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## A VACUUM ULTRAVIOLET ATOMIC EMISSION DETECTOR

## QUANTITATIVE AND QUALITATIVE CHROMATOGRAPHIC ANALYSIS OF TYPICAL C, N, AND S CONTAINING COMPOUNDS\*

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## SUMMARY

Vacuum ultraviolet atomic emission detection of effluent gases from a chromatographic column is a very sensitive and selective method for qualitative and quantitative elemental analysis of carbon, nitrogen, and sulfur compounds. A low pressure microwave discharge through helium, with added trace amounts of molecular oxygen, produced complete fragmentation of all compounds used and generated intense atomic emissions in the vacuum ultraviolet. Photometric measurement of these monochromator-isolated atomic emissions was successfully used to establish absolute concentration calibrations for the elements carbon, sulfur and nitrogen in various compounds. This detection method is sensitive, highly selective, and has a range of linearity greater than four decades.

## INTRODUCTION

Atomic and molecular emission detection has been successfully used by a number of groups in gas chromatographic (GC) applications<sup>1-8</sup>. This detection method is highly sensitive and frequently very selective. The technique consists of introducing chromatographic column effluents containing trace quantities of compounds into a discharge excited either by means of microwave power or high voltage d.c. or a.c. Fragmentation of the compound by electron bombardment and by collision processes involving rare gas metastable species produces electronically excited atoms as well as electronically excited diatomic fragments. Emissions from these species, isolated by means of a monochromator, are used to detect the presence of the compound in the effluent rare gas stream. Thus, the emitted spectral wavelength is frequently an indication of the elemental composition of the effluent compound. Various methods of

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producing discharges, the nature of the rare gas, column materials, and pressure conditions have been investigated in order to evaluate the linearity, sensitivity, and selectivity of this detection method<sup>1-8</sup>.

Our interest in vacuum UV atomic emission sources has prompted this investigation of vacuum UV chromatographic detection as a means for performing both qualitative and quantitative elemental analysis. Previous work has been confined to the visible and near-UV region of the spectrum, posing some limitation on the elements that can be measured. Our main goal has been to employ atomic emission measurements to obtain quantitative measurement of total atomic content in the effluent compound. Unfortunately, oxygen and hydrogen analyses were not possible, but many other common elements (*e.g.*: C, N, S, Cl, Br, I, P, etc.) were detectable through measurement of vacuum UV resonance and non-resonance atomic transitions.

In the present work only C, N and S were extensively investigated. These are particularly important elements in air pollutants. Instrumental calibrations (of typical air contaminants) are difficult or impossible for standard mixtures which are unstable or difficult to store, ( $\text{SO}_2$ ,  $\text{NO}_2$ , etc.). Conditions are described below in which essentially complete fragmentation of the compound can be achieved in a rare gas discharge and linearity between emission signal and atom content in the molecule can be realized. It is thus possible to establish concentration calibrations for a particular atom using a stable and easily stored compound. This calibration is then valid for many other compounds containing the same element.

## EXPERIMENTAL

The experimental design is schematically shown in Fig. 1. Experiments were performed in basically two different configurations. Samples were analyzed through their vacuum UV emission spectra either continuously (configuration I) as shown in

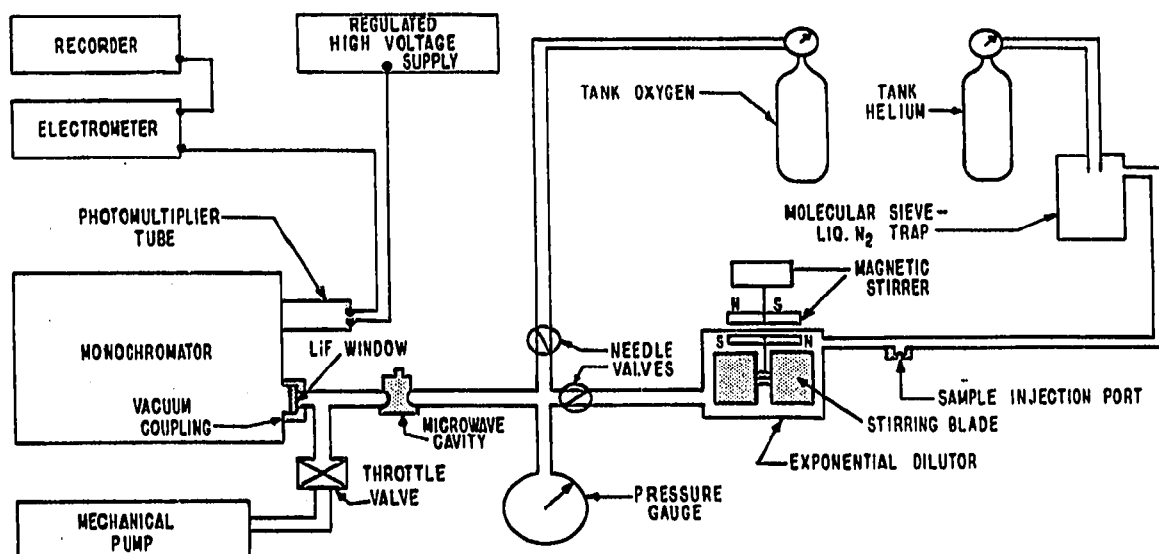


Fig. 1. Schematic drawing of apparatus showing essential components. In this configuration (I) the lamp is connected directly to the outlet of the exponential dilutor. With a chromatographic column replacing the dilution (configuration II) the apparatus is used as a chromatographic detector.

Fig. 1 or by passing them through a chromatographic column (configuration II). In the latter method the LOVELOCK<sup>9</sup> exponential dilutor was replaced by a temperature-controlled chromatographic column, all other components remaining the same. In either configuration a 1 or 5 ml sample diluted with He was injected into the injection port.

The essential components of the apparatus consist of a vacuum monochromator ( $f/10$ ) used to isolate atomic-line wavelength positions below 2000 Å, a liquid N<sub>2</sub>-trapped mechanical pump required to evacuate the discharge (lamp) section, and helium purified to remove trace carbon and nitrogen impurities such as CO, N<sub>2</sub>, CO<sub>2</sub>, by means of a bakeable (2000 cm<sup>3</sup>) trap containing 5 Å molecular sieve cooled to liquid nitrogen temperature. The helium discharge is excited by means of a 2450 MHz microwave (diathermy) unit employing a small, tuneable EVENSON microwave cavity<sup>10</sup>. The chromatographic column or exponential dilutor was operated at 1 atm pressure of He. The inlet to the lamp consists of a variable flow needle valve which can be adjusted so that the pressure in the lamp discharge is about 2 Torr total pressure (1 Torr = 133.32 N·m<sup>-2</sup>). At this pressure a stable discharge through helium can be maintained. The microwave cavity, in this configuration, is about 10 cm from the entrance slit of the monochromator and the discharge in the 10 mm I.D. quartz tube is viewed end-on through a lithium fluoride window.

The pressure in the lamp is measured with a precision-dial Bourdon gauge (0–20 Torr) and the volume flow is monitored by venting the exhaust of the mechanical pump through a soap bubble flowmeter.

The various intense atomic line spectral positions and electronic transitions appearing in the vacuum UV have been previously determined and tabulated<sup>11</sup> under experimental conditions somewhat similar to those employed here. For most of the experiments, the carbon 1930.9 Å (<sup>1</sup>P<sub>1</sub><sup>o</sup> → <sup>1</sup>D<sub>2</sub>) line was used to monitor carbon containing compounds, the 1742.7 Å nitrogen line (<sup>2</sup>P<sub>1</sub> → <sup>2</sup>P<sub>o</sub>) line for nitrogen containing species, and 1826.3 Å sulfur line (<sup>3</sup>S<sub>1</sub><sup>o</sup> → <sup>3</sup>P<sub>o</sub>) for sulfur. The monochromator entrance slit setting was generally 0.05 mm; a LiF-window, CsTe photomultiplier was used to measure the line emission through a 0.05 mm exit slit. The electrometer time constant was about 1 sec. Carbon and nitrogen background signals from the helium carrier gas flowing through the lamp were subtracted out using the electrometer offset circuit. The liquid nitrogen-cooled molecular sieve trap was found to significantly lower carbon and nitrogen background signals, and considerably helped the signal-to-noise ratio. The response of the lamp section to compounds eluting from the GC column was sufficiently fast due to the almost thousand-fold pressure drop between the column and detector that the rather large detector (lamp) volume of 50 cm<sup>3</sup> produced adequate detector response time and resolution.

An additional feature of the detection system shown in Fig. 1 is the oxygen supply inlet. It was found that carbon and sulfur compounds eventually left deposits on the walls of the lamp. This was particularly noticeable for longer-chain hydrocarbon and other oxygen-free compounds. Molecular oxygen was introduced upstream of the discharge at a very low flow rate relative to the helium (O<sub>2</sub> pressure = 10–100 mTorr) but in large concentrations relative to those of the effluent compounds. Oxygen atoms produced in the microwave discharge were found to be very effective in keeping all of the carbon and sulfur in the discharge zone by rapidly removing deposits from the walls.

With the LOVELOCK exponential dilutor in line with the emission lamp the injected sample was diluted at a constant rate with He and the response at a particular spectral position was monitored as a function of a known concentration of sample passing through the lamp section. The dilution was calculated from

$$C = C_0 \cdot e^{-Kt} \quad (1)$$

where  $C$  is the concentration at time  $t$ ;  $C_0$ , the concentration at  $t = 0$ ; and the constant  $K$ , obtained from slope of a semilog plot of  $C$  against  $t$ , is related to the volume of the dilution flask  $V(\text{cm}^3)$ , and the volumetric flow rate,  $\varphi$  ( $\text{cm}^3\text{sec}^{-1}$ ), through

$$K = \varphi/V \quad (2)$$

Both  $V$  and  $\varphi$  can be accurately measured. If the response of the detector is truly linear with the concentration of sample exiting from the dilution flask, then a linear plot of  $\log(s)$  vs.  $t$  is obtained where  $s$  is the photomultiplier current and the value of  $K$  obtained from the slope will agree with the value of  $K$  calculated from eqn. 2.

In configuration II, with the chromatographic column replacing the exponential dilutor of Fig. 1, samples were prepared as follows. A gas syringe of 1 ml volume, filled to atmospheric pressure with a particular compound was injected into the exponential dilutor (external to the detection apparatus) at the He inlet side through a "T" fitting equipped with a rubber septum seal. At set time intervals, 1- or 5-ml samples were extracted from the exit side of the dilutor (vented to the atmosphere) and these were injected into the injection port inlet to the GC column. In this way chromatograms were developed for large variations in sample size, and the absolute concentrations could be estimated from the known (measured) flow rate through the dilutor and the volume of the dilution flask ( $300 \text{ cm}^3$ ). Linearity of the detector in the chromatographic mode of operation could again be verified by plotting  $\log(s)$  vs.  $t$  and comparing the slope with the calculated slope attained from eqn. 2 using the flow rate through the dilution flask. Mixtures of two or more compounds were prepared in sample flasks equipped with a rubber septum at known dilution in helium. These were sampled at atmospheric pressure with a 1 ml syringe and injected into the chromatograph.

Although several column materials were employed, depending on the compounds investigated, the majority of experiments were performed with Porapak-N in a 1/4 in.  $\times$  1 ft. long stainless-steel column. Only experiments with this column are reported below. It should be noted, however, that other column packing materials, e.g., molecular sieve, silica gel, and squalane gave equally satisfactory results. The column temperature was controlled by means of a water bath, the temperature of which was measured by a mercury immersion thermometer. Employing a  $160,000 \text{ cm}^3\text{sec}^{-1}$  mechanical pump, unthrottled, and maintaining about 1-2 Torr pressure in the lamp section of the detector resulted in flow rates of about  $200 \text{ atm cm}^3\text{sec}^{-1}$  through the chromatographic column in configuration II. In configuration I, with the exponential dilutor replacing the column, typical flows averaged about  $100 \text{ atm cm}^3\text{sec}^{-1}$ . In both modes of operation the pressure in the column or the dilutor was slightly over 1 atm.

## RESULTS

*Configuration I: Lovelock dilutor*

Experiments employing the apparatus in configuration I (shown in Fig. 1), were designed to test the linearity of the detector as well as to test the response of the detector as a function of atomic composition of a test compound. A plot of the log of photomultiplier currents against time according to eqn. 1 should yield a straight line

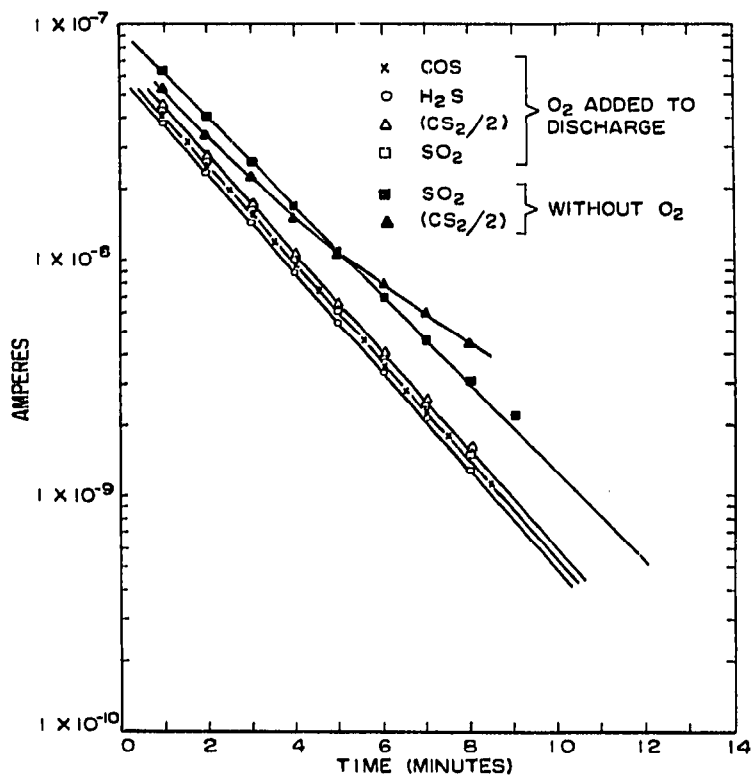


Fig. 2. Detector response  $S$  (A) at the sulfur 1826.3 Å line as a function of dilution time (min). Initial sample size the same for each compound,  $4 \times 10^{-9}$  moles ( $\sim 10^{-4}$  cm<sup>3</sup>atm). Slope calculated from flow rate and dilutor volume,  $0.52 \text{ min}^{-1}$ ; slope measured from lower family of curves,  $0.39 \text{ min}^{-1}$ ; figure shows the effect of oxygen added to discharge (lower curves); absence of oxygen (upper curves) shows non-linear behavior.

plot. Linear behavior on a semilogarithmic plot in itself, however, does not demonstrate detector linearity unless the slope agrees with that obtained through eqn. 2.

Fig. 2 displays detector response using the sulfur 1826.3 Å emission line for various sulfur containing compounds: COS, H<sub>2</sub>S, SO<sub>2</sub>, and CS<sub>2</sub>. The  $K$  values obtained from the slopes agree within experimental error  $\pm 5\%$  with the calculated value (eqn. 2) provided that a supplementary oxygen flow is maintained. In the absence of oxygen, the initial response toward sulfur is somewhat larger. The Schumann-Runge absorption bands of molecular oxygen account for the attenuation in signal when O<sub>2</sub> was added. The slope for sulfur atom response without added oxygen is considerably lower than the value calculated from the volume of the dilution flask and the helium flow rate. Sulfur polymers deposit on the walls of the lamp and are removed very slowly, thus accounting for a delayed response and smaller slope. The

effect is much more pronounced for  $\text{CS}_2$  than for  $\text{SO}_2$ , and distinct curvature can be noted on the semi-logarithmic plot (Fig. 2). A distinct light brown film was observed to develop over long operating times. After operating the lamp without oxygen for some time, addition of oxygen to the discharge was found to cause a rapid removal of the deposit with a sudden development of a very large sulfur atom emission signal. By continuously passing oxygen through the discharge no deposit forms and the response to the sulfur number in the parent compound is linear. The relative response of the signal is approximately the same for  $\text{COS}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $(\text{CS}_2/2)$  as shown by the lower family of curves (Fig. 2). The total spread of these (10%) is in fair agreement with the precision of preparing the standard mixtures and syringe sampling ( $\sim 5\text{--}10\%$ ).

The choice of the emission line may affect linearity between the atomic emission signal and atom concentration. Emission lines from transitions terminating on the ground electronic state of the atom can be strongly reversed due to self-absorption by the ground state atoms in the discharge. In the limit of high concentration the atomic emission signal may be slowly varying or may even be invariant with increasing atom concentration<sup>12</sup>, whereas in the limit of low atom concentration it is always a linearly increasing function. Both oxygen and hydrogen atomic emissions, for example, observed at the 1303 Å and 1216 Å resonance lines, respectively, exhibit essentially negligible response toward oxygen and hydrogen containing compounds added to the discharge. This behavior results from the high background of hydrogen and oxygen atoms in the "pure" helium discharge since it is essentially impossible to remove trace amounts of water from the lamp and connecting tubing.

Fig. 3 demonstrates two distinctly different response characteristics to sulfur

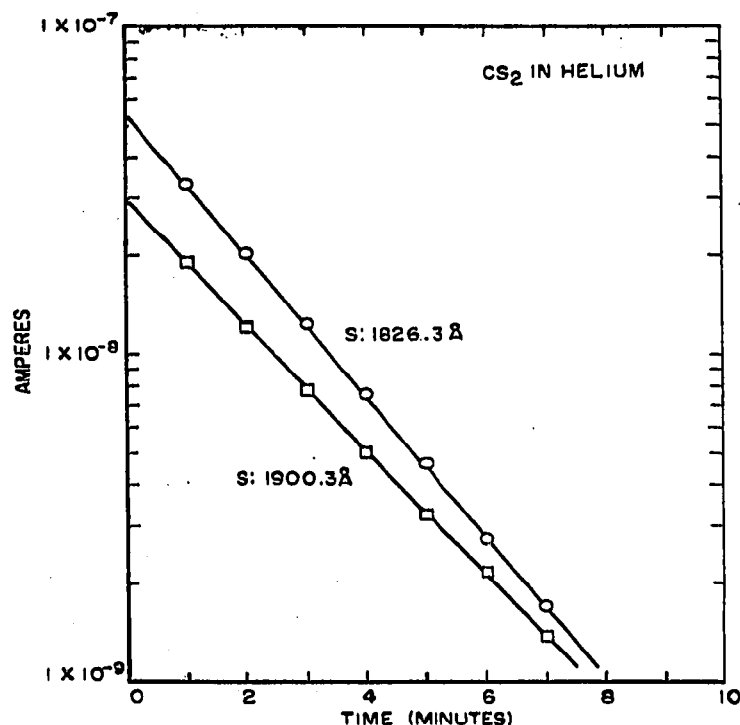


Fig. 3. Effect of line reversal on linearity: detector response at 1826.3 Å ( $J = 0$ ) sulfur line and at the 1900.3 Å ( $J = 2$ ) sulfur line. The upper curve (1826.3 Å) yields a slope which agrees exactly with the calculated slope (from flow rate and dilutor volume) *i.e.* demonstrates linear response.

atoms depending on the choice of the sulfur emission line. The sulfur 1826.3 Å line responds properly, *i.e.*, the slope agrees with the value calculated from eqn. 2. The 1900.3 Å sulfur emission line, however, is apparently not linearly dependent on sulfur atom (or sulfur compound) concentration but depends approximately on the 0.9 power of concentration. Both sulfur emission lines terminate on the ground electronic state of the sulfur atom; however, the 1826.3 Å terminates on the  $J = 0$  state, while the 1900.3 Å line connects to the  $J = 2$  state. The latter is the lower energy level, *i.e.*, the most populated level. If the multiplets are populated according to Boltzmann statistics, at room temperature the relative populations of the  $J = 0, 1, 2$  levels are respectively about 1, 10, 100. Since the Boltzmann distribution is approximately obtained in the discharge, the emission line terminating on the least populated ground electronic state multiplet level ( $J = 0$ ) is considerably less self-reversed than the most populated level ( $J = 2$ ). The slope of the exponential dilution plot for 1900.3 Å (Fig. 3) should slowly change and in the limit of very low concentration approach that of the 1826.3 Å curve.

Complications of this type can be completely avoided if line transitions are chosen which do not connect to the ground electronic state of the atom. While this criterion can be realized for C, S, and N atoms using the respective 1930.9 Å, 1826.3 Å, 1742.7 Å emission lines, the only observable emissions for oxygen (1303 Å) and hydrogen (1216 Å) in the vacuum UV terminate on the ground state and preclude analysis for these atoms in this spectral range. The strong Balmer- $\alpha$  line ( $n = 2$ , 6562 Å) in the visible region of the spectrum, however, has been used successfully to measure hydrogen atom concentrations in hydrogen and deuterium mixtures<sup>13,14</sup>.

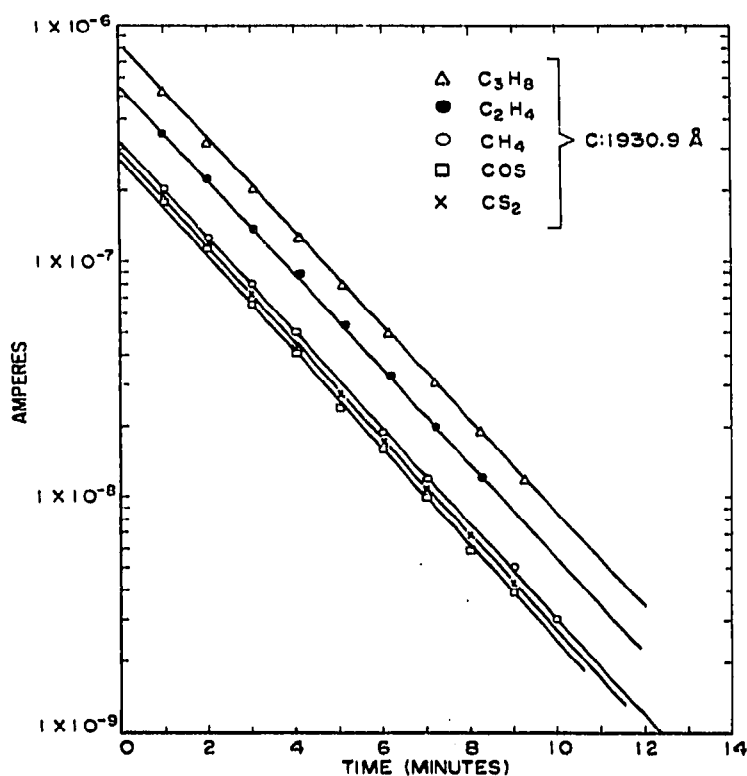


Fig. 4. Configuration I; demonstrates detector linearity and linearity on carbon number in compound. Initial sample size the same for each measurement,  $4 \times 10^{-9}$  moles ( $\sim 10^{-4}$  cm<sup>3</sup>atm).

Fig. 4 demonstrates the detection linearity for various carbon compounds. These curves were developed with an oxygen flow maintained. As found for sulfur compounds, the slopes for carbon compounds agree with the value calculated from the volume flow and the volume of the dilutor. The relative response also appears independent of the carbon containing compound (*e.g.*, COS, CS<sub>2</sub>, CH<sub>4</sub>) but follows closely the number of carbon atoms in the compound, (*e.g.*, equal amounts of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> give responses in the ratios 1:2:3). Deviations from linearity were observed also as in the sulfur case, although the deviations were somewhat less pronounced. Non-linearity in signal *vs.* carbon atom number in the carbon compound was observed in absence of supplementary oxygen flow. Deviations from linearity were severest for the higher molecular weight hydrocarbons.

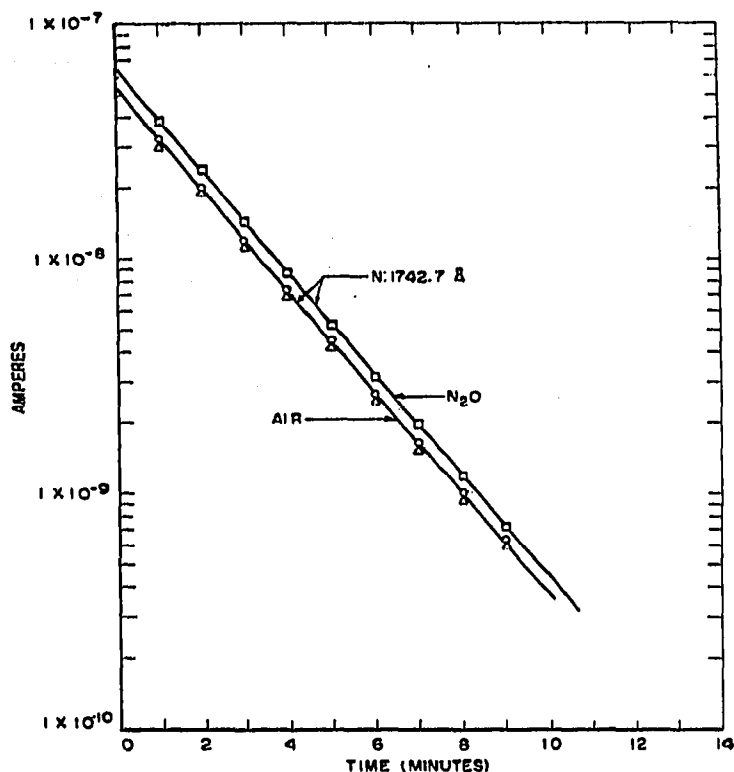


Fig. 5. Configuration I, equal volume samples of air in helium and N<sub>2</sub>O helium. Initial sample size  $4 \times 10^{-9}$  moles ( $10^{-4}$  cm<sup>3</sup>atm). Correcting for oxygen in air demonstrates equal response to nitrogen content for both samples.

Response to nitrogen, using the 1742.7 Å N emission line, is depicted in Fig. 5 for two compounds containing two nitrogen atoms, N<sub>2</sub>O and N<sub>2</sub>. As expected, equal sensitivities were realized as well as linear detector response. Dependence of detector linearity on oxygen flow for these two compounds was not evident.

#### Configuration II: chromatographic column application

Typical chromatograms are shown in Fig. 6. GC traces of a multi-component mixture containing approximately equimolar amounts of H<sub>2</sub>S, COS, N<sub>2</sub>O, cyclopropane (*c*-C<sub>3</sub>H<sub>6</sub>) and in addition containing the impurities air plus CO<sub>2</sub>, are shown with the monochromator peaked on the nitrogen, sulfur, and carbon emission lines. At a



constant amplification throughout, the various traces show that there is no apparent response toward sulfur and carbon compounds at the nitrogen emission line. Further amplification by two orders of magnitude reveals a response toward both carbon and sulfur compounds about  $10^{-3}$  times less than the photometric response toward nitrogen. Similarly, response toward carbon, *e.g.*  $c\text{-C}_3\text{H}_6$ , at the sulfur position is between  $5 \times 10^{-2}$  and  $1 \times 10^{-3}$  times the response toward sulfur, *e.g.*,  $\text{H}_2\text{S}$  or  $\text{COS}$ . Selectivity is here defined in the usual way, *i.e.*, the relative response to  $\text{H}_2\text{S}$  at the

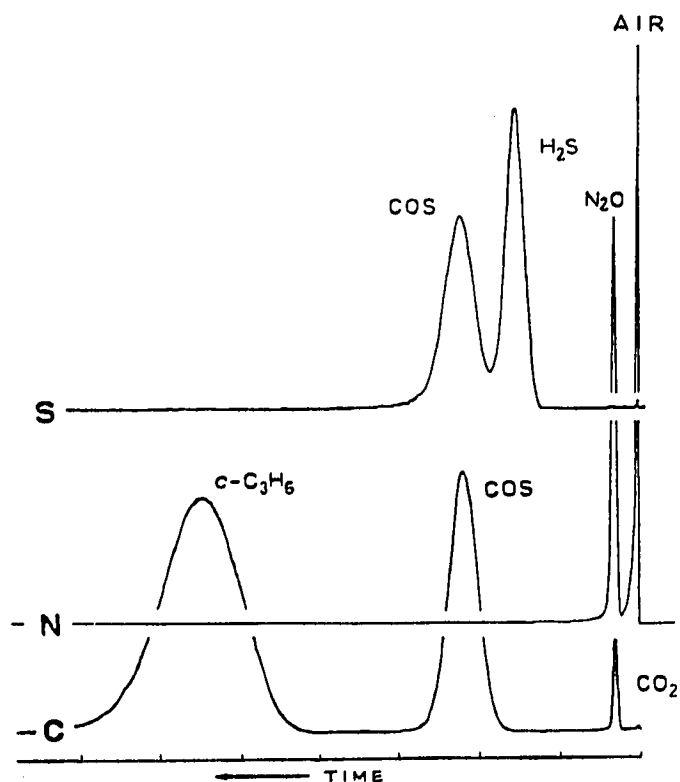


Fig. 6. Configuration II, equimolar mixtures of  $\text{COS}$ ,  $\text{H}_2\text{S}$ ,  $\text{N}_2\text{O}$ , and cyclopropane:  $2 \times 10^{-7}$  moles ( $\sim 5 \times 10^{-3} \text{ cm}^3/\text{atm}$ ) containing trace air and  $\text{CO}_2$  impurities. Detector response at the sulfur  $1826.3 \text{ \AA}$  (top), nitrogen  $1742.7 \text{ \AA}$  (middle) and carbon  $1930.9 \text{ \AA}$  (bottom) atomic line positions.

sulfur emission line position compared to the response at the sulfur position to a compound containing only carbon, *e.g.*,  $c\text{-C}_3\text{H}_6$ . Molecular emissions of  $\text{CO}$ ,  $\text{NO}$ , and  $\text{O}_2$ , are minimal in this wavelength range and do not coincide with the atomic wavelength positions so that the selectivity, to a good approximation is limited by light scattering in the monochromator. Selectivity values of about  $10^3$  to  $10^4$  are expected from the stray radiation properties of the monochromator.

Selectivity values lower than  $10^3$  are sometimes observed which depend on the sample size, column, the composition of the gas mixture, and the oxygen flow rate. While oxygen removes essentially all of the sulfur and carbon passing through the lamp a displacement effect is sometimes noticeable for multi-component samples. For example, a carbon-containing compound passing through the lamp can liberate trace quantities of sulfur from the walls due to a sulfur compound which has just previously eluted from the column and formed deposits. This can result in selectivity

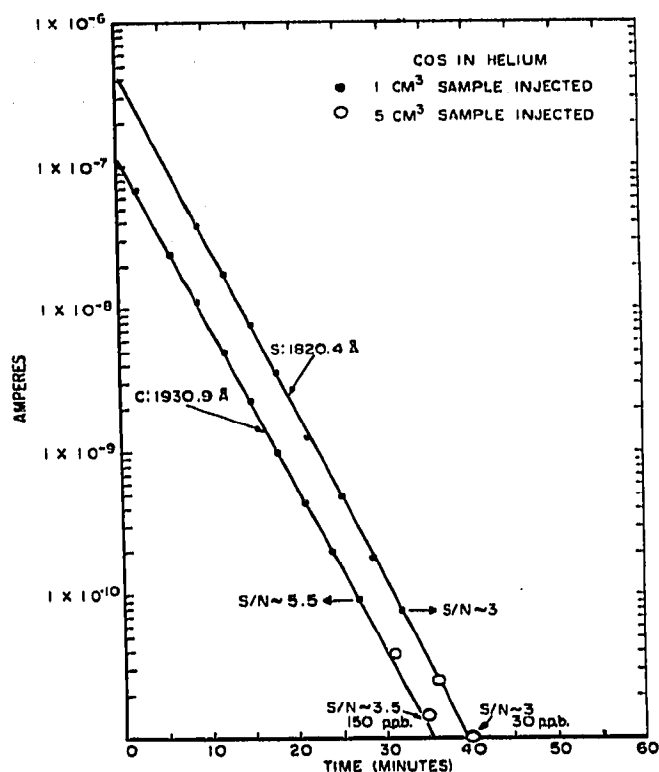


Fig. 7. Sulfur and carbon response from COS using exponential dilutor plus column. Semilog plot of peak height (A) vs. time. Column Porapak-N,  $\frac{1}{4}$  in.  $\times$  1 ft., 25°, helium carrier. Carbon atomic emission at 1930.9 Å; sulfur atomic emission at 1820.4 Å 0.05 mm slits. Photomultiplier dynode voltages 2.5 kV and 3.0 kV for C and S respectively. Helium flow rate in exponential dilution flask = 90 cm<sup>3</sup>/min, volume = 300 cm<sup>3</sup>. Initial injection 0.5 ml COS into mixing flask.

values as low as 200. In general, selectivities observed here are in the 10<sup>3</sup> range or better, when an oxygen flow is maintained.

Fig. 7 demonstrates linearity of the column plus detection system. Samples of COS taken as a function of time from the exponential dilutor were injected into the chromatograph injection port and the peak heights, measured in amperes, were plotted on semilog paper. Both carbon and sulfur atomic emissions were monitored. This test of linearity examines not only the detector linearity but also the sampling from the dilutor plus column. Once again,  $K$  obtained from the slope agrees within several percent of the value calculated from eqn. 2 using the flow rate through the dilutor and the dilutor volume. The range of linearity appears to be at least four orders of magnitude, ranging from large sample sizes 10 Torr cm<sup>3</sup> to sample sizes less than 10<sup>-3</sup> Torr cm<sup>3</sup>.

The detection limit of the present apparatus, sampling at the lowest concentration limit with a 5 ml injection syringe, is about 100 p.p.b. for carbon and about 30 p.p.b. for sulfur. The limit, for this instrument, is arbitrarily fixed as a measurement which can be made at a signal to noise ratio of about 3:1. Sulfur determinations are somewhat more sensitive than carbon because of a lower background level for sulfur than for carbon with only "pure" helium flowing through the lamp.

A number of parameters affect the ultimate sensitivity; these were only qualitatively investigated. They include the distance of the discharge to the monochromator slit, the slit width, the tuning of the microwave cavity (which affects back-

ground noise of fluctuations), the pressure in the discharge, and the microwave power level. The best discharge can be maintained in the lamp at a pressure of about 1 to 5 Torr. At higher pressures in the lamp a higher concentration of eluting compound can be achieved with a potential increase expected in signal. In fact at low pressures in the discharge the detector signal increases linearly with increasing pressure. However, the emission signal becomes insensitive to increasing pressure at pressures greater than about 10 Torr where the microwave coupling is impaired.

Most experiments were performed with 0.05 mm slits. However, as expected, the absolute signal intensity increased with increasing slit width and a somewhat improved signal to noise ratio could be obtained at the larger slit settings. Little dependence of signal on microwave power level settings was observed. An increase in power level of about a factor of two produced an increase in signal by less than 20%. Therefore very constant sensitivity ( $\pm 5\%$ ) was obtained for various sample sizes for many hours and even days at a fixed microwave power setting.

The microwave power level had little effect on the relative sensitivity *vs.* number of atoms in the compounds with oxygen flow maintained. In the absence of oxygen flow, however, higher molecular weight compounds containing more than one particular atom, as previously noted, produced less than a linear response with increasing atom content. Higher microwave power levels tended to improve linearity undoubtedly due to greater fragmentation and less polymer formation on the discharge tube walls. To ensure complete fragmentation of effluent compounds the helium flow direction was maintained from the back toward the front of the lamp *i.e.* toward the direction of the monochromator slit.

As previously noted, the percentage of oxygen introduced in the lamp is not critical. For very small sample sizes the polymer build-up problem is less severe and very little oxygen flow is required to achieve precise linearity between signal and atomic concentration. At higher concentrations, oxygen pressures as high as 50 mTorr are required to maintain linearity. In the absence of oxygen, with large sample size, large satellite peaks were frequently observed for carbon and sulfur containing compounds. These satellite peaks came immediately following the compound peak position. The satellite resulted from carbon and sulfur slowly eroding from the walls of the discharge tube after compounds had eluted from the column. Addition of oxygen produced larger initial peaks and completely eliminated the satellite peaks.

The precision obtainable with this detection system can be roughly assessed from the various figures. Fig. 5, for example, displays two separate determinations of an air sample with several hours between separate injections. The long term reproducibility is well within the precision of syringe sampling and presumably with a more precise sample injection technique the detection system reproducibility should at least match deviations of individual points from the straight line dilution curves ( $\sim 2-5\%$ ).

## DISCUSSION

The first systematic investigations of UV-visible atomic emission chromatographic detection were reported by BACHE AND LISK<sup>4-7</sup>. Selective analysis of drugs and pesticide residues was demonstrated by using the most intense phosphorous, sulfur, chlorine, bromine, and iodine lines in the UV-visible spectrum. In addition to achieving sensitive and highly selective qualitative detection, they were also able to

attain a fair degree of linearity of detector response for different organic compounds containing various amounts of a given element and different types of chemical bonds. This was achieved by analyzing very small concentrations of sample and by employing high power densities in a capillary discharge lamp. Reasonably intense atomic emissions were achieved through the use of helium carrier gas. Earlier experiments by these workers with argon carrier gas resulted in intense molecular and somewhat weaker atomic emissions.

Here we have extended their work to detection in the vacuum UV region and demonstrated nitrogen and carbon analysis. We have been concerned primarily with precise chromatographic detection of simple gaseous systems useful in physical-chemical, photochemical, and air pollution applications. The range of linearity of the detection systems and linearity with atom number found in the present work suggests a potential use rivaling the flame ionization detector. The detection sensitivity utilizing atomic vacuum UV emissions compares favorably with flame-ionization detection.

Detection limits obtained by BACHE AND LISK<sup>4-7</sup>, using visible and near UV atomic emission lines are somewhat smaller than those found in this work. Selectivity, however, appears to be better in the vacuum UV than in the visible, limited principally by light scattering in the spectrometer. No attempt has been made to achieve maximum sensitivity. Molecular fragment detection (as opposed to atomic detection) obtainable under higher pressure conditions by other workers appears to be as much as several orders of magnitude more sensitive than atomic emission detection. However, molecular emission detection is frequently not linear and requires separate calibration for each compound. Sensitivity varies markedly with the type of fragment emission measured and frequently requires the presence of impurities in the discharge (*e.g.* nitrogen, to obtain CN emission from hydrocarbons). For quantitative purposes, therefore, atomic emission appears to be potentially more useful in spite of the lower limits of detection possible by other means.

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