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Chemiluminescence Detector Based on Active Nitrogen for Gas Chromatography of Hydrocarbons

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A sensitive detector for hydrocarbons has been demonstrated on the basis of the spectrophotometric determination of the intensity of the $\text{CN}(\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+)$ emission that results from the introduction of the sample into active nitrogen. The most intense spectroscopic feature of the CN flame is the $\Delta\nu = 0$ sequence at 383 to 388 nm. Both saturated and unsaturated samples, with or without halogen constituents, are detectable by monitoring the same feature. A minimum detectable limit of 100 pg has been demonstrated for vinyl fluoride. The introduction of HCl gas into the active nitrogen flow catalyzes the production of CN ultraviolet emission. The sensitivity to simple alkanes is generally improved by the addition of HCl. Methane, for example, was detected in this manner. Spectral evidence indicates the method can be made specific to compounds that contain metal atoms by monitoring atomic lines and CN emission simultaneously. The specificity of the method to other classes of species, such as oxygen-containing compounds, is discussed.

The emergence of capillary bore gas chromatography has created a dual requirement for general detectors of increased sensitivity and for more versatile specific detectors. The most widely used general detector is the flame ionization detector (FID). The advantages of this device are the low detection limit (10 to 100 pg), the large dynamic range (up to 10^7), and a response that is generally proportional to the number of CH_2 groups.

There are, however, certain environments where flammables are in constant use and the open flame of the FID would be hazardous or undesirable. An alternative technique has been developed in which hydrocarbons are mixed with active nitrogen produced by a low-power microwave discharge to excite ultraviolet emission from the CN radical. The resultant chemiluminescence is detected optically, its intensity being directly proportional to the amount of hydrocarbon introduced into the active nitrogen stream. Thus the general, linear response characteristic of FID detection is maintained, yet the flame is eliminated. Coupling this detector to a gas chromatograph is a straightforward procedure. In addition, the active nitrogen breaks apart organic compounds containing metal atoms and causes the metal atoms to fluoresce. Such spectral features could be used to obtain selective chromatograms simultaneously with the universal chromatogram based on CN emission. This development is based on a system previously developed by Sutton and co-workers for metals and gas-phase organometallics, i.e., Metastable Transfer Emission Spectrometry (MTES) (1, 2).

In the following sections, the underlying physical chemistry upon which the technique is based is discussed, the experimental apparatus is described, results obtained in this lab-

oratory with vinyl fluoride and with mixtures of compounds are given, and current conclusions and projections are presented.

BACKGROUND

When hydrocarbons are mixed with active nitrogen, strong chemiluminescence results, primarily from two systems in CN (3). Photon yields as high as 4% have been measured for the $\text{CN}(\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+)$ transition in this flame (4). The most intense feature of this system is the $\Delta\nu = 0$ sequence at 383 to 388 nm (Figure 1). Past experience in this laboratory (4) and the literature reviews (5) indicated that the reaction of active nitrogen with hydrocarbons to produce CN emission is almost universal, suggesting that a simple, sensitive detector for hydrocarbons could be designed on the basis of the quantitative detection of this emission.

EXPERIMENTAL

The experimental setup is shown in Figure 2. A 12-mm o.d. quartz tube makes two right-angles past Wood's horns into a quartz tube of square cross section 30 mm on a side that acts as the viewing region. Nitrogen is metered through a micrometer valve into the 12-mm quartz tube at a rate of 80 to 150 mmol/min (≈ 1.8 –3.4 std L/min). Provision is also made for metering additional gases into the primary flow both before and after the discharge region. A choke valve between the quartz tube and the vacuum pump permits the control of the pressure in the system.

Active nitrogen is produced by enclosing the 12-mm quartz tube in a McCarroll cavity and applying 70 to 90 W from a Raytheon microwave generator. The resulting discharge in the flowing nitrogen creates the characteristic straw colored afterglow downstream.

Just upstream of the viewing region, sample gases are injected perpendicular to the flow through a 0.05-mm i.d. stainless-steel capillary tube. This tube couples the gas chromatographic column, which normally operates at 1 atm, with the flow tube, which normally operates in the 8- to 30-Torr region. The capillary also serves to inject the sample into the mainstream of the active nitrogen flow, ensuring optimal mixing of the sample and the active nitrogen.

Samples can be injected into the flow either in the continuous mode or in a pulsed mode. The former mode is useful for scanning the spectral region for signature spectra and impurity detection; the latter is useful for the gas-chromatographic and sensitivity measurements.

In the continuous mode, the sample is metered directly through the capillary tube. Poiseuille flow is expected to develop. The back pressure on the capillary and the outlet pressure, are monitored. These data enable us to calculate, using well known equations, the flow rate, dn/dt , of molecules through the capillary. A more detailed discussion of these calculations is given in Ref. 6.

The pulsed mode is primarily designed to couple a gas-chromatographic column to the flow system. Samples are injected with a Condyne, Inc., LOV-6-6 multiport valve; a short piece of 1.6-mm i.d. stainless steel tubing serves as the sample reservoir.

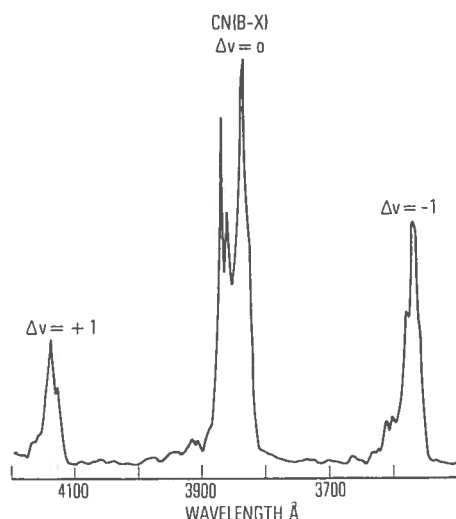


Figure 1. Spectrum of $(\text{CN } B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ chemiluminescence for hydrocarbons added to active nitrogen afterglow

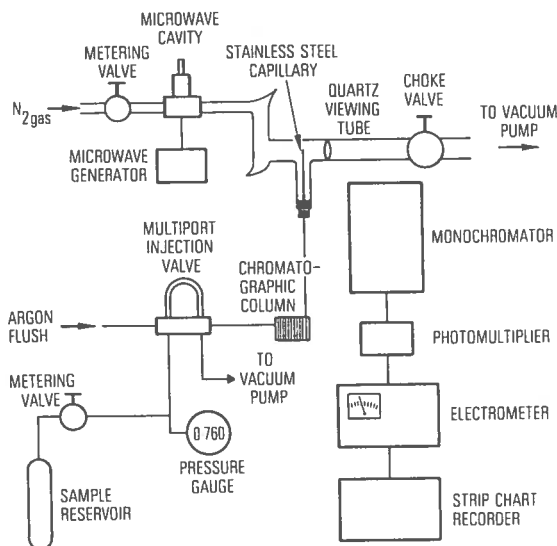


Figure 2. Schematic of active nitrogen detector fitted to a capillary bore gas chromatograph

The WCOT stainless steel column is 30 m long of 0.75-mm i.d., and is coated with SE-30. An argon flow of 1.5 std mL/min is the carrier. (Argon is used instead of helium, because helium quenches active nitrogen.) The column can also be bypassed with a piece of 1.6-mm i.d. stainless steel tubing, thus permitting samples to be tested directly by injecting them into the active nitrogen flow.

Conventional chromatograms are made by observing the time-dependent fluorescence of the B-X system of the CN molecule downstream (5 to 10 cm) as it flows out of the capillary. With relatively large samples (100 ng), a purple glow can be seen simultaneous with the detector signal, a result of the presence of the $\Delta v = -1$ sequence of the B-X band system fluorescing near 420 nm.

The fluorescence is monitored photoelectrically through a Jarrell-Ash 0.5-meter Ebert scanning monochromator with an RCA 1P28 photomultiplier fitted at the exit slit. The phototube is biased with 700 V, which maximizes the signal-to-noise ratio. The photomultiplier signal is sent through a Keithley Model 417 picoammeter and then to a stripchart recorder. Current values ranged from 10^{-10} to 10^{-7} A. The entrance slits of the monochromator were opened from 250 to 400 nm, yielding a maximum spectral slit width of 0.6 nm. The monochromator was tuned to the $\Delta v = 0$ sequence of the B-X system at 383 nm which is the strongest of the CN violet system (Figure 1).

One of the products of the reaction of hydrocarbons with active nitrogen is a polymer containing CN (7). As this product accumulates in the system, background CN emission is increased.

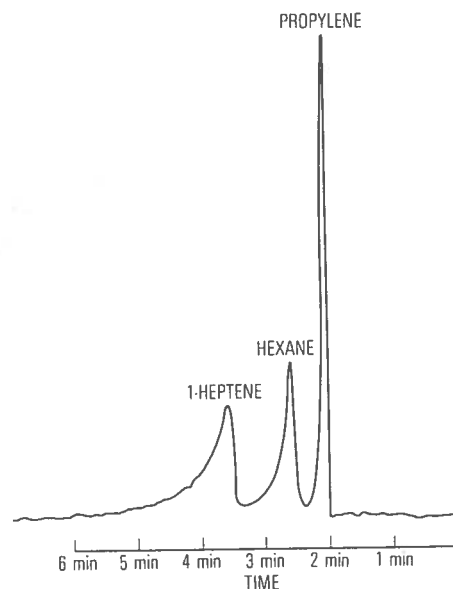


Figure 3. Intensity of $\text{CN}(B-X) \Delta v = 0$ emission feature as function of time (The individual peaks can be correlated with known constituents of the sample.)

This background emission can be eliminated by running pure oxygen through the discharge while heating the quartz tube with heating tape for a few hours.

Since repeated excitation-emission cycles may occur for each molecule, the reduction of the flow speed permits a longer dwell time for a given molecule within the viewing region, as well as reducing the turbulence within the flow tube for a less noisy signal. In addition, since the excitation of the $\text{CN}(B^2\Sigma^+)$ state is collision dependent (3), increasing the system pressure increases the signal intensity by several orders of magnitude. A pressure of 20 to 25 Torr is optimal, as it improves the signal and keeps the background within a reasonable limit.

RESULTS

The spectrum shown in Figure 1 was obtained (with varying intensity) whenever any of the following compounds were introduced into the active nitrogen stream: vinyl fluoride, propylene, 1-pentene, *n*-hexane, 1-heptene, octene, hexafluorobenzene, and 1,3,5-trifluorobenzene. An identical spectrum was obtained for many additional compounds by Capelle and Suchard (4). The remaining results were obtained by monitoring the $\Delta v = 0$ feature at 383 nm as a function of time with a 0.5-m Jarrell-Ash monochromator configured as shown in Figure 2.

The results for a sample containing a mixture of three hydrocarbons in nitrogen are shown in Figure 3. The three peaks correspond to 0.51 μg of propylene, 1.5 μg hexane, and 1.8 μg 1-heptene. They were identified by separately determining the retention time for each compound. Note that the signal-to-noise ratio is excellent and there is little or no base-line drift. The asymmetry observed in the peaks is a characteristic of "homemade" systems. It is caused by the dead volume and the noninert nature of the stainless-steel capillary. With careful construction and the use of a glass lining, the peaks can be sharpened and their symmetry improved.

For quantitative work, a detector with a large dynamic range that provides a simple functional response is highly desirable. Vinyl fluoride was selected as a prototype to determine the performance of the system in these two areas because of its high vapor pressure at room temperature and short retention time in the gas chromatograph. These two properties facilitated the rapid preparation and analysis of the vinyl fluoride-nitrogen mixtures. Vinyl fluoride was also selected since it is anticipated that the system will respond similarly to vinyl chloride. Vinyl chloride is of environmental im-

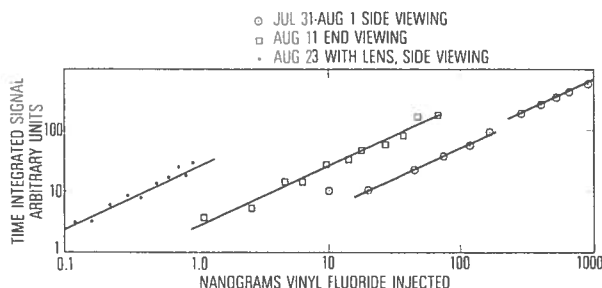


Figure 4. Time-integrated intensity of CN(B-X) $\Delta v = 0$ chemiluminescence as function of nanograms of vinyl fluoride injected into gas chromatograph

portance because of its widespread use in the plastic industry and the reports that long-term exposure results in a high incidence of cancer.

Figure 4 is a plot of the time-integrated emission intensity of the CN(B-X) $\Delta v = 0$ feature as a function of the amount of vinyl fluoride injected into the gas chromatograph. The different sets of data were taken on different days with different optical configurations. However, all the lines through the individual sets were deliberately drawn with unity slope. It is thus concluded that the integrated signal is directly proportional to the amount of the sample injected into the chromatographic column. Figure 4 also demonstrates that the detector has a linear response in sample concentration over four orders of magnitude with no sign of saturation. The current minimum detection limit for vinyl fluoride is 100 pg. We feel this performance, can be markedly improved for several reasons discussed in the following section on Conclusions and Projections.

It has been shown (5) that some simple alkanes, e.g., methane, react slowly with active nitrogen at room temperature, but will react quickly to completion at 250 °C. It has also been demonstrated that the addition of a small quantity of HCl to the active nitrogen results in a "spectacular" increase in the CN B-X emission (8). This increase was also observed in this system. A 1% mixture of HCl in nitrogen is metered in after the discharge, between the two Wood's horns. When the HCl is turned on, the gas flow immediately turns the characteristic lilac color associated with CN emission with an accompanying increase in the background 383-nm CN feature. This effect is most likely caused by the catalytic effect of the HCl on the residual polymerized CN present.

When the time-integrated intensity at 383-nm is plotted vs. the amount of methane injected with 27 $\mu\text{mol}/\text{min}$ of HCl continuously metered in, a line with a unity slope results. The response of the system is linear over three orders of magnitude of CH_4 concentration without saturation. The detection limit is 4 ng. Without added HCl, the detection limit is approximately 200 ng.

Another promising aspect of this technique is the possibility of observing several fluorescence features simultaneously. In this manner, the same apparatus could serve both as a general and a specific detector. For example, the detection of metal alkyls by active-nitrogen-induced fluorescence has previously been demonstrated (6). The spectrum obtained when trimethyl aluminum is injected into active nitrogen is shown in Figure 5. It is obvious from the spectrum that this compound could be selected from a series of eluents by the synchronous detection of the aluminum 396.1-nm line and the CN(B-X) bands. The presence of oxygen in the sample results in NO γ -band emission. This emission has been used to detect air leaks in the system and to identify compounds with oxygen-containing functional groups. Similarly, alcohols have been identified among the eluents by monitoring $\text{OH}(\text{A}^2\Sigma^+ - \text{X}^2\Pi)$ emission. These tests suggest that a detector that can

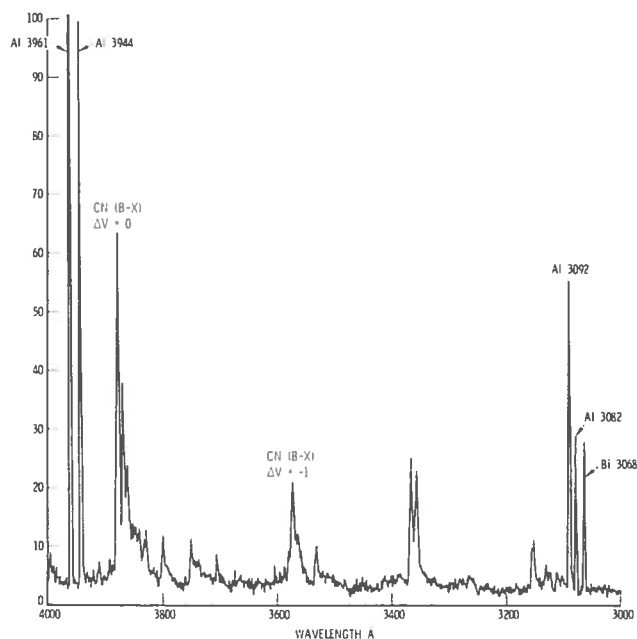


Figure 5. Fluorescence spectrum obtained for trimethyl aluminum mixed with active nitrogen

yield specific structural information along with a conventional chromatogram may eventually be developed.

CONCLUSIONS AND PROJECTIONS

A universal hydrocarbon detector with simple inexpensive components suitable for gas chromatography has been demonstrated that does not use open flames.

For a variety of reasons, this device can be improved to be competitive with or exceed the 10- to 100-pg sensitivity of the FIDs. The monochromator has an F number of 8, with a maximum spectral bandpass of only 0.6 nm. The fwhm of the $\Delta v = 0$ features is approximately 5.0 nm. A simple lens-filter-photomultiplier system might decrease the minimum detectable limits by a factor of 100. Currently, the sensitivity is limited by background fluorescence and dark current. Sharpening the peaks by minimizing the "dead" volume and photon counting could substantially reduce these respective limitations.

The characteristics of our detector can be summarized by comparison with the photoionization detector. Both are nonflame devices capable of general response and large dynamic range. Both have responses that depend on photochemical properties of the sample. However, by monitoring emission features in addition to the CN B-X system the active nitrogen detector offers promise for simultaneous general and specific operation, and the active nitrogen detector is impervious to carrier gas impurities.

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