the peak profile under these conditions. The shape of the simulated profile is highly sensitive to the ratio of quantum yields, ϕ_{PI}/ϕ_{NO} , but not to their absolute values. If the quantum yield for photoionization of NO is assumed to be unity, the quantum yield for Penning ionization is required to be 0.020 84 for the conditions of Figure 3, and the shape of the profile is sensitive to changes in the fourth significant figure of ϕ_{PI} . Small deviations of NO concentration and/or ϕ_{PI} from the conditions of Figure 3 result in either positive or negative peaks. For example, Figure 4 compares the simulated results for NO concentrations of 3.00×10^{16} , 3.62×10^{16} , and 4.00×10^{16} molecules cm^{-3} with all other parameters held the same as in Figure 3. Similar results can be obtained by changing only the quantum yield for Penning ionization or by simultaneously changing both NO concentration and ϕ_{PI} . These results qualitatively confirm the validity of eq E2. Although the shapes of

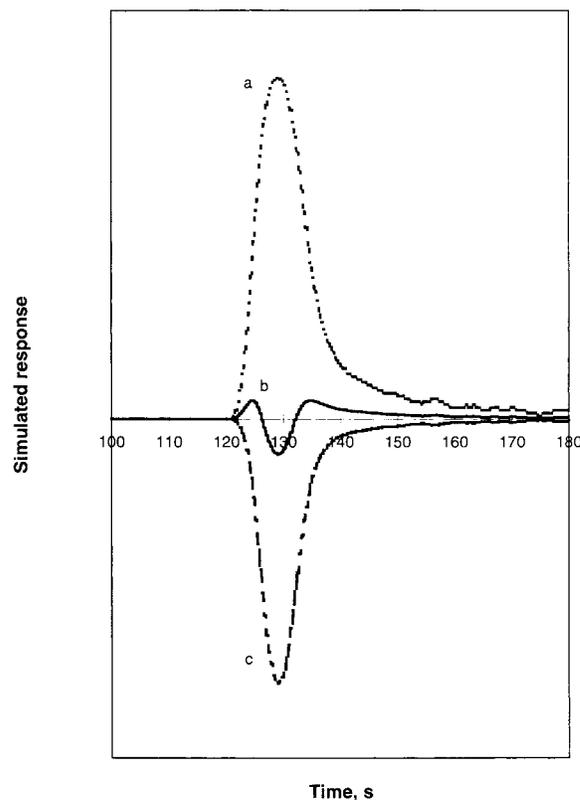


Figure 4. Simulated effect of NO concentration on the response to an injection of 9.56×10^{-8} mol of Ar for NO concentrations of (a) 3.00×10^{16} , (b) 3.62×10^{16} , and (c) 4.00×10^{16} molecules cm^{-3} . Other simulation parameters are the same as for Figure 3. Note that the simulations predict a change from a positive peak (dominated by Penning ionization) to a negative peak (dominated by competitive absorption) over a small change in concentration of NO.

positive, negative, and mixed profiles can be fit quite well with eq E2 using the parameters of Figure 3, a single set of parameters could not be found that quantitatively describes all profiles. Thus, it is likely that there are other factors that contribute to the magnitude of the signal. One such factor appears to be a dependence of the ion collection efficiency on NO and Ar concentrations. Ion loss through recombination of positive ions with electrons is expected to be enhanced at higher NO and Ar concentrations. This may account for the curvature, for example, in the plot of background signal vs NO concentration of Figure 2. Similar curvature occurs in the working curve for Ar at higher concentrations when a fixed, low concentration of NO is used. Also, as the absorbance becomes optically thick, the collection efficiency may change due to formation of ions at different average distances from the collection electrodes. Neither of these factors that affect ion collection efficiency, is accounted for by eq E2.

Other explanations for the enhanced photoionization signal observed in response to argon at low NO concentrations were considered. Senum¹⁰ found that argon is a good choice of carrier gas for chromatographic systems employing a PID in its normal mode of operation, as it provides a 40% increase in response to ionizable compounds relative to the observed response when nitrogen or helium is used as the carrier gas. Senum attributed this effect to enhanced drift velocity, which increases the ion collection efficiency by reducing the extent of recombination of positive ions with electrons. A simple calculation shows that this

effect is several orders of magnitude too small to explain the signal enhancement we observed for Ar at low NO concentrations. The Hornbeck–Molnar reaction put forth by Gawlowski et al.¹⁶ as an explanation of the helium ionization detector response to hydrogen is not likely to be important to the method described in this paper, since a significant source of hydrogen atoms is lacking. Photolysis of water vapor could be a source of H atoms, but the use of dry, ultrahigh-purity gases precludes this effect as a likely explanation for signals produced.

To substantiate that the mechanism of Penning ionization is responsible for the enhanced photoionization of NO in the presence of argon, the experiment was performed using a 10.2-eV lamp, a wavelength not absorbed by Ar atoms. The lack of response by the detector to argon under these conditions supports the mechanisms of detection proposed above, both of which rely on resonant absorption of the radiation by argon.

Calibration and Headspace Analysis. Calibration standards were prepared by dynamic dilution of argon in helium using mass flow controllers. The resulting gas stream was sampled with a gastight syringe, and 50- μ L volumes were injected onto the GC column by overfilling an injection loop. A working curve for detection by Penning ionization over the range of 1.17–3.17 nmol of Ar was highly linear with $r^2 = 1.00$. Ten replicate injections of each standard were measured; the relative standard deviation was 5% of the measured peak height at 2 nmol of Ar. The limit of detection, defined as the number of moles of argon producing a signal equal to 3 times the peak-to-peak noise was determined to be 81 pmol of Ar. Considering the peak width of 5.8 s (1σ), the limit of detection for Penning ionization is 14 pmol of Ar s^{-1} . Thus, a 5- μ L sample of ambient air, which contains 1.94 nmol of Ar, may be analyzed by this method with a signal-to-noise ratio of ~ 70 .

The detection system also responds to oxygen and nitrogen by competitive absorbance, although on a molar basis the response is ~ 2 orders of magnitude greater to argon than to either oxygen or nitrogen because argon has a much higher extinction coefficient for the resonant emission of an Ar lamp. Competitive absorbance detection (NO concentration $\sim 0.4\%$) was used to construct working curves for argon, nitrogen, and oxygen. These working curves were linear with $r^2 = 0.993$ for argon, 0.975 for oxygen, and 0.926 for nitrogen.

Headspace analysis of water equilibrated with helium/argon mixtures containing Ar mixing ratios in the range 0–1.8% was demonstrated using the technique of Penning ionization. Stan-

dards were prepared by submersing a 120-mL screw cap bottle under water inside a solvent bubbler. He/Ar gas mixtures of known composition were bubbled through the water inside the bottle for 30 min. A TFE-lined rubber septum cap (Alltech) was sealed onto the bottle while under water; care was taken to exclude any bubbles remaining in the bottle or trapped under the cap. The bottle was then removed from the bubbler, and a 20-mL headspace was created by simultaneous removal of water and addition of helium using hypodermic syringes. The standard was equilibrated for 15 min by gentle swirling, and aliquots of headspace were transferred to the sample loop of the injection valve with a gastight syringe. The working curve obtained for headspace analysis of water using this method was highly linear with $r^2 = 0.995$. The Ar signal for a headspace injection of a water sample equilibrated with ambient air had a signal-to-noise ratio of ~ 12 and corresponded to a standard equilibrated with gas containing 0.95% Ar.

CONCLUSIONS

Quantification of argon using a nitric oxide-sensitized photoionization detector coupled with gas chromatographic separation has been demonstrated. Nitric oxide is added to the detection system postcolumn and provides a background ion current that is affected by the presence of argon in the detection cell. Argon passing through the detection cell absorbs the resonant emission from an argon lamp. An increase or decrease in the background ion current results, depending on the concentration of nitric oxide used in the system. Low concentrations of NO result in a positive response to argon relative to baseline due to the process of Penning ionization, while high concentrations of NO yield a negative response resulting from competitive absorbance. Both detection mechanisms provide a linear response to argon. The detection system also responds linearly to oxygen and nitrogen by competitive absorbance, although the response to these gases is much weaker than that of argon. The method is applicable to the determination of Ar in air and in natural waters by headspace analysis.

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