

A STUDY ON THE USE OF ICP-OES FOR THE DETERMINATION OF
NONMETALS IN ORGANIC SOLUTION

by

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ABSTRACT

The application of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) to the determination of total oxygen, nitrogen and sulphur in organic solution has been studied. Near-infrared emission lines of the three nonmetals have been used and detection limits in xylene have been established. Oxygen was determined for the first time by ICP-OES in a non-gaseous sample.

The characteristics of the inductively coupled plasma when used with an organic aerosol have been studied with respect to the completeness of atomization and potential interference from the complex excitation environment. Spatially resolved atomic and molecular emission profiles have been collected as part of these investigations.

The nonmetal emission intensities were found to depend on the boiling point of the compounds containing the nonmetal because a redistribution effect in the nebulizer chamber was leading to an enrichment of volatile solutes in the aerosol stream to the plasma. Response factors for a series of compounds have been determined.

The utility of the method was shown by establishing working curves and by testing certified standards for sulphur.

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CHAPTER I

INTRODUCTION

1.1 OBJECTIVE

The inductively coupled plasma (ICP) has become very popular as an excitation source in analytical atomic spectroscopy. It is widely used for the analysis of geological, industrial, biological and environmental samples. The vast majority of these applications involve aqueous solutions of metals. In principle, inductively coupled plasma optical emission spectroscopy (ICP-OES) could also be a simple and rapid method for the determination of nonmetals in organic solutions. However, the development of this application has been slow because of problems encountered with the introduction of organic solvents and the lack of strong emission lines for some nonmetals (in particular for the important elements oxygen, nitrogen and sulphur) in the usual analytical region (200–700 nm) of the spectrum.

The problems associated with organic solvent introduction have been diverse. Soot deposits on the plasma torch and instabilities of the plasma itself have been encountered. The observation of molecular emission has brought the degree of atomization into question and

nebulizers have not been well characterized for organic solvents.

Most nonmetals of groups V, VI and VII have their sensitive resonant emission lines in the vacuum-ultraviolet region (100 - 200 nm). The detection of wavelengths below about 200 nm requires evacuation (hence vacuum-ultraviolet) or purging of the optical path (including the monochromator) to eliminate absorption by atmospheric oxygen. Also, light absorption by quartz becomes appreciable below 200 nm. Most analytical ICP-spectrometers can operate successfully down to about 180 nm when purged, so sulphur, which has strong resonant lines at 180 nm, and possibly nitrogen with lines at 170 nm can be determined on an instrument which can be evacuated or purged. For the measurement of the resonant lines of oxygen (130 nm) appropriately blazed gratings and special detectors are necessary.

Recently, a torch for stable use with organic solvents has been developed and the different aspects of organic aerosol production and introduction into the plasma have been described fairly well. Also, ICP emission lines of the nonmetals have been reported in the far red to near-infrared region (700 - 950 nm) and applications with gaseous sample introduction have been described. This spectral region is not normally used for analytical atomic spectroscopy but is easily accessible for conventional spectrometers.

This thesis presents an investigation into the feasibility of determining nonmetals in organic liquids with an ICP-optical emission spectrometer employing those near infrared emission lines. The test matrix consisted of solutions of organic compounds containing O, N or S in xylene. The method has potential utility in the petroleum industry, where monitoring of sulphur and nitrogen is crucial in the refining process, because these elements act as catalyst poisoners. Another potential application is liquid-chromatography, where element selective detection with ICP-OES had gained much attention recently, but has not included these three nonmetals.

1.2 THE INDUCTIVELY COUPLED PLASMA

The first use of an ICP as an excitation source for atomic spectroscopy was reported independently by Greenfield [1] and Fassel [2] 20 years ago. Since then it has become very popular because of its good detection limits, high precision, accuracy and versatility compared to older spectroscopic methods like dc arc- and spark-emission, atomic absorption and x-ray-fluorescence. Other plasma sources have been developed, the direct-current plasma, the microwave-induced plasma (MIP) and the capacitively-coupled plasma (CMP), but the ICP has been most exploited.

The basic components of an ICP-optical emission spectrometer are shown in Figure 1. The radio frequency generator supplies the energy necessary to sustain the plasma. The plasma itself is located in the plasma box, which also contains the units for input power matching and control of gas flow rates. Samples are usually introduced as aerosols which are produced in either concentric or cross-flow pneumatic nebulizers. The spectrometer normally is based on a grating and readout is usually achieved with a photomultiplier tube (PMT). Scanning monochromators contain one exit slit - PMT combination, so that only one element can be determined at a time. Adaption to the determination of a different element is easily achieved by rotating the grating to read a different wavelength. Direct readers contain a number of PMTs, each reading one fixed line. The number of PMTs corresponds with the number of elements which can be determined simultaneously. Its flexibility is limited, because the PMTs have to be repositioned each time the determination of a new set of elements is required. Photodiode arrays as detectors can be used to observe a small spectral window. This allows, in favourable cases, the simultaneous determination of a few elements while retaining the flexibility of a scanning monochromator. Also, because a spectral window not just the intensity of the analytical line is measured, changes in continuum background

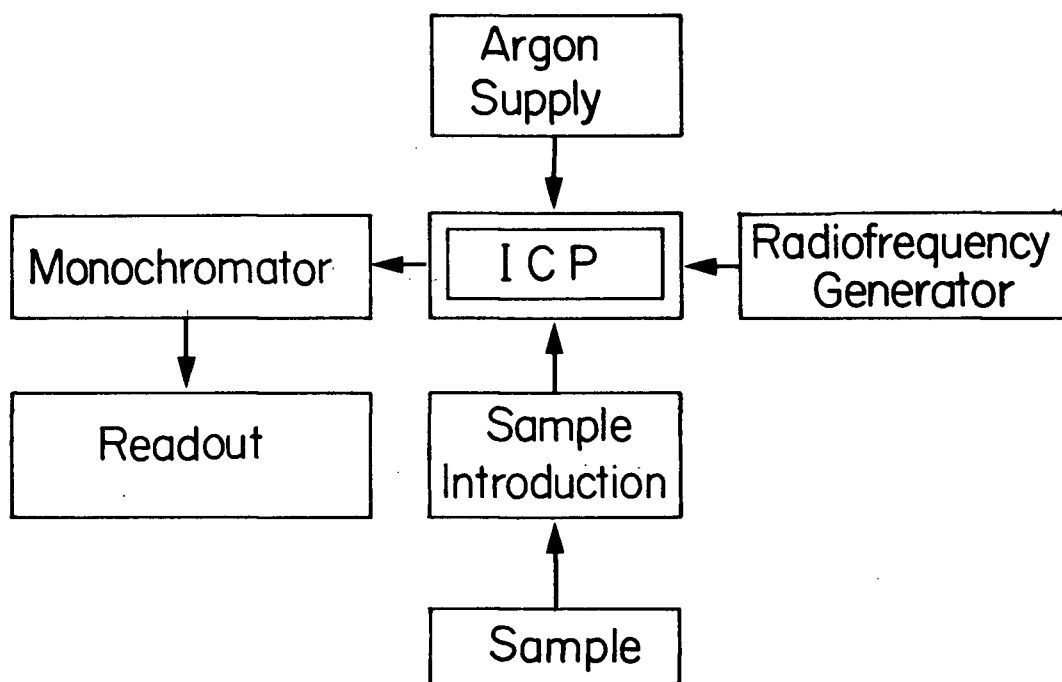


Figure 1. Block Diagram of an ICP spectrometer.

intensity can be easily recognized and corrections made. However, these detectors have not yet found commercial application in atomic spectroscopy.

A diagram of the ICP itself is given in Figure 2. The two essential parts, torch and load coil, are included in the picture. The torch is made from three concentric quartz tubes: the outer, the intermediate and the nebulizer tube. Accordingly three gas flows are employed: plasma, auxiliary and nebulizer gas flow. The plasma gas flow is the main gas flow, and a toroidal shaped plasma is formed at the load coil by induction of energy from the radio frequency current. The auxiliary gas flow serves to lift the plasma off the intermediate tube to prevent melting of the torch and is not always required. The sample aerosol is introduced axially through the nebulizer tube into the central (or aerosol) channel. Energy from the toroidal region is transferred into the central channel by diffusion and the sample is atomized, excited and ionized as it travels through the plasma. The strongest analyte emission intensity is normally observed at 10 to 20 mm above the load coil and originates from ionic and atomic species. The terms, energy addition zone, initial radiation zone and normal analytical zone were coined by Koirtzmann et al. [3] and are generally accepted. Two versions of the ICP are in use. The low power argon-ICP uses a relatively small torch and low flow rates

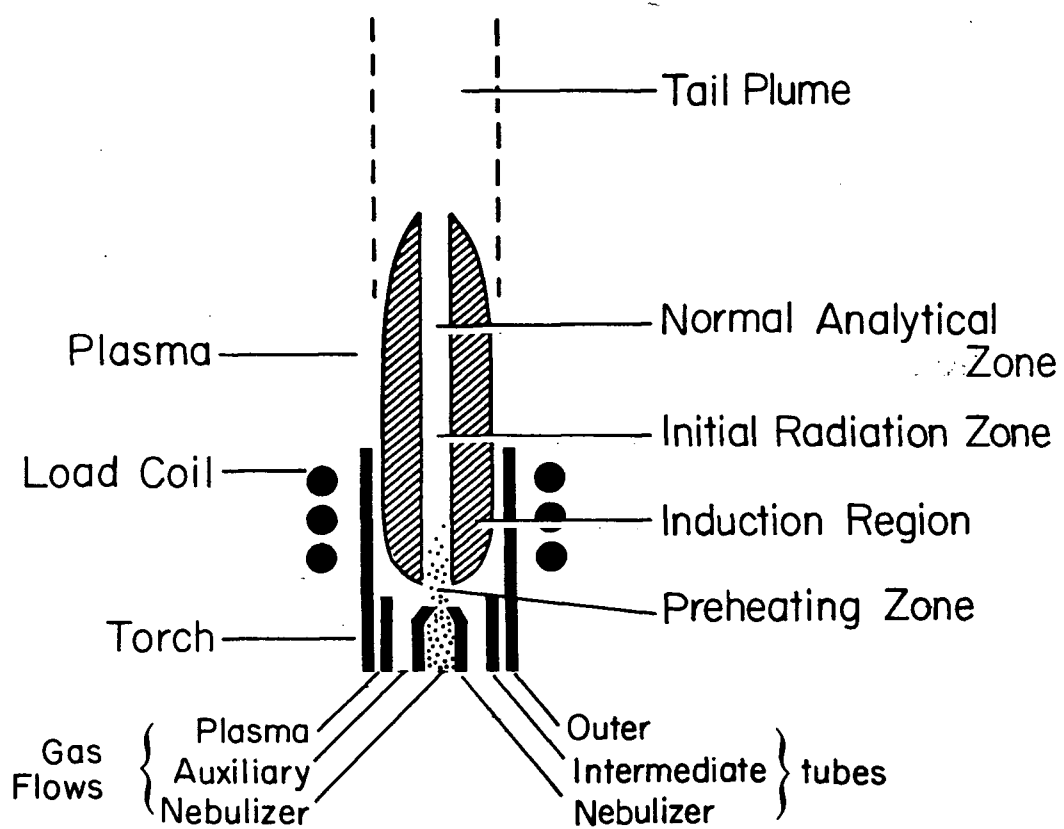


Figure 2. The Inductively Coupled Plasma.

of argon. Radio frequencies between 27 and 50 MHz are used and the rf input power is between 0.5 and 2.5 kW. High power nitrogen/argon-ICPs use larger torches and flow rates and the plasma gas flow consists of nitrogen. Frequencies are between 4 and 27 MHz and power input between 4 and 7 kW. The two types of ICPs show quite different characteristics. The work reported herein was done with a low power Ar-ICP and the references to publications made are concerned with this type of the ICP except where specifically stated otherwise. Inductively coupled plasma spectroscopy and its applications have been reviewed repeatedly [4-10].

1.3 APPLICATIONS TO ORGANIC SAMPLES AND NONMETALS

The first report on the use of ICP-OES for an organic matrix appeared in 1968 [11]. Detection limits for Al, Fe and Ni in oil were given. Greenfield and Smith presented working curves for a few metals in engine oil diluted with xylene in 1972 [12] and in 1976 Fassel et al. [13] presented a more thorough investigation into the determination of wear metals in lubricating oils with an ICP. The determination of trace metals in a variety of petroleum products has subsequently been reported [14,15]. The use of an ICP-OES as an element selective detector in liquid chromatography when using an organic mobile phase was first reported by Gast et

al. in 1979 [16] and later by Hausler and Taylor in 1981 [17,18]. In these studies organometallic compounds were used and emission from metals only (exception silicon) was detected.

Several of the easily accessible nonmetals have been determined in aqueous solutions, and Windsor and Denton have demonstrated elemental analysis of volatile organic compounds introduced as vapours by ICP-OES [19]. They used wavelengths between 190 and 660 nm and measured the elements B, C, H, I, P, S and Si. The important elements oxygen and nitrogen could not be determined, because no strong lines are available in this wavelength region. Heine, Babis and Denton proceeded to examine the spectral region between 120 and 185 nm [20]. A vacuum spectrometer was used and the optical path from the plasma to the spectrometer purged with helium to avoid absorption by molecular oxygen. Strong emission lines for O, N and also C, Br, S and Cl were found [20]. Fry and coworkers in a series of nine papers [21-29] surveyed the far red to near-infrared region (700 - 950 nm) and sensitive lines for N, O, F, Cl, Br, S, C and H were found. They used these lines for element selective detection of oxygen and nitrogen in gas-chromatographic effluents [24,25].

Element selective detection or even elemental analysis of GC-effluents using atomic emission spectroscopy has

received much attention, because such data increases the specificity of the method. However, microwave induced-plasmas have proven to be more useful than ICPs because their lower inert gas consumption matches the gas flow rate of the GC better and helium MIPs possess higher temperatures than the Ar-ICP. Element selective detection for chromatography by plasma emission spectroscopy has been reviewed by J.W. Carnahan et al. [30].

Few references to the determination of nonmetals in organic solvents have appeared in the literature. Of the three elements oxygen, nitrogen and sulphur, only the two latter ones have been determined in organic solvents. Wallace [31,32] determined sulphur in NBS (National Bureau of Standards) oil samples which were diluted with xylene or methyl isobutyl ketone (MIBK). Three lines around 180 nm were tested on a purged instrument. Wallace [32] reported a detection limit of 0.05 mg/l for sulphur. Hausler determined nitrogen in xylene using the 174.3 nm line on a purged instrument. The detection limit was reported to range from 5 to 100 ppm [33]. Both elements, sulphur and nitrogen have also been determined successfully in aqueous solutions using vacuum-ultraviolet lines [34,35].

1.4 FUNDAMENTALS OF ORGANIC SAMPLE INTRODUCTION

If ICP-OES is to be successful for the determination of nonmetals in organics, the measured emission intensity has to be a simple function of the concentration of the analyte in the sample. However, interference effects exerted on an organic sample as it passes through a nebulizer-ICP system are potentially more severe than in the usual case of aqueous solutions. The critical aspects of aerosol production, the torch, the plasma, and the spectrum, are listed in Table I and will be discussed below in the light of the current literature.

TABLE I

Organic Sample Introduction

<u>Step in Analysis</u>	<u>Critical Aspect</u>
Aerosol Production	Sample Delivery Rate Nebulizer Efficiency
Torch	Soot Deposition
Plasma	Vapour-Effect Plasma Temperature Incomplete Atomization Entrainment of Air
Spectrum	Spectral Overlap with Molecular Band Emission

1.4.1 AEROSOL PRODUCTION

The two nebulizer types frequently used are the concentric (or Meinhard) and the cross-flow nebulizer. Both work on the same principle. A flow of liquid is shattered by a high velocity stream of gas to produce droplets with a more or less well defined size distribution. Nebulizer chambers are designed to remove droplets larger than a certain cutoff-diameter to avoid loading effects in the plasma and incomplete desolvation. A large part of the sample entering the nebulizer is therefore lost for the analysis and leaves the spray chamber through the drain. The fraction of the originally nebulized sample which reaches the plasma, defines the nebulizer efficiency.

SAMPLE DELIVERY RATE:

Sample transport to the nebulizer is usually assured by the VENTURI effect and governed by the POISEUILLE equation. The delivery or aspiration rate Q is defined by the viscosity of the solvent η , the length of the capillary L of radius R and the driving pressure P :

$$Q = \frac{\pi R^4 P}{8\eta L}$$

Of these variables the viscosity and possibly the

pressure difference are sample dependent and therefore delivery rates and emission intensities vary. Also, the pressure difference depends on the nebulizer gas flow rate. To make free aspiration possible and assure constant delivery rates, viscous oil samples are diluted with an appropriate solvent (see e.g. [13]). The limitations set by the POISEUILLE equation can also be overcome by using a pump to control the flow of sample to the nebulizer (force-fed as opposed to free aspiration) (see e.g. [36,32]).

NEBULIZER EFFICIENCY:

The droplet size distribution is an important parameter to be considered, since the finer the aerosol is, the higher the nebulizer efficiency and the emission intensity will be. No exact theoretical model is available to predict droplet size distribution, but an empirical formula, the NUKIYAMA-TANASAWA equation, originally designed to describe carburetor operation is usually quoted. Its validity for concentric nebulizers used in atomic spectroscopy has recently been thoroughly examined by Gustavsson [37,38].

$$d_o = 585 \frac{\sqrt{\sigma}}{v\sqrt{\rho}} + 597 \left(\frac{\mu}{\sqrt{\sigma\rho}} \right)^{0.45} \left(\frac{1000Q_l}{Q_g} \right)^{1.5}$$

d_o = mean droplet diameter (m), v = velocity of gas (m/s)
 σ = surface tension (dyne/cm), μ = viscosity (poise)
 ρ = density of the liquid (g/ml)
 Q_l = volume flow liquid, Q_g = volume flow gas

σ , ρ and μ are liquid properties and therefore the size distribution varies as different samples are used for a given nebulizer.

Moreover, evaporation of solvent from the droplets serves to change the original size distribution. Cresser and Browner have presented an equation to predict evaporation from droplets [39], and Boorn et al. have published theoretical data on a series of solvents based on that equation [40]. Obviously spray chamber temperature will have an effect on evaporation, and heating during an analysis and the resultant drift of nebulizer efficiency can cause instabilities in the observed analytical signal [17]. To overcome this problem, Hausler and Taylor have used a jacketed water cooled spray chamber [17]. A different approach is to locate the spray chamber distant from the plasma outside the plasma box [36].

Both, delivery rate and nebulizer efficiency, cause larger amounts of organic solvents to reach the plasma (higher transport efficiency) compared to water and the emission intensity in ICP-OES is higher. Therefore the term 'solvent enhancement effects' has been used. Nebulizer efficiencies for a controlled aspiration rate were reported to be 22, 8, 6, and 1.5 % for benzene, xylene, nitrobenzene and water respectively [41]. Reviews of aerosol production in atomic spectroscopy have been compiled by Cresser [38]

and Browner and Boorn [39,40].

1.4.2 TORCH

The design of the torch has proven to be critical when organic aerosols are introduced into the ICP. Fassel et al. reported carbon like deposits on the rims of the two inner tubes of the torch when MIBK or xylene was aspirated [13], and Boumans and Lux-Steiner have described an optimized torch design for organic aerosols to overcome this problem [45]. The following summarizes the main features found desirable:

- (1) A Tulip shaped intermediate tube, outer diameter of that tube as large as ease of ignition would allow.
- (2) Tapered rims of inner and intermediate tube.
- (3) The rim of the nebulizer tube located slightly below the rim of the intermediate tube.

In addition, Greenfield et al. [46] suggested, that the top of the nebulizer tube possesses a long, narrow channel. This provided for efficient penetration of the aerosol into the plasma and therefore good stability.

1.4.3 PLASMA

VAPOUR EFFECT AND PLASMA TEMPERATURE:

Boorn and Browner have published an extensive investigation on the effects of organic solvents on the ICP itself [36]. They found, that the maximum aspiration rate compatible with stable operation was strongly correlated with a theoretical solvent evaporation factor. The evaporation factor is a measure of the rate with which the solvent evaporates from aerosol droplets. The maximum aspiration rate was defined as the highest possible rate which did not cause appreciable carbon deposits on the torch after one hour of operation. They measured line intensities for metals in different solvents and found intensities in volatile solvents lower than expected by transport efficiency considerations. They argued, that solvent vapour loading causes lowering of the temperature in the plasma. From some spatially resolved emission data they also concluded, that the vapour loading effect was more significant low in the plasma. In contrast, high power Ar/N-ICPs pose no difficulties with respect to the vapour effect, and highly volatile solvents (e.g. acetone) can be introduced without any problems [47].

Boumans and Lux-Steiner [45] undertook a detailed study of a 50 MHz low power ICP with metals in MIBK to find

optimum analytical conditions (detection limits) with respect to flow rates, rf input power, sample feed rate and viewing height. They found that an input power between 1.4 and 1.8 kW for MIBK aspiration produced similar excitation conditions to those with water aspiration between 0.8 and 1.4 kW. A similar study by Miyazaki et al. [48] using diisooctyl ketone (DIBK) suggested again that the major difference to an aqueous plasma (the terms 'aqueous plasma, xylene plasma, organic plasma' etc. will be used to refer to the type of aerosol introduced) was the need for an increase in rf input power by about 0.5 kW when optimizing signal to noise ratios (S/N) for metals. To further clarify this power aspect, Blades and Caughlin [49] have acquired spatially resolved information on temperatures in a xylene plasma; xylene being a common solvent used for the determination of metals in oils. They found, that temperatures generally are lower in the xylene plasma compared to the aqueous one and an increase of about 0.5 kW yields the same temperatures for the xylene plasma. These three latter studies showed that the ICP is quenched even by solvents with higher boiling points than water. The evaporation factors of xylene and water in particular are very close [36], so that the quenching of the plasma cannot be attributed to the vapour effect alone. Therefore a further organic quenching effect must take place. Boumans and Lux-Steiner suggested, that the

presence of organic solvent leads to increased enthalpy of the carrier gas and the presence of molecular constituents increases the thermal conductivity of the plasma and so requires higher input power to achieve similar excitation conditions [45]. Also it has to be considered, that transport efficiencies are higher for organic solvents and therefore also the sample load. Whatever the causes, the excitation temperature in an organic plasma can be expected to be generally lower for a given power when analysing organic samples and the vapour effect limits the use of highly volatile liquids.

INCOMPLETE ATOMIZATION:

Boorn and Browner [36] have also listed a number of molecular species detected when organics were aspirated. The observed diatomic fragments (C_2 , CH, CN, CS, OH, NH, NO and CCl) were detected by their emission bands. They also presented plots of emission intensity as a function of height along the central axis for CI, C_2 and CN for several solvents. CI and C_2 intensities steadily decreased from the lowest height measured (5mm) whereas CN increased first to peak at about 15 mm above the loadcoil. For pyridine, the only nitrogen containing solvent, an intense CN peak was found low in the plasma. Similar studies had been conducted by Truitt and Robinson with solvents introduced as vapours

[50]. Emission from a molecular band of NH has been used for the determination of nitrogen [51].

The presence of these molecular species indicates that atomization is not complete (although fragmentation to the diatomic level is obviously achieved), at least not at all locations in the plasma. This could give rise to poor sensitivity, when measuring emission from the nonmetals which are part of a complex organic molecule. Also, the degree of atomization might vary for different molecular structures because of differences in bond strength and cause a matrix interference effect.

Northway and Fry [21] have investigated this potential interference effect for gaseous sample introduction. The oxygen emission intensities from equal volumes of O_2 and CO gas were compared and their ratio plotted as a function of rf input power. They found that the theoretical ratio of 2:1 was only achieved at an input power as high as 2 kW. Therefore a structural interference effect is indicated for oxygen determinations when the rf input power is not sufficient and possibly also when other operating conditions (gas flow rates, viewing height) are not favourable. Northway and Fry chose CO for their investigation because it is the molecule with the highest dissociation energy (11.1 eV).

ENTRAINMENT OF AIR:

When determining oxygen and nitrogen, contamination poses a major interference problem, because the plasma is exposed to surrounding air. Fry and co-workers have presented plots of oxygen [24] and nitrogen [22] emission intensities as a function of viewing height to illustrate this entrainment and suggested the use of an extended torch to exclude atmospheric gases [24]. They also reported oxygen and nitrogen contamination of the argon gas which was attributed to impurities in the tank and leakage into the tubing. Fry et al. have also shown that emission intensities of oxygen, sulphur and carbon decayed less rapidly with viewing height when extended torches were used. This was explained by the lack of quenching of the plasma by atmospheric N_2 , CO_2 and O_2 [24,28,52].

1.4.4 SPECTRUM

Band emission from molecules can cause considerable spectral interference. Even aqueous plasmas exhibit some molecular emission due to molecules formed with entrained atmospheric gases. Wallace [53] suggested the use of a torch extension to reduce some interferences caused by NO, OH and CN emission. Naturally, molecular emission is more severe when organics are introduced and spectral overlaps more

numerous. Boorn and Browner [36] have listed a number of such potential interferences and this aspect has also been investigated by Xu et al. [54].

1.4.5 SUMMARY

The literature review has led to the following conclusions. Samples with different physical properties could not be compared, because of the effects taking place at the aerosol production step, and therefore matrices should be matched by dilution. The spray chamber should be cooled to minimize instabilities caused by heat build up in the plasma box. A special torch for organic aerosols must be used. The rf input power should be set high to maximize the degree of atomization, and this potential interference should be examined. An effective solution to the interference from entrained air must be found. A survey of the reported nonmetal NIR lines should be carried out to find the most intense lines for the xylene plasma and the chosen lines had to be examined for spectral overlaps with molecular band emission.

The study reported in the following chapters was done in essentially three steps. First, analytical lines were established and the completeness of atomization examined. Secondly, the interference from air was investigated and

operating conditions optimized. Finally, the feasibility of the method was tested by comparing the response from samples of different composition, establishing detection limits and working curves and by analysing certified samples.

CHAPTER II

EXPERIMENTAL

2.1 INSTRUMENTATION

A block diagram of the instrumentation is given in Figure 3. The ICP used was a commercially available unit manufactured by Plasma-Therm Inc., Kresson N.J. The source consisted of a HFP-2500E, 27.18 MHz, 2.5 kW radio frequency generator, an AMN-2500E automatic matching network, an APCS1 automatic power control system and a PT-2500 plasma torch assembly. A concentric glass nebulizer (Plasma-Therm Inc., model GN 5601) was used for sample introduction. Free sample uptake was employed except where mentioned. The spray chamber was of the conventional concentric barrel type (Plasma-Therm Inc., model SC-5037). To minimize instabilities due to heat build up in the plasma box the spray chamber was water cooled using a coil of tightly wrapped plastic tubing. The water temperature was approximately 10 °C.

A 0.35 m Czerny-Turner monochromator (Model 270, Schoeffel-McPherson, Acton MA) with a grating with 1200 grooves/mm blazed at 500 nm was used. An image of the plasma was formed at the entrance slit of the monochromator by a plano-convex fused silica lens of 50 mm diameter and 150 mm focal length. The imaging distance was adjusted to provide

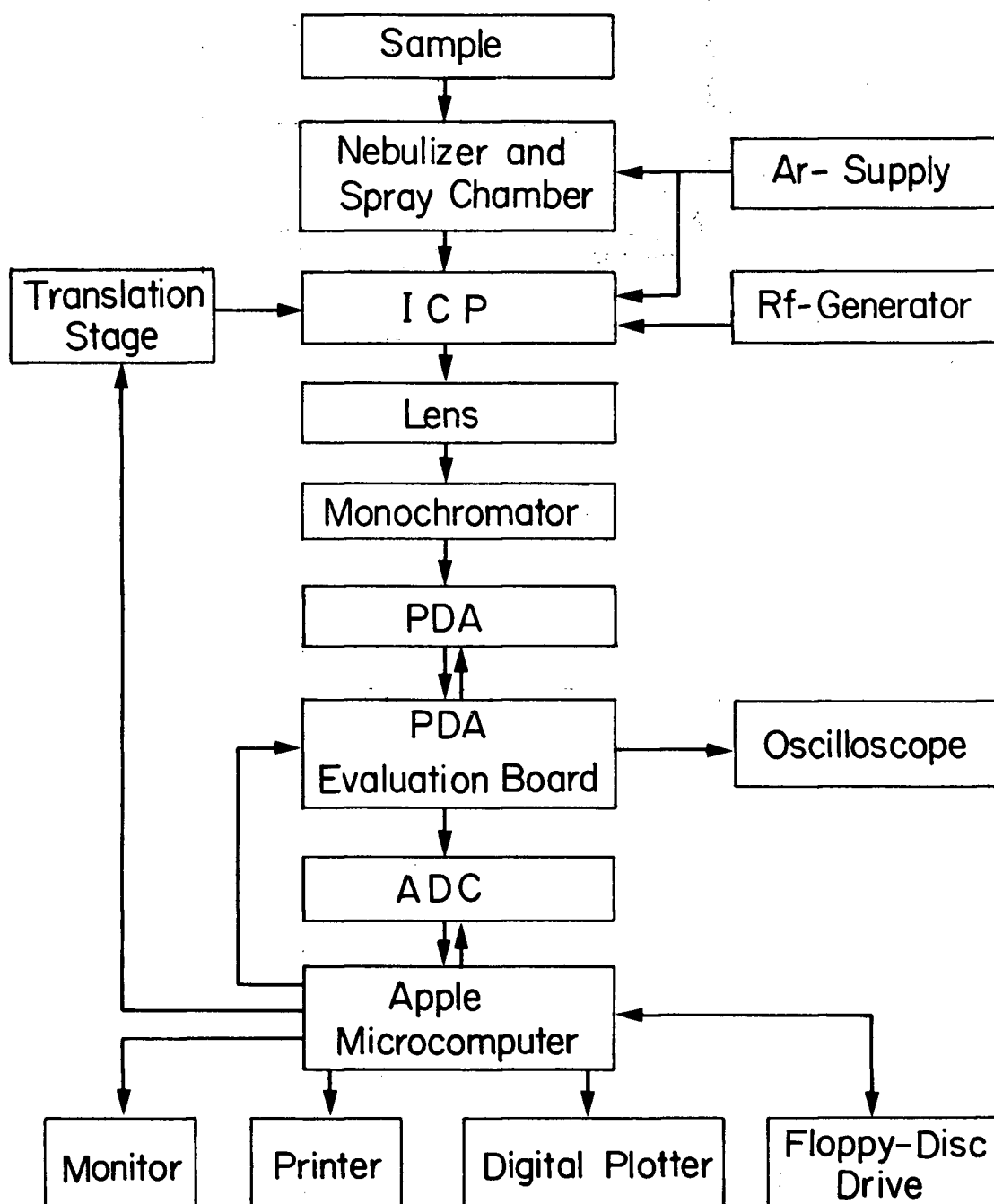


Figure 3. Block Diagram of the Instrumentation.

an image magnification of 1. The viewing height was altered by moving the lens vertically. The entrance slit was 100 μm wide and its height restricted to 1 mm by an aperture. A long pass filter (Opticon, model RG63) was used to cut off wavelengths shorter than 630 nm to prevent multiple order interferences. All three elements, ICP, lens and monochromator were mounted and aligned on an optical railbed. The detector used was a 1024 element photodiode array (Reticon RL-1024S) mounted in the exit focal plane of the monochromator. The dimensions of the total light sensing area were 25.5 mm by 2.5 mm. This provided for a simultaneous readout of a spectral window which was 38 nm wide at 900 nm. Electronic readout of the photodiode array was accomplished with an RC-1024SA evaluation board from Reticon. The integration time capability of this board has been increased by adding 9316 integrated circuit counters as described in Ref. [55], so that it could be varied between 50 ms and 10 s in 50 ms increments. The array output signal was displayed on an oscilloscope (Kikisui, Model 5650). Analog to digital conversion of the array analog readout was achieved by a AI13 12-bit analog to digital converter from Interactive Structures (Bata-Cynwyd, PA). The digitized output was acquired with an Apple II plus microcomputer, which was also used to control the operation of, and data acquisition from the array evaluation board (including

integration time) and the digital to analog converter by a 6502 machine language program. Further data processing (signal averaging, background subtraction, Abel inversion etc.) was done in Applesoft Basic. Spectra and processed data were stored on 5 1/4 inch floppy discs and displayed on the Apple monitor, on a digital plotter (WATANABE WX 4671) or a printer (OKIDATA 92).

The plasma box was mounted on a linear translation stage driven by a stepper motor (Daedal Inc. model 4979, Harrison City, PA) which allowed horizontal movement perpendicular to the optical axis in increments of 0.0127 mm. A combination of movements of the lens and the translation stage thus enabled observation of any desired region of the plasma. The translation stage was interfaced to the microcomputer so that its movements could be software controlled.

A piston pump (model NH-SY, Fluid Metering Inc., Oyster Bay, NY) was used in experiments where controlled sample delivery was employed. Pulses were damped by a few millilitres of air contained in a syringe connected to the solvent line downstream from the pump.

The argon supply was of welding grade and reagent grade chemicals were generally used. A mixture of xylene isomers was used as the solvent.

An rf input power of 2 kW was used throughout the study

and the plasma and auxiliary gas flow rates were 12 l/min and 2 l/min respectively. The nebulizer gas flow rate and the viewing height varied.

2.2 TORCH

The quartz torch was constructed at the UBC glass shop from precision-bore quartz tubing. The dimensions are provided in Figure 4. The torch shows some of the features found desirable for organic aerosols by Boumans and Lux-Steiner [45]. It was designed to tolerate high aspiration rates of organic solvents without extinction of the plasma and to be resistant to soot buildup on aerosol and intermediate tubes. Using both criteria our torch compares well with those used by other authors. Xu et al. [54] reported that their 27 MHz Ar plasma was extinguished when more than 1 % acetone was mixed to water aspirated into the plasma via a concentric nebulizer. No data on the torch was given. It was found that our torch tolerated at least 70 % acetone in water when operated with the same flow rates and rf power as Xu et al. Boorn and Browner [36] reported operation free of carbon deposits for a controlled aspiration rate of 0.1 ml/min acetone via a cross-flow nebulizer for a period of one hour. The torch they used was a Plasma Therm Model T1.0. Using their working conditions

and criteria, it was found that our assembly tolerated a delivery rate as high as 0.4 ml/min acetone.

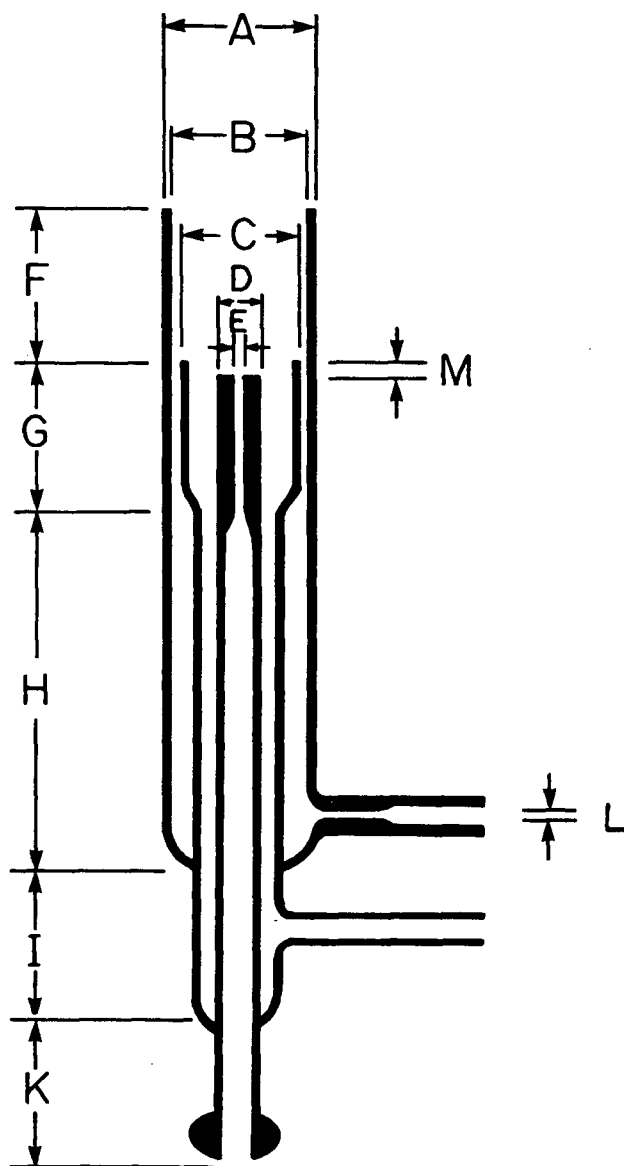


Figure 4. ICP Torch

Dimensions: A 20.37 mm, B 17.39 mm, C 15.86 mm, D 5 mm, E 1.48 mm, F 20 mm, G 20 mm, H 43 mm, I 20 mm, K 25 mm, L 1 mm, M 3 mm.

2.3 ACQUISITION OF EMISSION PROFILES

After choosing the desired viewing height, profiles of emission intensity were acquired in the following manner. The translation stage was moved in 100 increments of 0.1905 mm each to allow the measurement of emission intensities at 100 locations across the width of the plasma. The so obtained lateral profiles represented the sum of intensities through the depth of the plasma as illustrated in Figure 5. I_{xn} stands for the observed lateral emission intensity at position x_n . Asymmetric Abel Inversion [56] was then used to calculate emission intensities as a function of radial position from this measured lateral data. The radii hereby are equivalent to the lateral distances. The intensities I_{rn} in Figure 5 represent the calculated emission intensities on 100 radii (r) left and right from the centre.

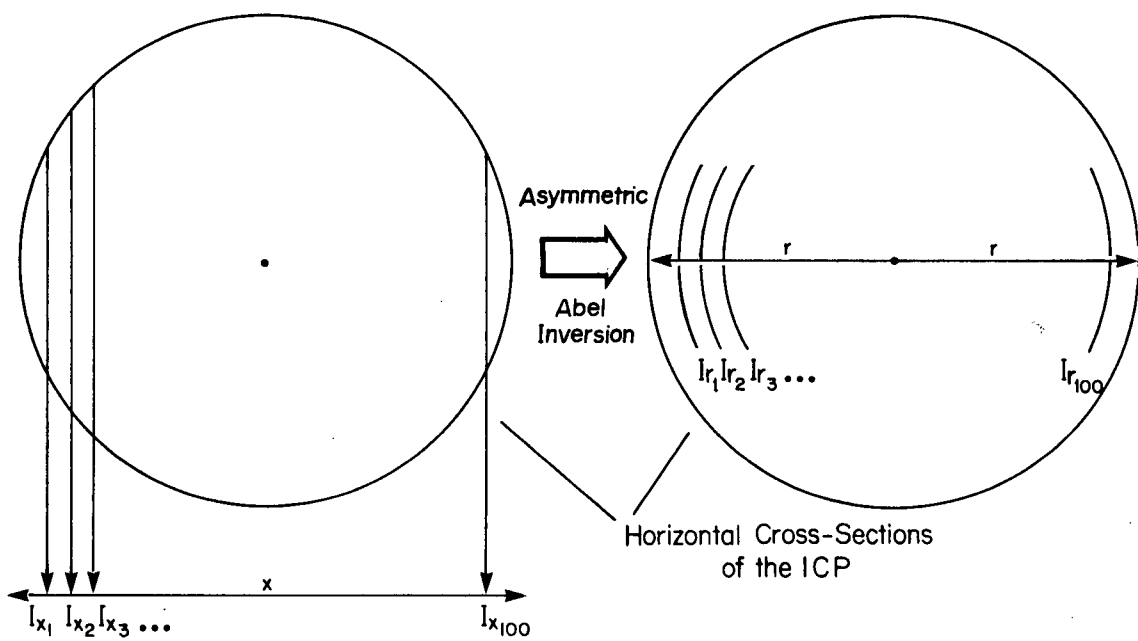


Figure 5. Asymmetric Abel Inversion.

CHAPTER III

RESULTS AND DISCUSSION

3.1 NEAR-IR OXYGEN, NITROGEN AND SULPHUR LINES

The publications of Fry and his colleagues [21,22,28] were used as a guide for the selection of analytical lines for the determination of oxygen, nitrogen and sulphur. Since our work involved nebulizing xylene as opposed to gaseous sampling, a survey of these lines was carried out, to find the most sensitive lines and to check on potential spectral overlaps with molecular species. A nebulizer gas flow rate of 0.75 l/min and a viewing height of 10 mm from the top of the load coil was employed for these studies.

In agreement with Fry et al. it was found that the 777.2 nm line was the most intense NIR emission line of atomic oxygen [21]. An emission spectrum of 1 % oxygen in xylene is provided in Fig. 6. The 777.2 nm line is not resolved from the nearby 777.4 and 777.5 nm OI lines, with the resolution provided by the experimental system described in Chapter II. However, the OI lines are free of spectral overlaps from the other plasma components and could thus be used as a group for oxygen determinations.

For nitrogen, all lines were found to be comparatively weak. The 868.0 nm line was most intense, again in agreement

with Fry et al. [22]. In practice, however, a line wing overlap with the intense 866.7 nm ArI line restricted the dynamic range of the NI line at long array integration times. Fig. 7 is an emission spectrum in the range from 848 nm to 880 nm. The 868 nm NI triplet and the nearby ArI line are identified in the figure. As a result of this partial overlap the 821.6 NI line was used for analytical determinations of nitrogen. A plot of the emission spectrum in the immediate region of this line is provided in Fig. 8. The 821.6 nm line is about half as intense as the 868.0 nm line.

For sulphur, the 921.3 nm line was found most intense, again in agreement with Fry [28], and was used for quantitative determinations. An emission spectrum between 905 nm and 932 nm is given in Figure 9. The SI 922.8 nm line is partially overlapped with the ArI 922.5 nm line with our experimental system, but as shown in Fig. 9, the subtraction of a spectrum from pure xylene makes this line visible.

It should be noted, that under the conditions of low rf input power, high nebulizer flow rate and low viewing height, the C₂-Phillips band (stretching from about 875 to 960 nm) was observed [57]. However, the effect of this band emission was not significant under the working conditions adopted for analysis. No other spectral interference from molecular band emission with any of the analytical lines was

found.

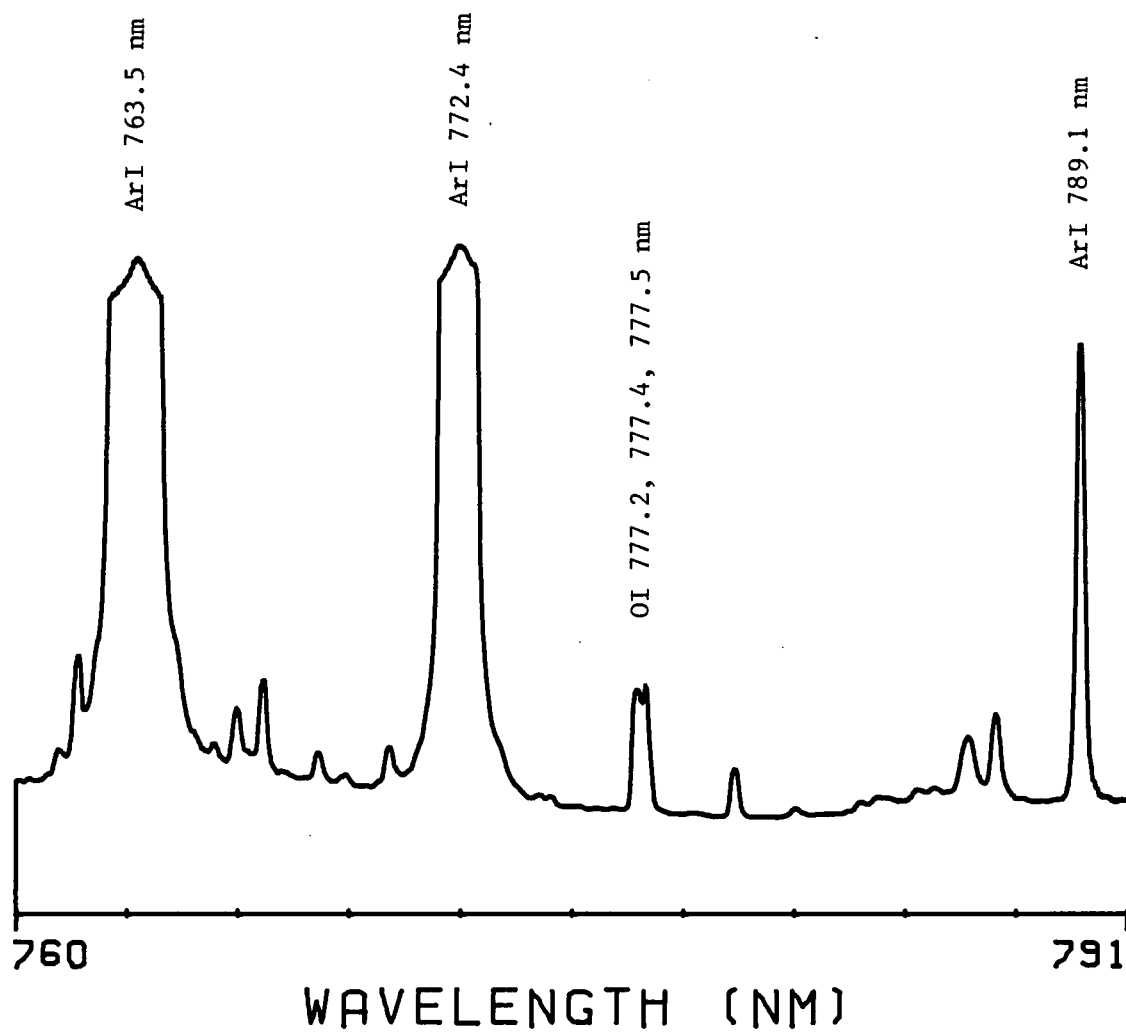


Figure 6. Emission Spectrum at 777 nm. Aerosol: Xylene with 1 % O added as Isopropanol. Integration time: 750 ms. Darkcurrent was subtracted.

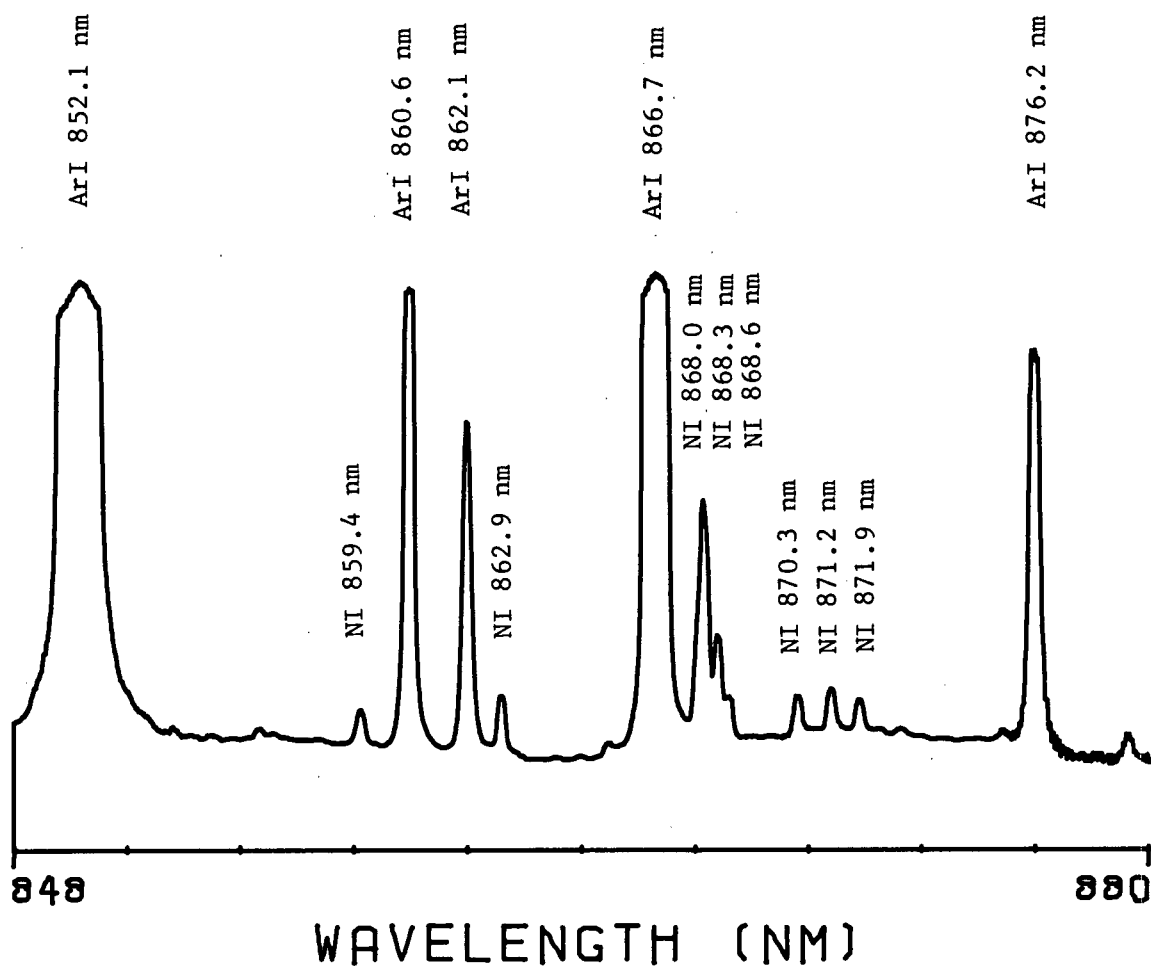


Figure 7. Emission spectrum at 865 nm. Aerosol: Xylene with 1 % N added as triethylamine. Integration time: 1.5 s. Darkcurrent was subtracted.

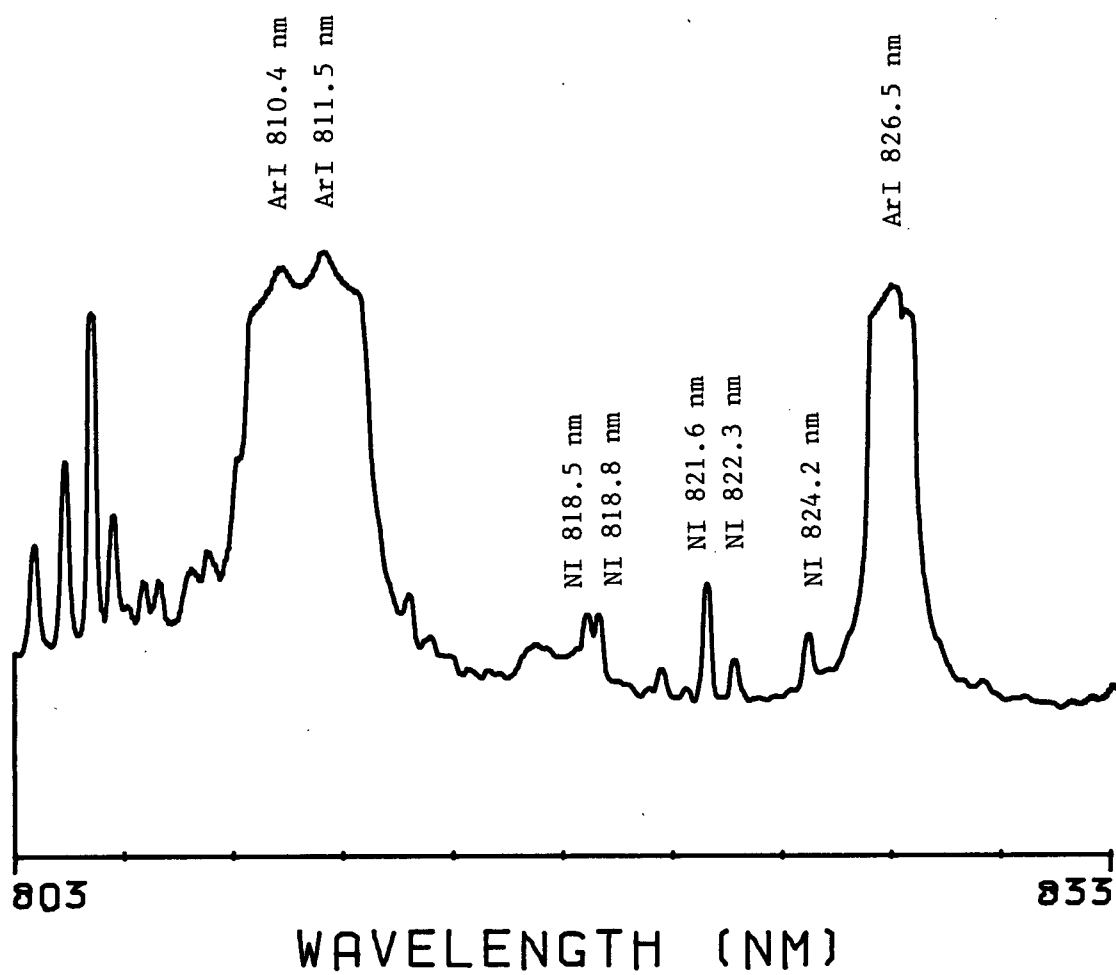


Figure 8. Emission spectrum at 820 nm. Aerosol: Xylene with 1 % N added as triethylamine. Integration time 1.5 s. Darkcurrent subtracted.

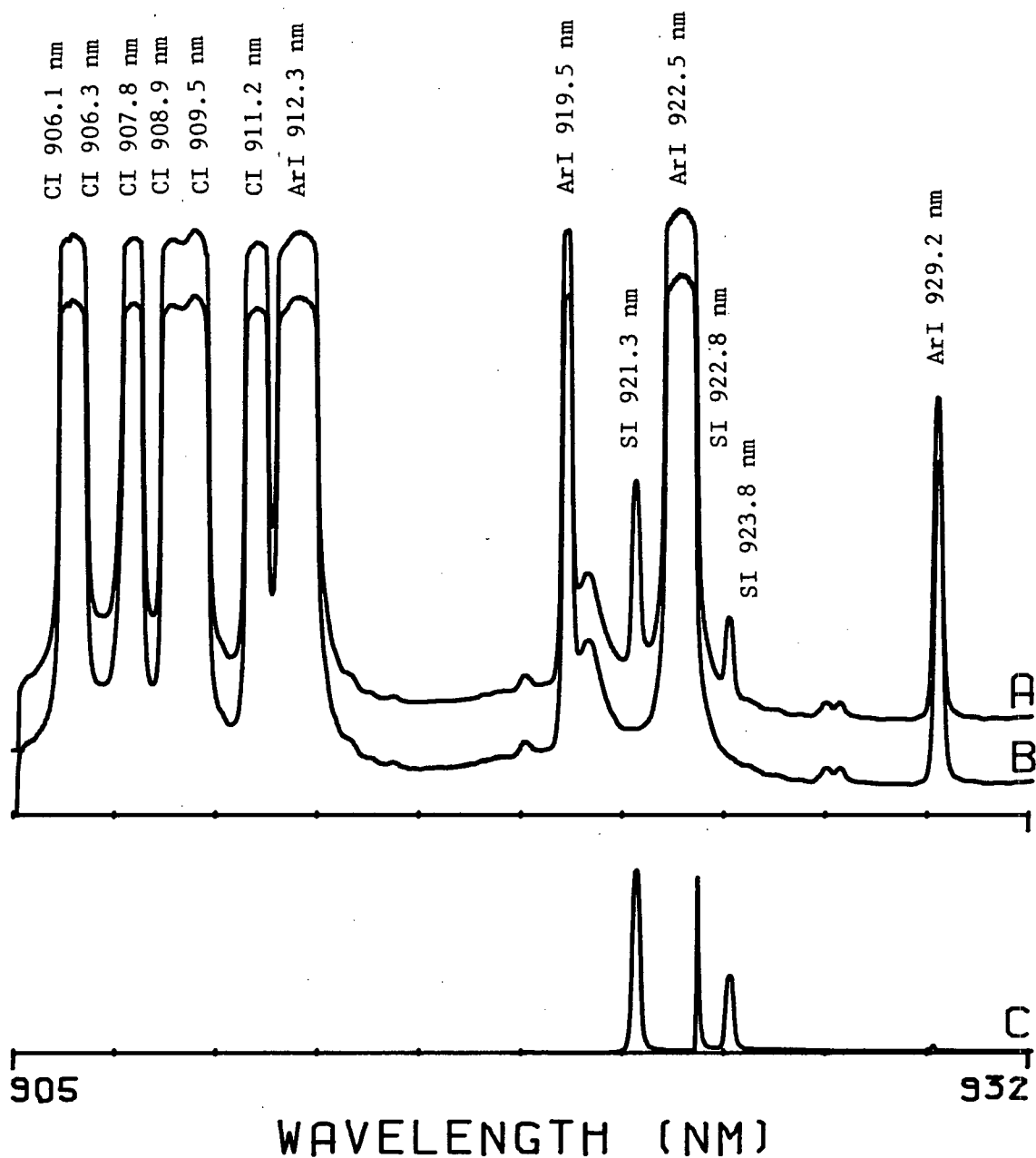


Figure 9. Emission spectra at 920 nm. Int. time 750 ms.
A: Aerosol: Xylene with 1 % S added as diphenyl-
disulfide. Darkcurrent subtracted.
B: Aerosol: Xylene. Darkcurrent subtracted.
C: Spectrum B subtracted from A, showing the partially
overlapped SI 922.8 nm line.

3.2 PHYSICAL APPEARANCE OF THE 'XYLENE-PLASMA'

When xylene or any other organic solvent is aspirated, the appearance of the plasma changes dramatically compared to the aqueous plasma. An organic plasma is depicted schematically in Figure 10. Intense green emission due to the C_2 Swan band at 515 nm is visible around the bottom of the plasma, on the sides up to the torch rim and also in the aerosol channel just above the nebulizer tube. The length of this core of green emission in the central channel increases with nebulizer flow rate and also when solvents, which are more volatile than xylene, are aspirated. For xylene, the tip of this green core was just above the load coil for a nebulizer gas flow rate of 0.4 l/min and at 15 mm above the load coil for 0.8 l/min. Above the torch rim, no green emission is visible on the outside of the plasma but violet emission due to the CN violet system at 415 nm is observed. This stretches all along the plasma and becomes more intense on the top.

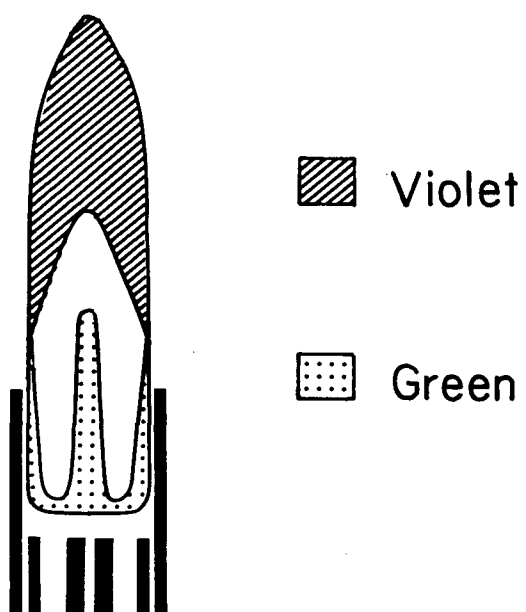


Figure 10. The ICP when xylene is aspirated.

3.3 COMPLETENESS OF ATOMIZATION

Atomization of organic molecules in the ICP is obviously not complete. However, this does not interfere with the determination of a particular nonmetal if, either the nonmetal sought for is not incorporated in the molecules present (i.e. atomization of that particular element is complete), or if the observed atomic emission originates from a region in the plasma where atomization is complete. Both aspects, i.e. which molecules are present and the spatial dependence of the completeness of atomization, were therefore examined. The obvious available tool was the emission from molecules and the corresponding atoms. Several points have to be considered when interpreting emission data from that point of view. Molecules which are present might not be detected by emission. Spatial emission data has to be correlated with a measure for the temperature in the plasma. Further, disappearance of emission from neutral molecules might be caused by ionization of these to positively charged molecules. However, this is unlikely because the ionization energies are generally higher than the dissociation energies.

The diatomic species detected by their emission [36] and some other molecules likely to be present are listed in Table II along with their dissociation and some ionization energies. The ionization energy of Ar is included for

comparison.

TABLE II

Dissociation and Ionization Energies for some Molecules

<u>Molecule</u>	<u>Dissociation Energy (eV)</u>		<u>Ionization Energy (eV)</u>
(Ar)			15.8 [58]
CO	11.1	[21]	14.0 [59]
N ₂	9.8	[22]	15.6 [59]
CN	8.2	[59]	
CS	7.6	[60]	
C ₂	6.5	[60]	
NO	6.5	[60]	
O ₂	5.1	[21]	12.2 [59]
OH	4.4	[60]	
CH	3.5	[47]	11.1 [59]

3.3.1 EMISSION FROM DIATOMIC MOLECULES

The accessible spectral range from about 200 nm to 1000 nm was searched for molecular emission band structure at several viewing heights. Faint ripple-structure in the background occurred in many spectral regions, but besides the already mentioned C_2 Phillips and Swan bands and the CN violet band, no strong identifiable molecular emission bands were found. The C_2 Swan band at 515 nm and the CN violet band at 415 nm are shown in Figures 11 and 12. The other diatomic species reported by Boorn and Browner [36], CH, CS, OH and NO, could not be detected (50 % 1,3-propanedithiol added to xylene and pure isopropanol were aspirated when searching for CS and OH respectively). These molecules might have been absent, but another explanation could be, that all these bands (except CH at 430 nm) lie in a region (200 - 400 nm) where the PDA is relatively insensitive compared to the PMT which Boorn and Browner used for their investigations. Therefore, this data is not very conclusive.

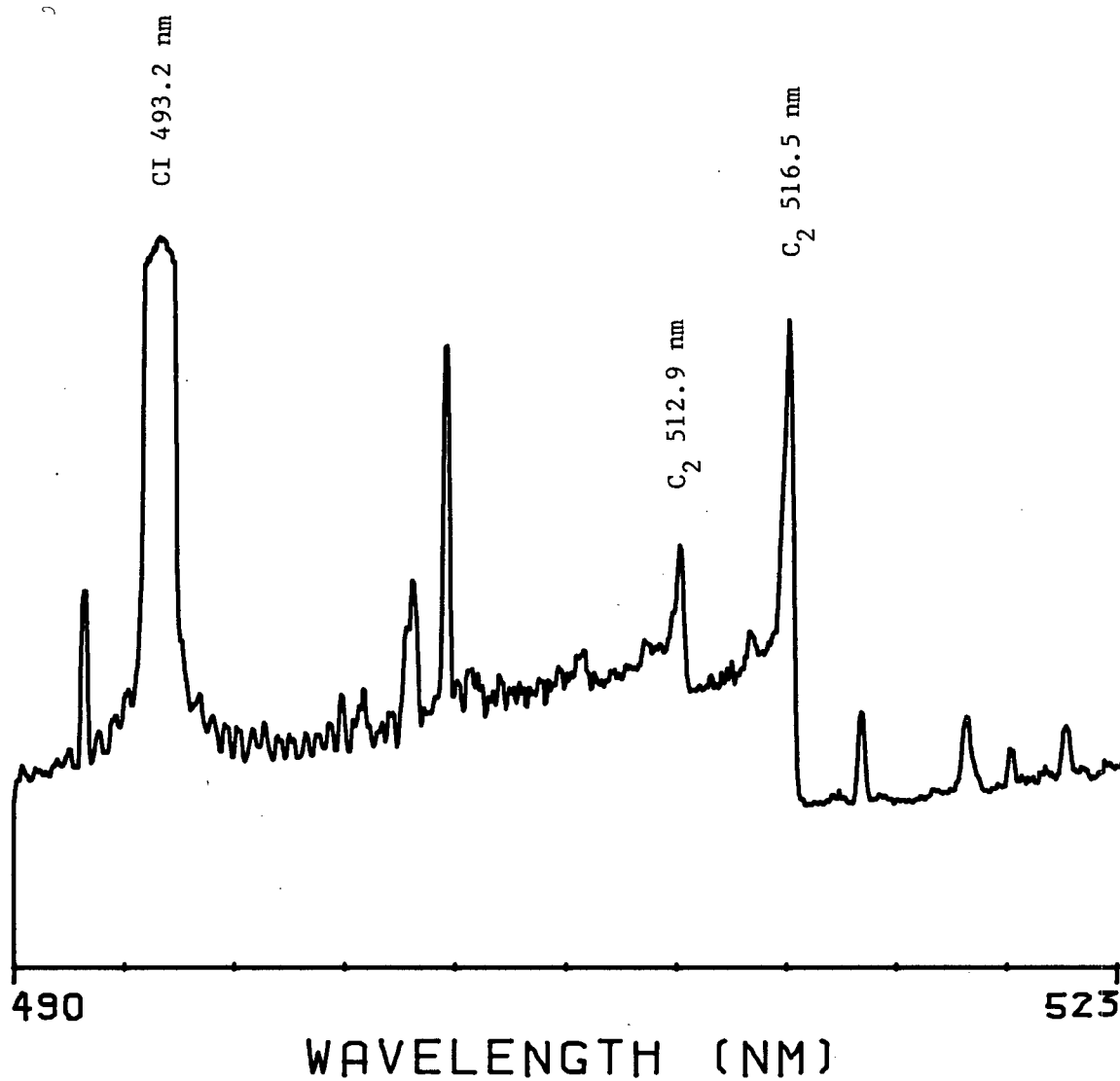


Figure 11. C₂ Swan band at 515 nm. Aerosol: Xylene
Integration time: 750 ms.

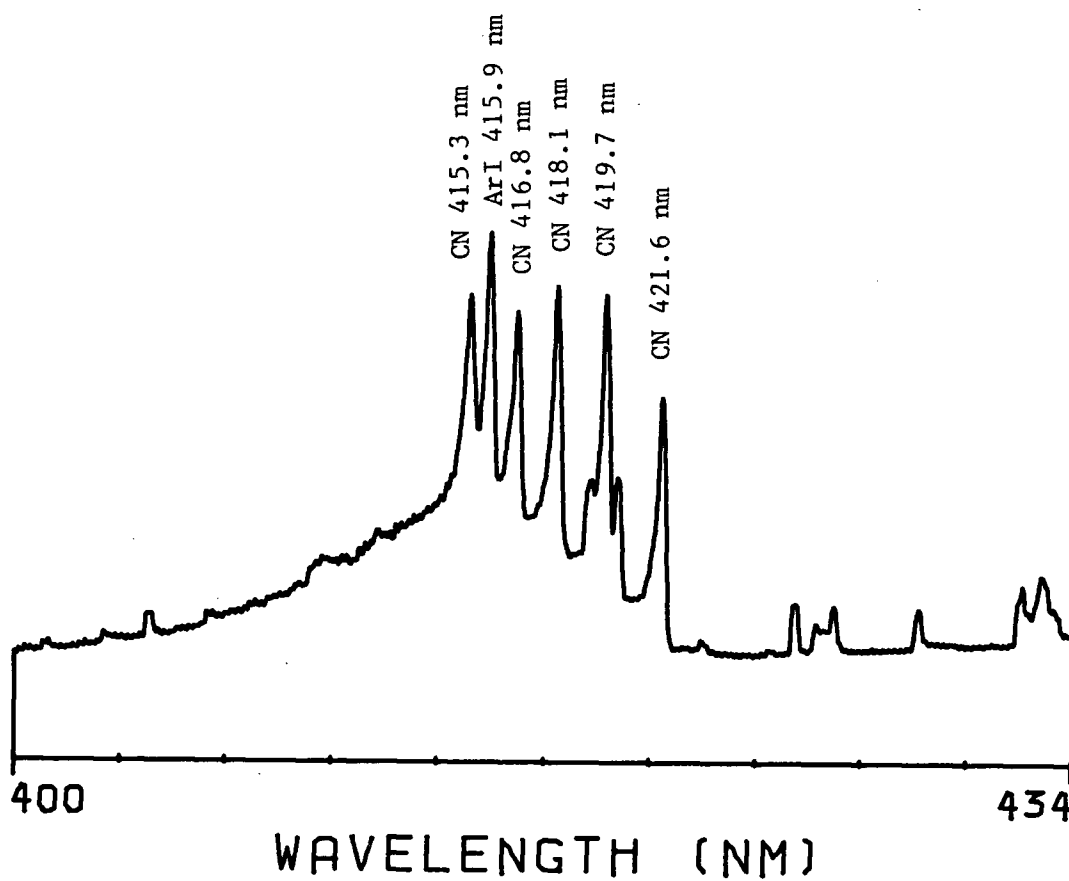


Figure 12. CN Violet band at 415 nm. Aerosol: Xylene
Integration time: 50 ms.

3.3.2 EMISSION PROFILES

Excitation temperature profiles acquired for the xylene plasma by Blades and Caughlin [49] are reproduced in Figure 13 because a qualitative picture of the temperature distribution in the ICP will be needed for the discussion of the subsequently presented profiles. Data for 2 kW, the input power level used throughout this work, was not obtained by Blades and Caughlin, but there should not be a substantial difference to the 1.25 and 1.75 kW plasma. Two main regions can be distinguished: a toroidal region above the induction zone and an axial region. In the toroidal region, the temperature is high at low heights and decreases with increasing height. In the axial region the temperature is generally lower than in the toroidal region but increases with height. Temperature profiles below 10 mm were not acquired, but the indicated trends can be expected to be more pronounced at lower heights.

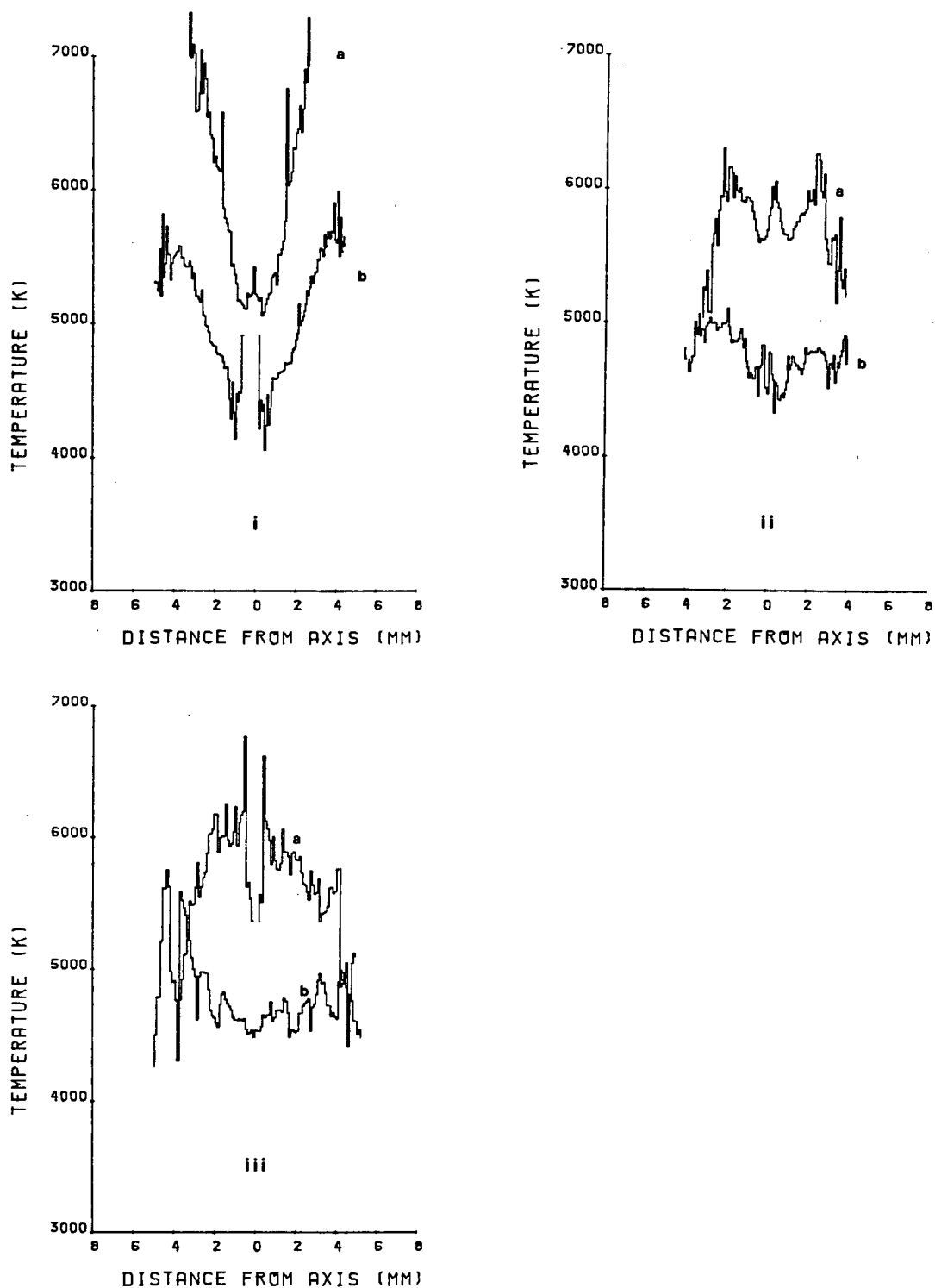


Figure 13. FeI Excitation Temperature profiles of the ICP when xylene is aspirated. a: 1.75 kW, b: 1.25 kW. (i) 10mm, (ii) 15 mm and (iii) 20 mm from the load coil. Taken from Blades and Caughlin [49].

The following profiles were all acquired above the torch rim, which was located 4 - 5 mm above the load coil. The nebulizer gas flow rate was adjusted to 0.70 l/min, so that the tip of the green C₂ core was visible 2 mm above the torch rim and that influence could show up in the measurements.

The wavelengths and integration times used for the acquisition of the presented profiles are provided in Table III. All profiles were corrected for variations in the background by measuring its intensity close to the analyte line and subtracting that value.

The viewing heights, with the top of the loadcoil as the reference point, are indicated in the profiles.

TABLE III

Experimental Conditions for the Acquisition of the Profiles

<u>Species</u>	<u>Wavelength</u>	<u>PDA Integration Time</u>
C ₂	516.5 nm	50 ms (Fig. 14)
		250 ms (Fig. 26)
CN	421.6 nm	250 ms
CI	907.8 nm	150 ms
SI	921.3 nm	1500 ms
OI	777.5 nm	1000 ms

3.3.2.1 C₂ AND CN EMISSION PROFILES

Lateral emission profiles of C₂ are given in Figure 14. Emission from C₂ is limited to the central channel and the profiles agree with the visually observed extent of C₂ emission.

The plots of CN emission (Figures 15, 16 and 17) show some CN in the central channel at low heights, which probably is due to nitrogen impurities in the xylene and argon supply. Strong CN emission is formed on the outer layers of the ICP which must be caused by nitrogen entrained from the surrounding air. This emission extends across the width of the plasma at larger heights. Adding pyridine to xylene (approximately 10 %) causes high CN emission intensities in the central channel at low heights, which must originate from the sample (Figure 18).

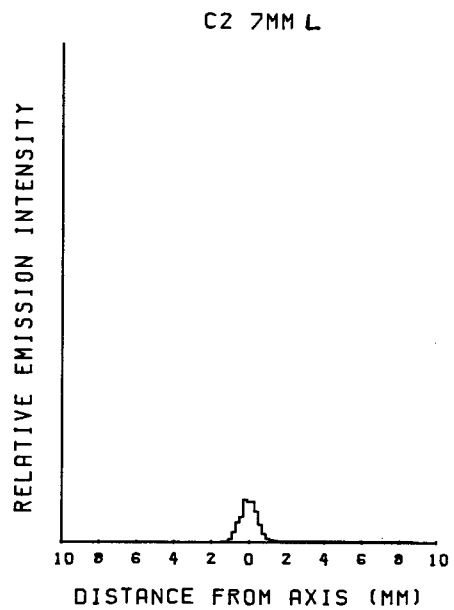
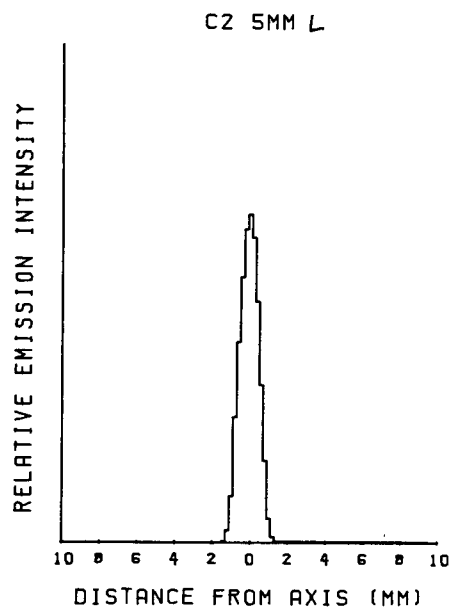


Figure 14. Lateral C₂ emission profiles.

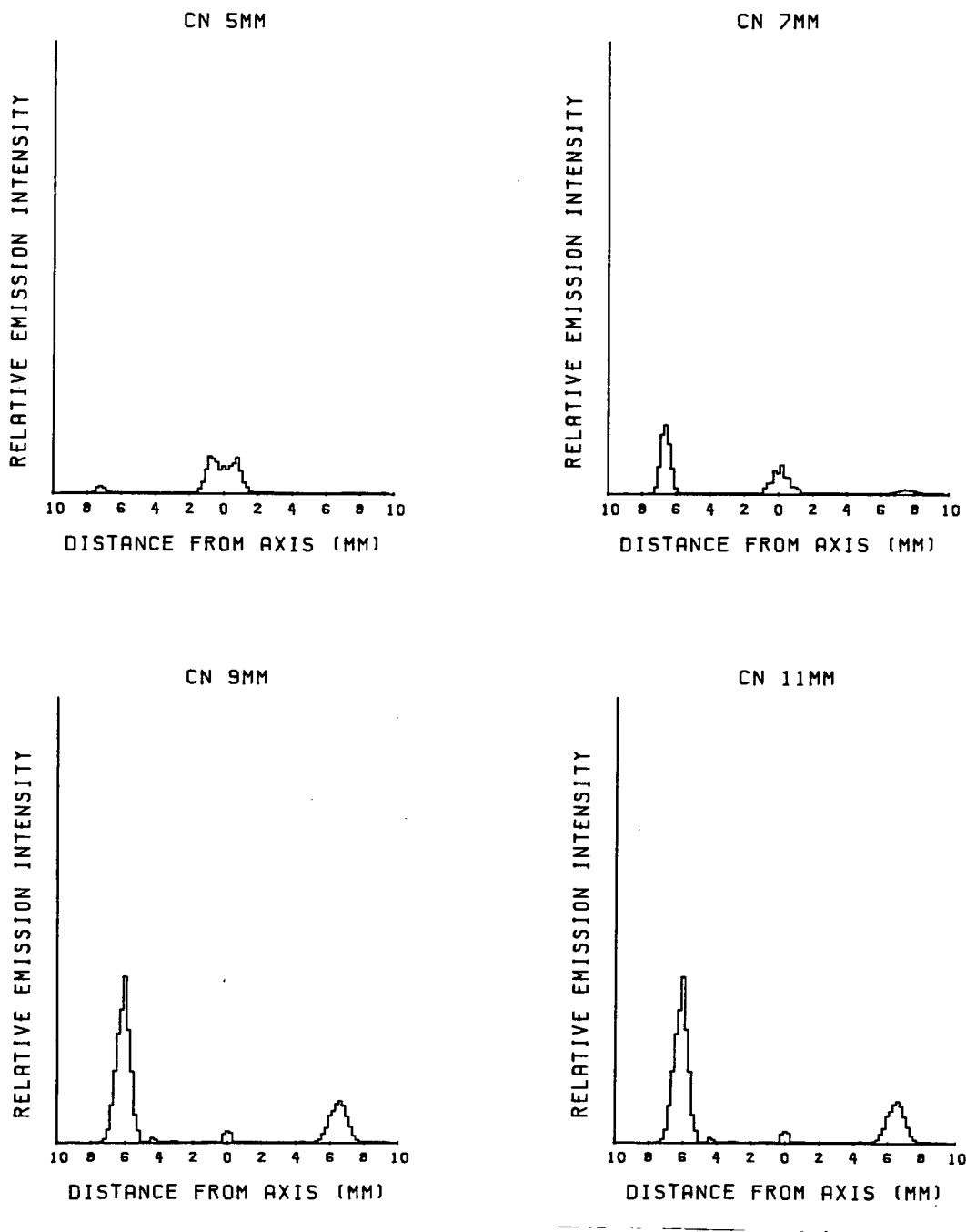


Figure 15. Radial CN emission profiles (1)

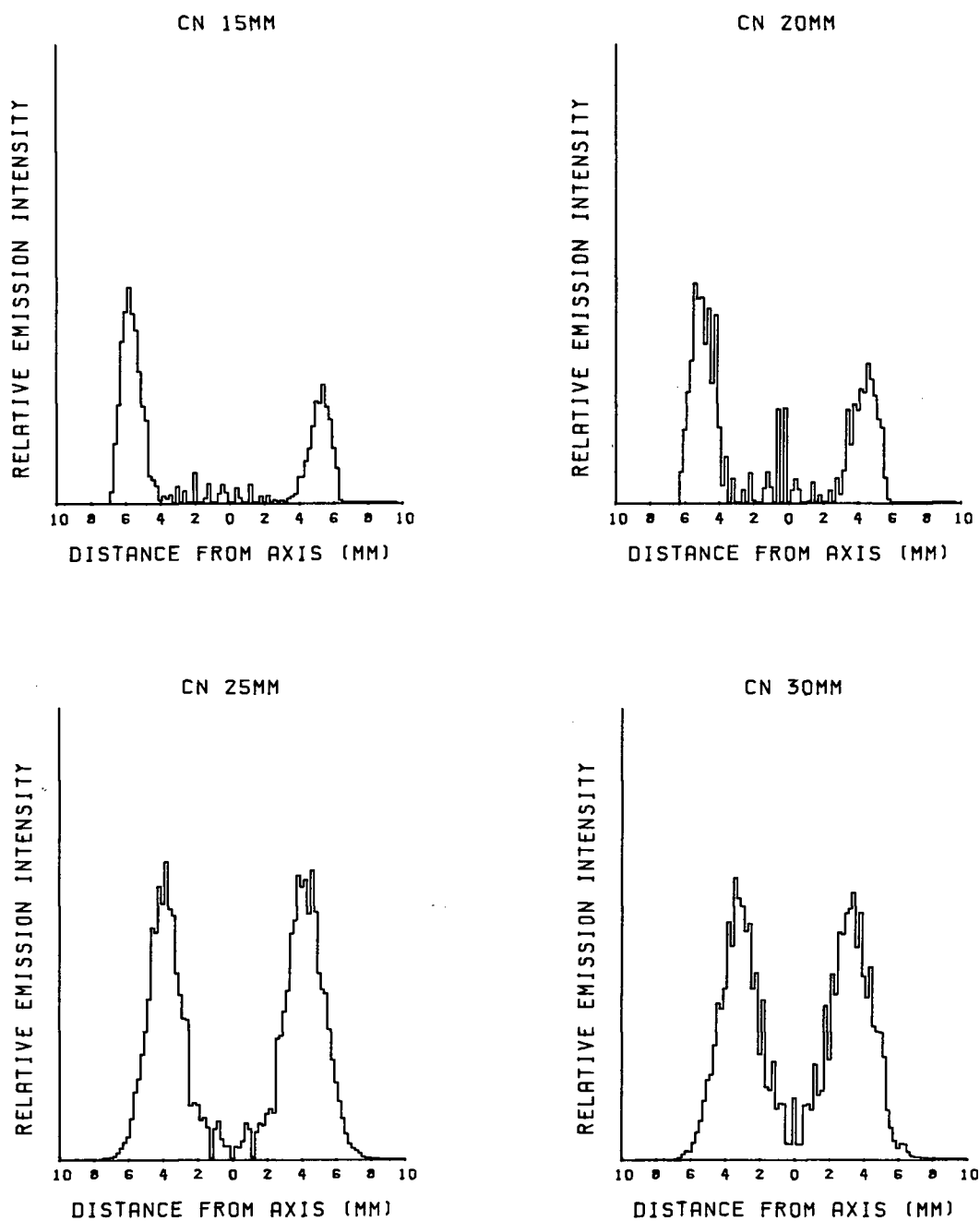


Figure 16. Radial CN emission profiles (2)

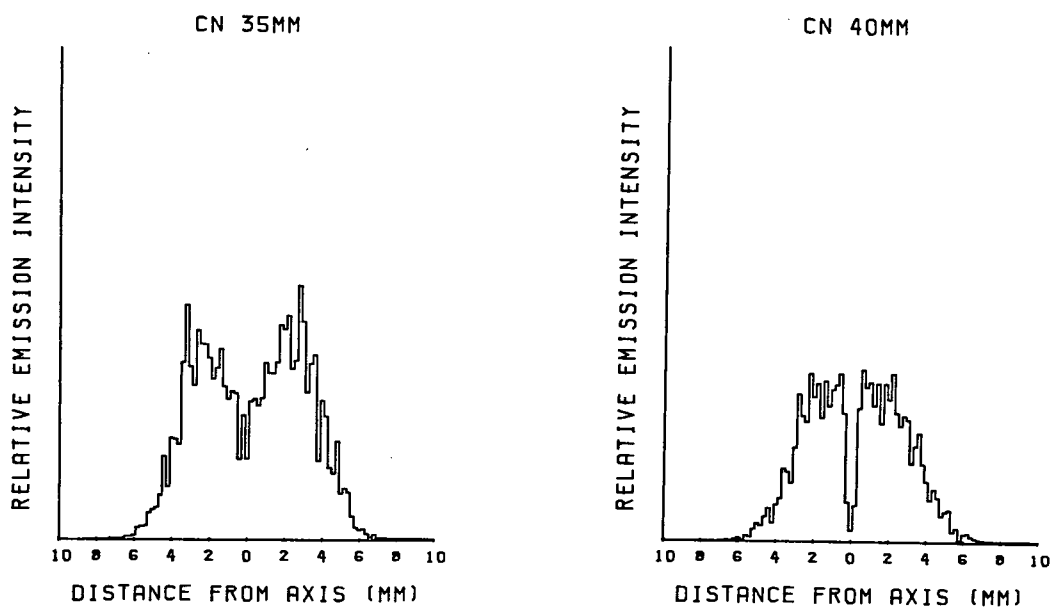


Figure 17. Radial CN emission profiles (3)

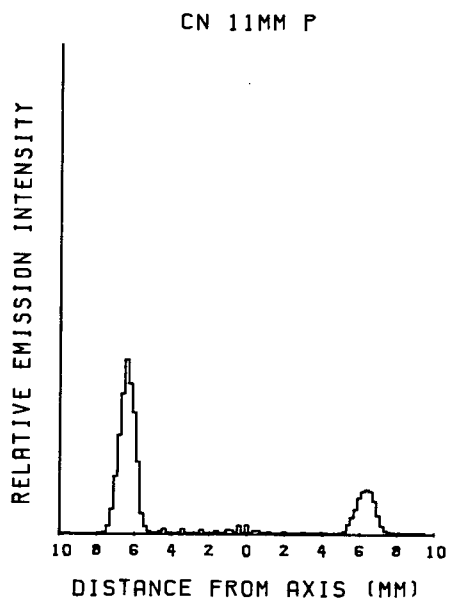
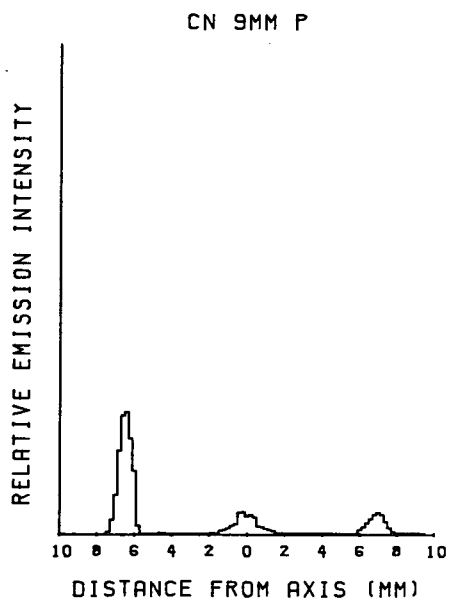
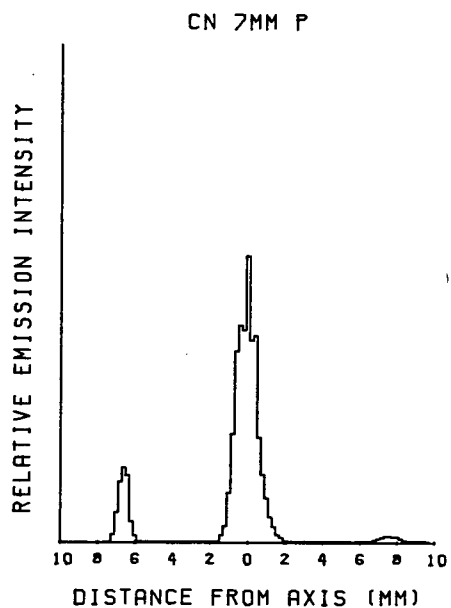
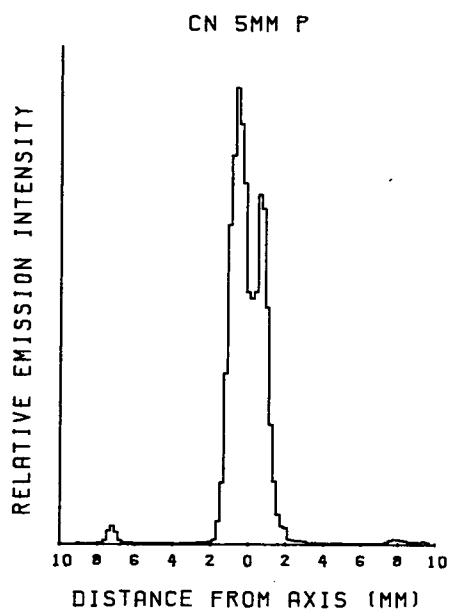
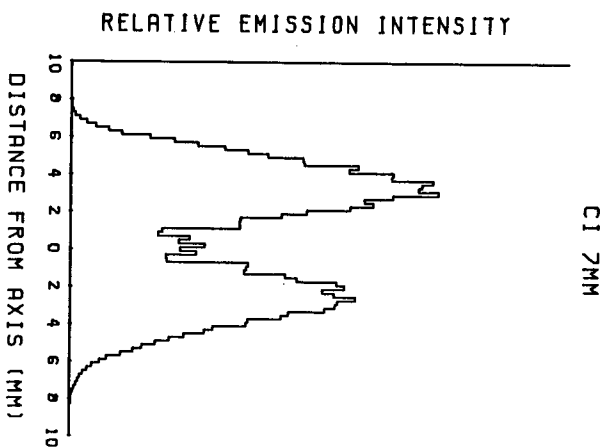
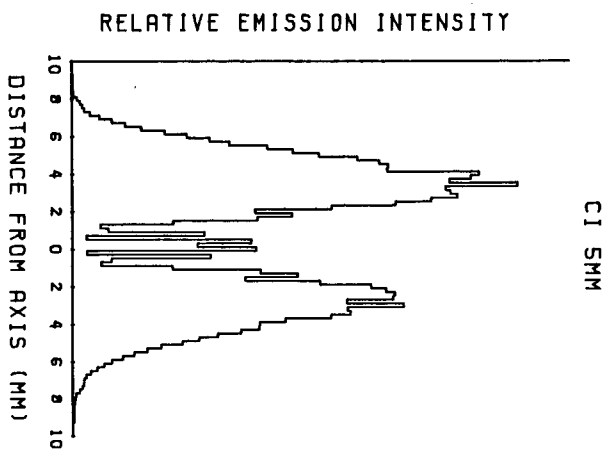


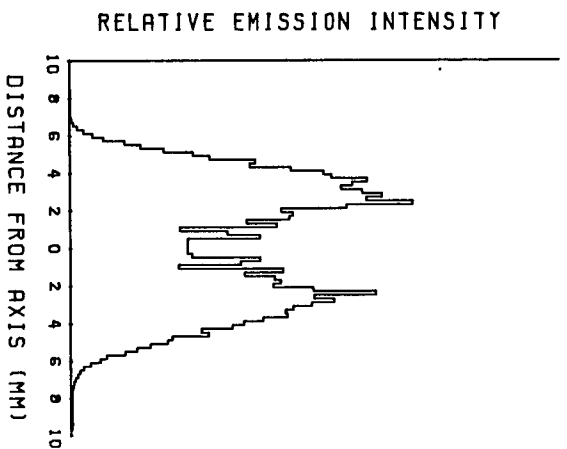
Figure 18. Radial CN emission profiles when 10 % pyridine added.

3.3.2.2 CI AND SI EMISSION PROFILES

The profiles of CI emission in Figures 19 and 20 and of SI emission in Figures 21 and 22 (20% dimethylsulfoxide in xylene) show emission from the toroidal region of the plasma at all heights. In the central channel, emission intensities are weak low in the plasma and increase with height.



CI 9MM



CI 11MM

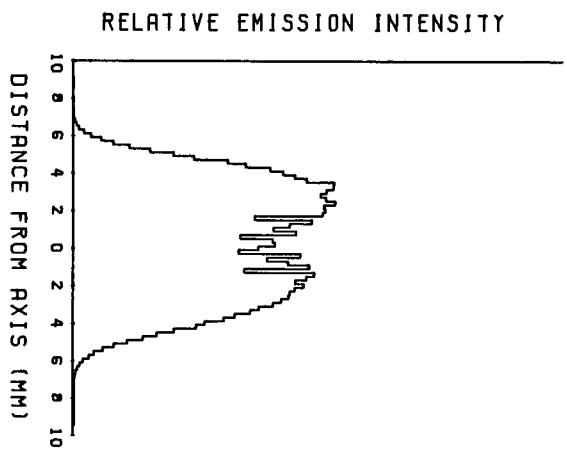


Figure 19. Radial CI emission profiles (1)

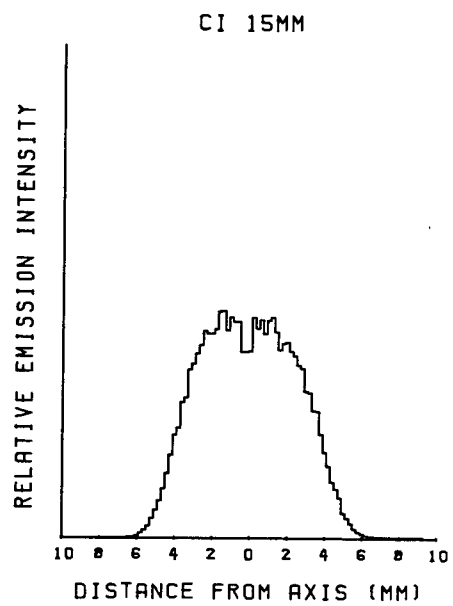
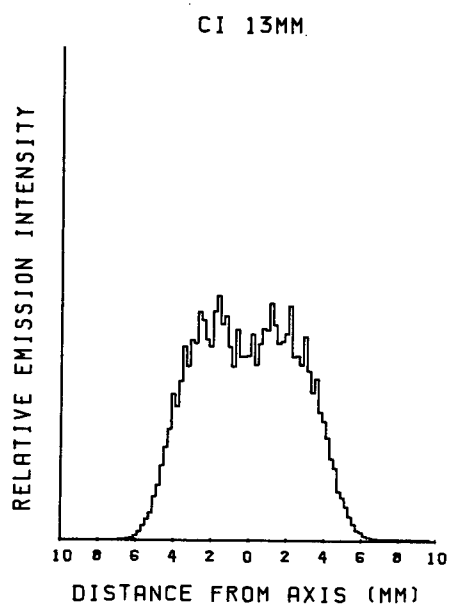


Figure 20. Radial CI emission profiles (2)

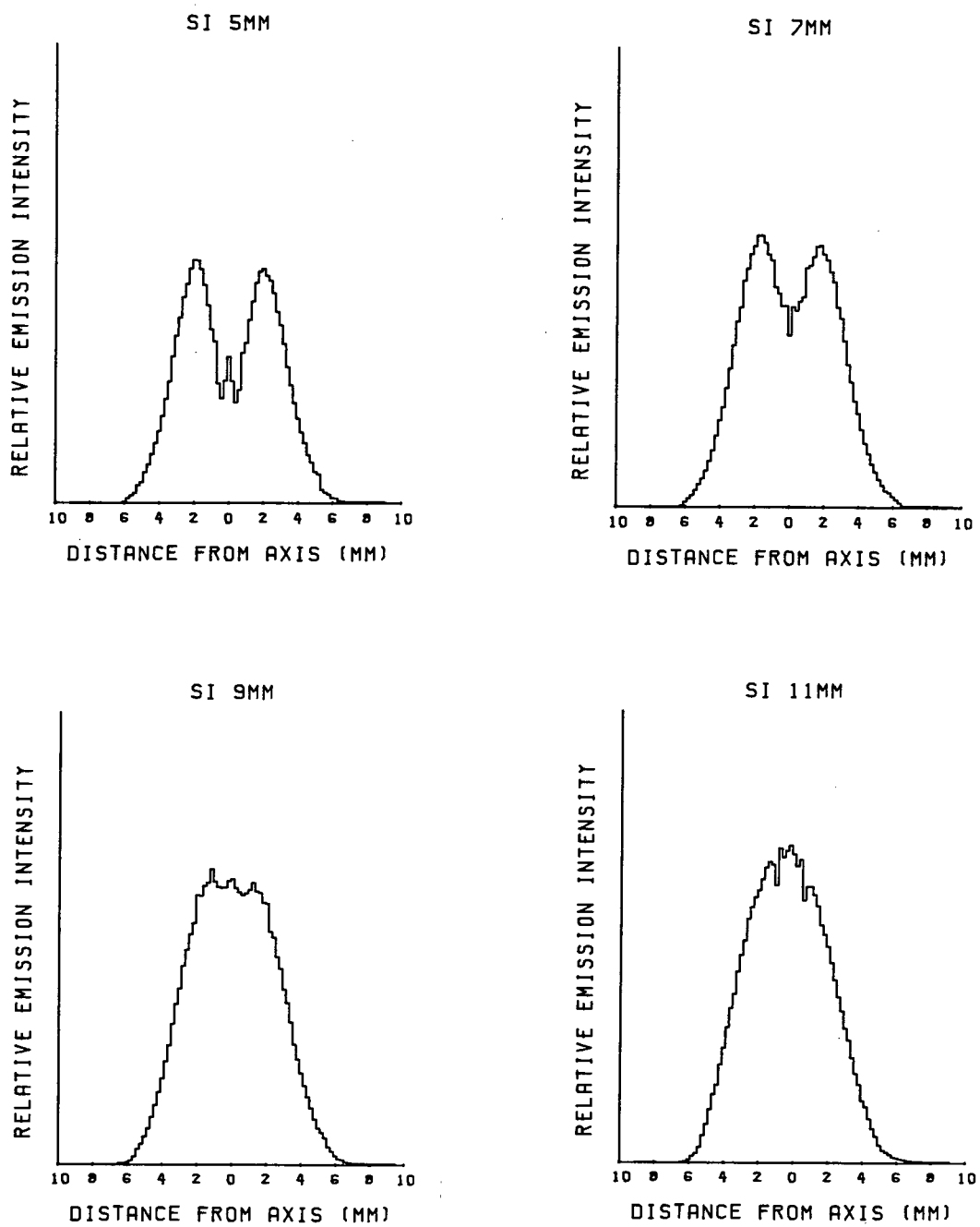


Figure 21. Radial SI emission profiles (1)

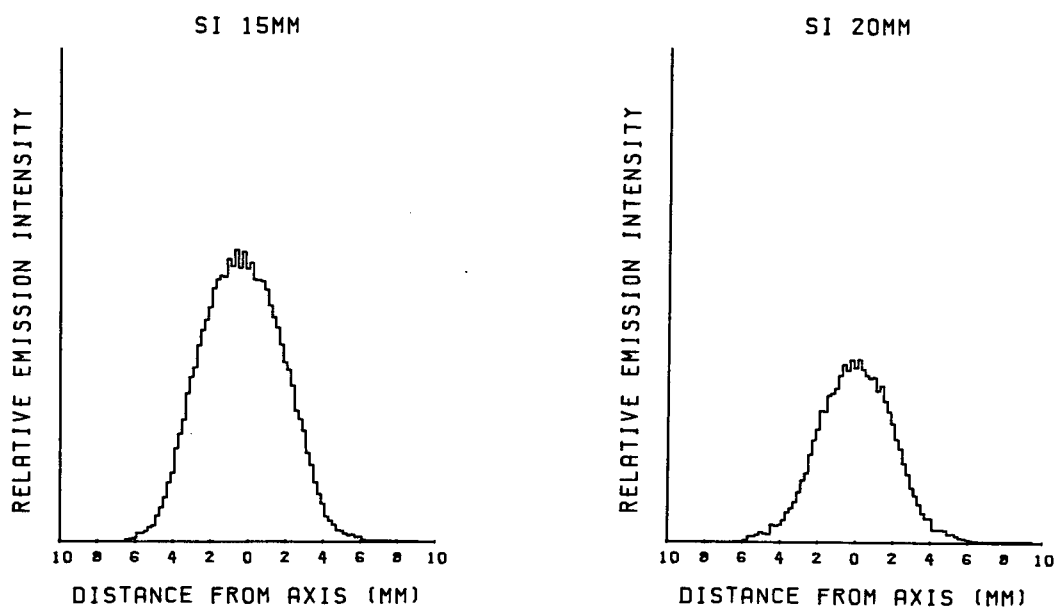


Figure 22. Radial SI emission profiles (2)

3.3.3. CONCLUSIONS

Emission from molecular species originating from the sample, C_2 and CN from pyridine, was observed low in the central channel but disappeared with increasing height. This agrees with the visually observed extent of the green core of C_2 emission. The fact that the strong molecule CN with a dissociation energy of 8.2 eV, disappeared in the central channel above this height suggests, that atomization is complete above a certain height in the aerosol channel. The height where this is achieved, presumably depends on the nebulizer gas flow rate, as the length of the visible C_2 core changes.

The profiles of atomic emission of CI and SI showing low intensities low in the central channel, comply well with the extent of molecular emission. The occurrence of emission from CI and SI in the low toroidal region of the plasma indicates, that the sample diffuses very rapidly sideways from the aerosol channel.

The fact, that at low heights, where atomization in the central channel is not complete, most of the atomic emission originates from the toroidal region, implies, that an interference from incomplete atomization is small and independent of viewing height.

3.4 OPTIMIZATION

3.4.1 ENTRAINMENT OF AIR

OI emission profiles taken at four heights are given in Figure 23. Oxygen is observed at the outer layers of the plasma, right at the torch rim (5 mm). With increasing height, more and more oxygen has been entrained and has travelled further towards the centre.

3.4.2 EXCLUSION OF AIR

A first attempt to eliminate this entrainment was made by simply placing a short piece of quartz tube on top of the torch. It was found that this crude device was not efficient for the exclusion of air and also blackened very rapidly with carbon deposits when aspirating xylene, making the observation of analyte lines impossible. Different shapes and sizes of "add-on" extensions were then tested to determine whether the deposition of carbon could be prevented. It was found that such a torch extension had to be sealed very carefully to the torch in order to completely exclude any oxygen. Figure 24 is a schematic drawing showing how the extensions were connected to the torch. The extension shown in Fig. 24 is a straight bore quartz tube. With that extension in place the plasma changes its

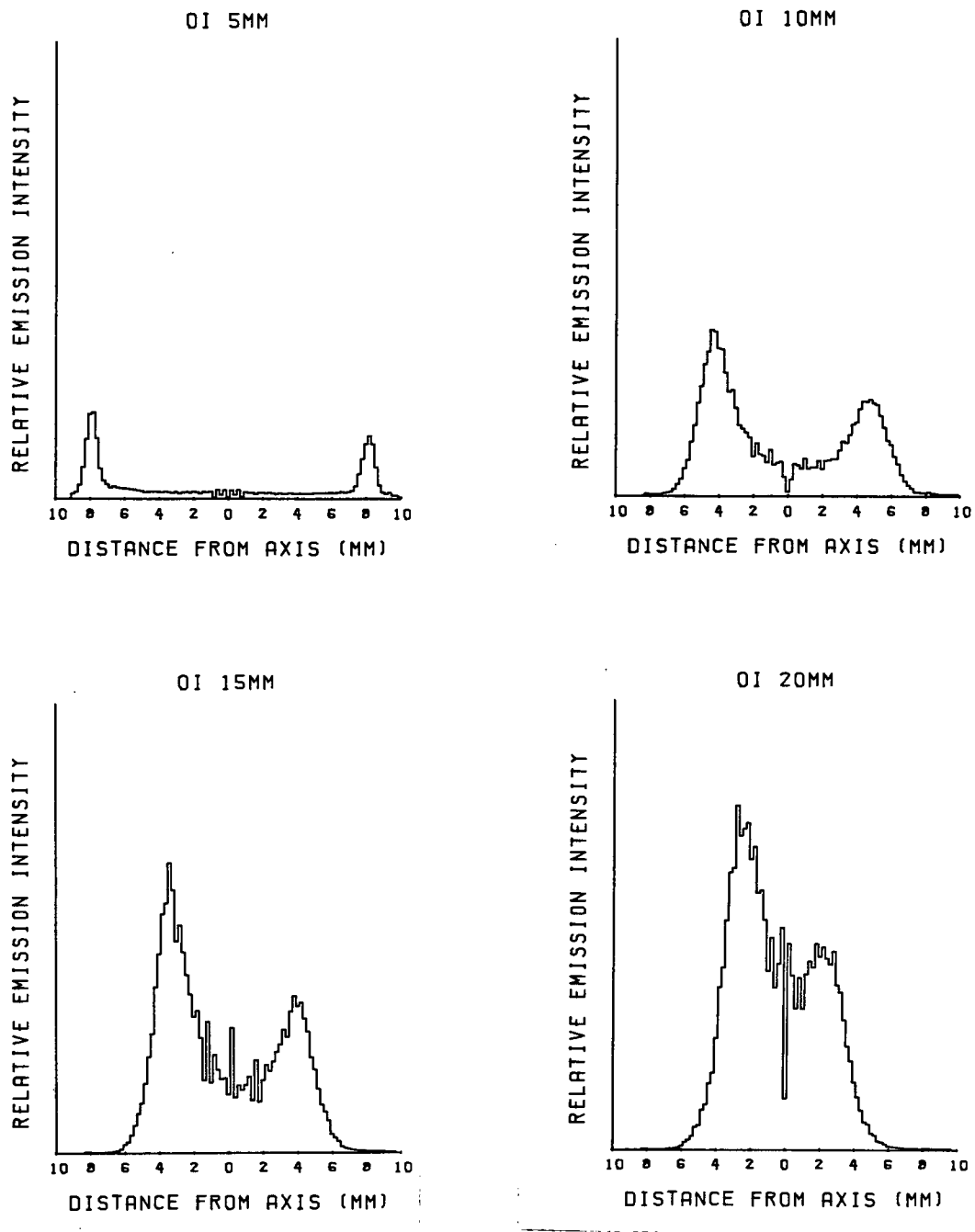


Figure 23. Radial OI emission profiles.

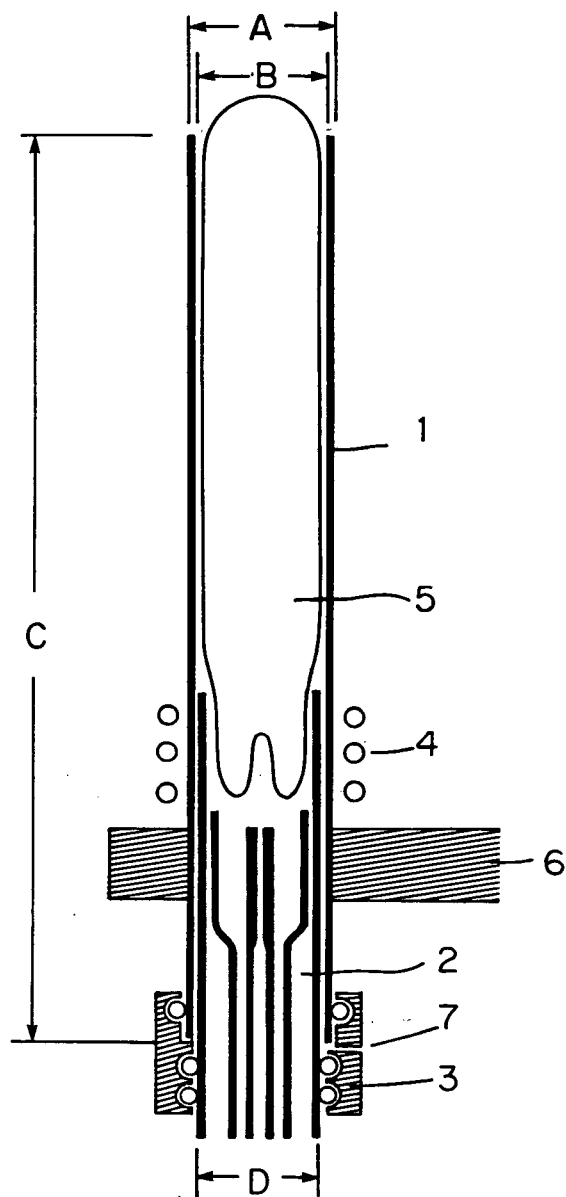


Figure 24. Torch and connector shown with straight tube extension in cross sectional view. 1. Straight tube extension. 2. Torch. 3. Connector (Teflon) with rubber O-rings. 4. Load Coil. 5. Plasma as depicted by its envelope of green C_2 emission. 6. Torch holder. 7. Bore for additional sheathing argon (see text). Dimensions: A: 25.5 mm B: 22 mm C: 150 mm D: 20.37 mm.

appearance. The visible tailplume normally only about 3 - 4 cm high persists up to about 1 cm beyond the top of the extension. Green emission caused by C_2 is no longer restricted to below the torch rim but extends to the top of the extension. Violet CN emission is no longer observed. Although the plasma changes its appearance with the extension, it was found that its excitation characteristics did not change significantly. An exact, spatially resolved evaluation, however, is not possible because the extension alters optical characteristics.

The straight tube extension of Fig.24 was found to be very effective for the exclusion of atmospheric gases. However, it is very susceptible to the buildup of carbon deposits. When aspirating xylene, the extension tends to blacken at about three cm above the load coil within a few minutes. After initial formation, the carbon deposits spread upwards and downwards, eventually coating the entire tube. The different extensions which were tried are depicted in Fig. 25. Removing the wall from the plasma as in Figs. 25a and 25b causes the plasma to flicker badly and oxygen exclusion is not complete. Narrowing the top as in Fig. 25c made the extension efficient, but the wall got blackened very rapidly. The solution finally arrived at, was to use the straight tube as extension and to isolate the plasma from the wall of the extension by introducing argon

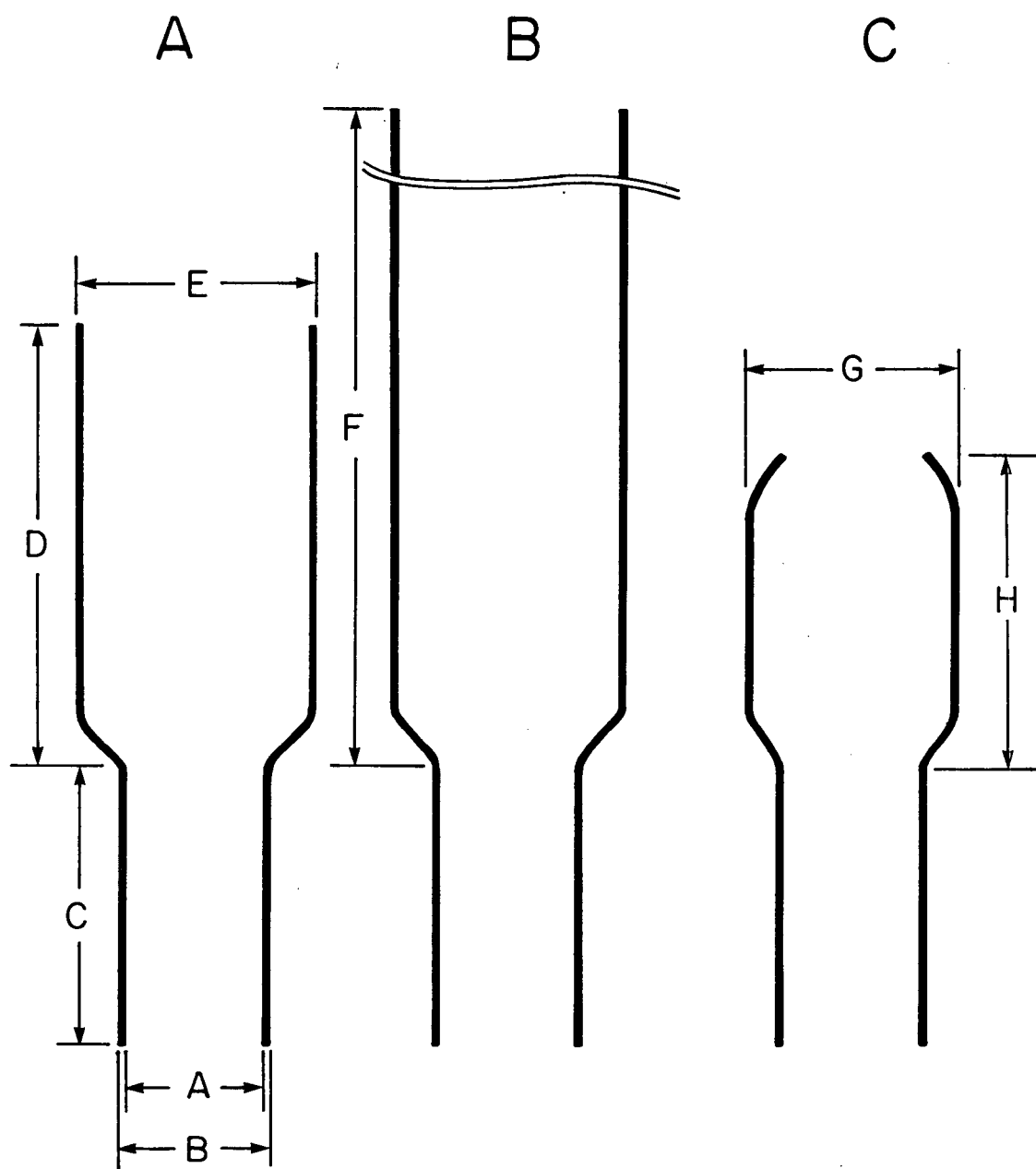


Figure 25. Cross sectional view of torch extensions.
Dimensions: A: 22 mm B: 25.5 mm C:45 mm D: 70 mm E: 38 mm
F: 150 mm G: 33 mm H: 45 mm

(approximately 2 l/min) tangentially through a hole in the connector (see Fig. 24) into the gap between torch and extension. This arrangement keeps the lower half of the extension free of carbon deposits when aspirating xylene. No problems in operation occurred, although occasional sputtering of the plasma was observed. The reason for this could not be found. Fig 26. shows radial profiles of C2 acquired with that set up showing C2 at locations where not normally present. The presence of C2 close to the wall of the extension explains also the sensitivity of it to soot build up since an other dicarbon molecule, acetylene, is found to be a major precursor for the formation of soot [60].

3.4.3 AMBIENT OXYGEN AND NITROGEN

Oxygen and nitrogen emission was observed even in the pure argon plasma, when entrainment of atmospheric gases was prevented, so those elements must be present as impurities in the argon tanks. These amounts were found to vary as different tanks were used. It was also found, that xylene, even of spectroscopic grade, contains oxygen in some form. Treatment with molecular sieves (3 A) and bubbling nitrogen through the solvent for several hours reduce this oxygen contamination effectively, so that this contribution is

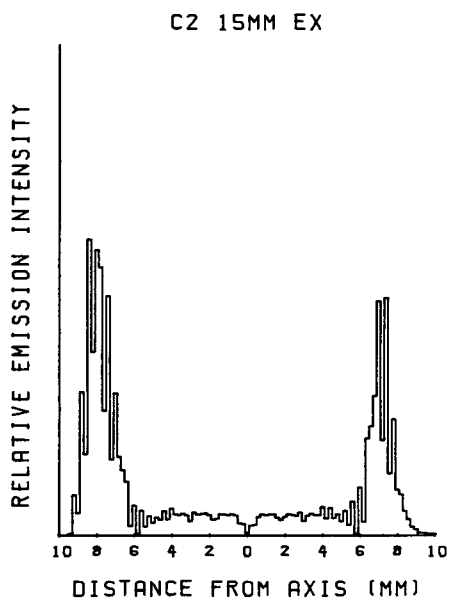
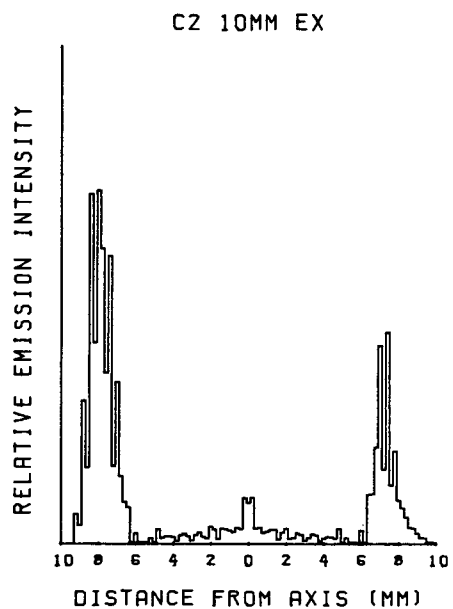
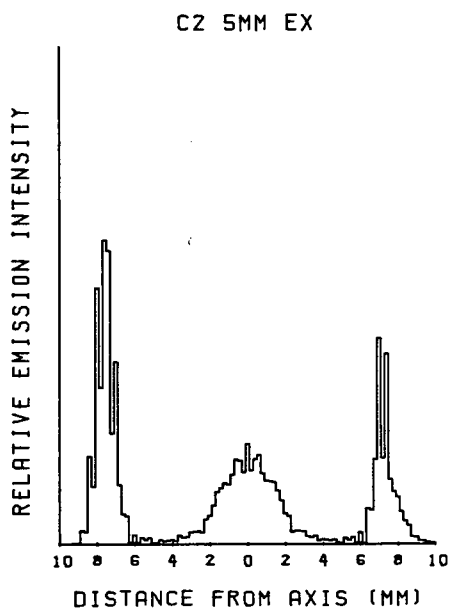


Figure 26. Radial C₂ emission profiles with straight tube extension in place.

small compared to the amount found in the pure argon plasma itself. Therefore all xylene used for the subsequent determinations was treated that way. No increase in ambient nitrogen emission could be detected when xylene was aspirated.

3.4.4 OPERATING CONDITIONS AND VIEWING REGION

Rf input power, gas flow rates and viewing height were optimized for maximum intensity with the adopted extension in place.

- Rf input power: Emission intensities were found to increase strongly with load power, therefore it was left at the original 2 kW.

- Plasma and auxiliary argon flow: Both flow rates did not influence the emission intensity significantly and were left at the original 12 and 2 l/min.

- Nebulizer argon flow rate and viewing area: Because the tip of the green C_2 core in the nebulizer channel rises with nebulizer argon flow rate it was expected, that the nebulizer gas flow rate and viewing height would be interdependent. Emission intensities versus viewing height along the center of the plasma were therefore acquired for several nebulizer gas flow rates. Vertical oxygen emission intensity profiles are given in Figure 27. The peak

intensity was found at a viewing height of 3 mm for all flow rates except 0.4 l/min. A flow rate of 0.5 l/min gave maximum peak emission intensity. A similar plot for sulphur (Fig. 28) shows highest emission intensity for a somewhat higher viewing height and nebulizer gas flow rate. A quick survey for nitrogen suggested, that the best viewing height for that element is also found in the region of a few mm above the load coil.

Because the radial intensity profiles (section 3.3.2.2) suggest, that most nonmetal emission at low heights does not originate from the central channel, lateral profiles of SI emission intensity were obtained (Fig 29) to check whether observation off the central axis was desirable. Only a slight dip at 5 mm was found, and observation was made at the centre.

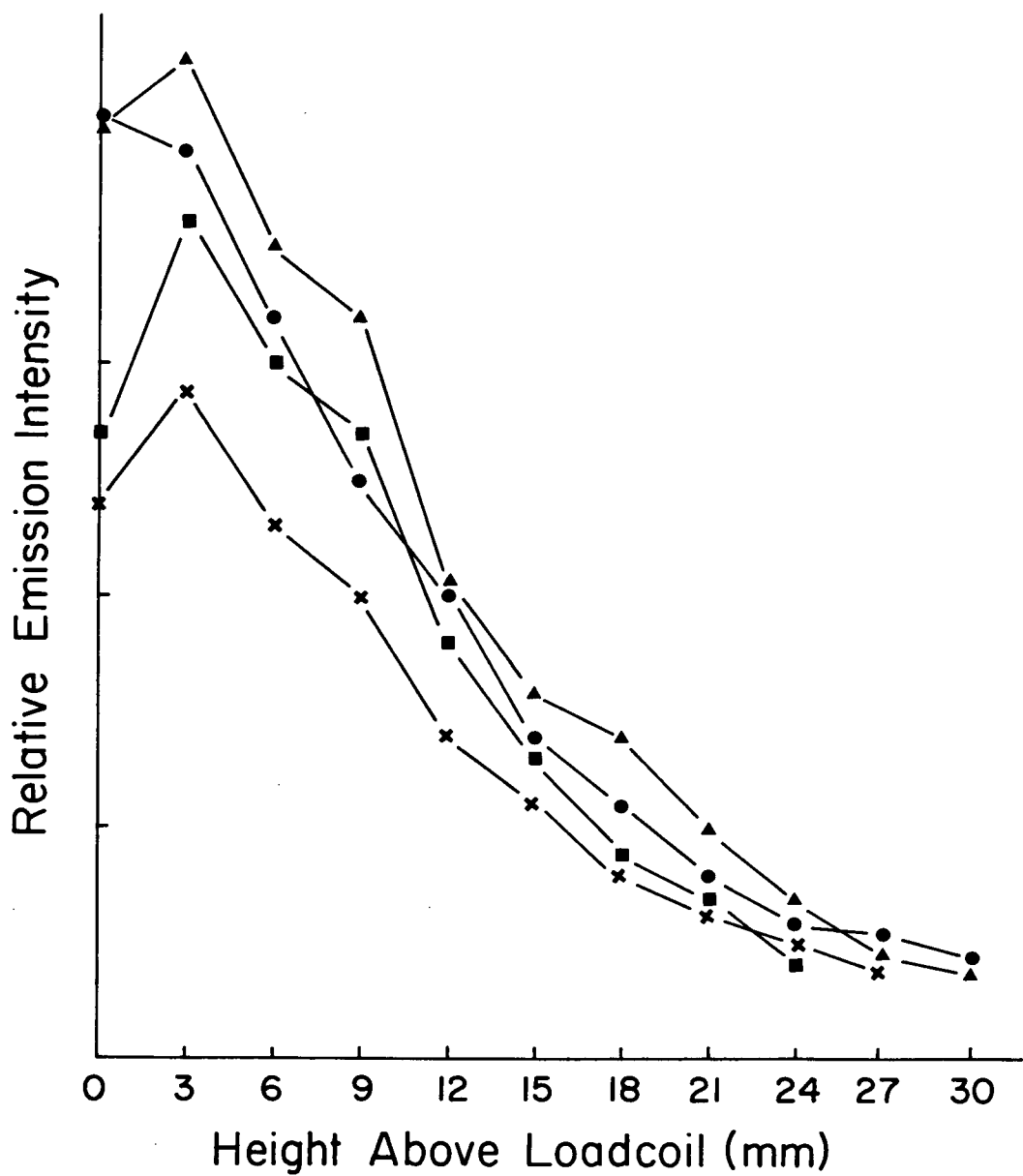


Figure 27. Oxygen emission intensities along the central axis when xylene mixed with octanol (1 % oxygen) aspirated. Straight tube extension in place. Four different nebulizer gas flow rates were employed.

● - 0.4 l/min ▲ - 0.5 l/min ■ - 0.6 l/min × - 0.7 l/min

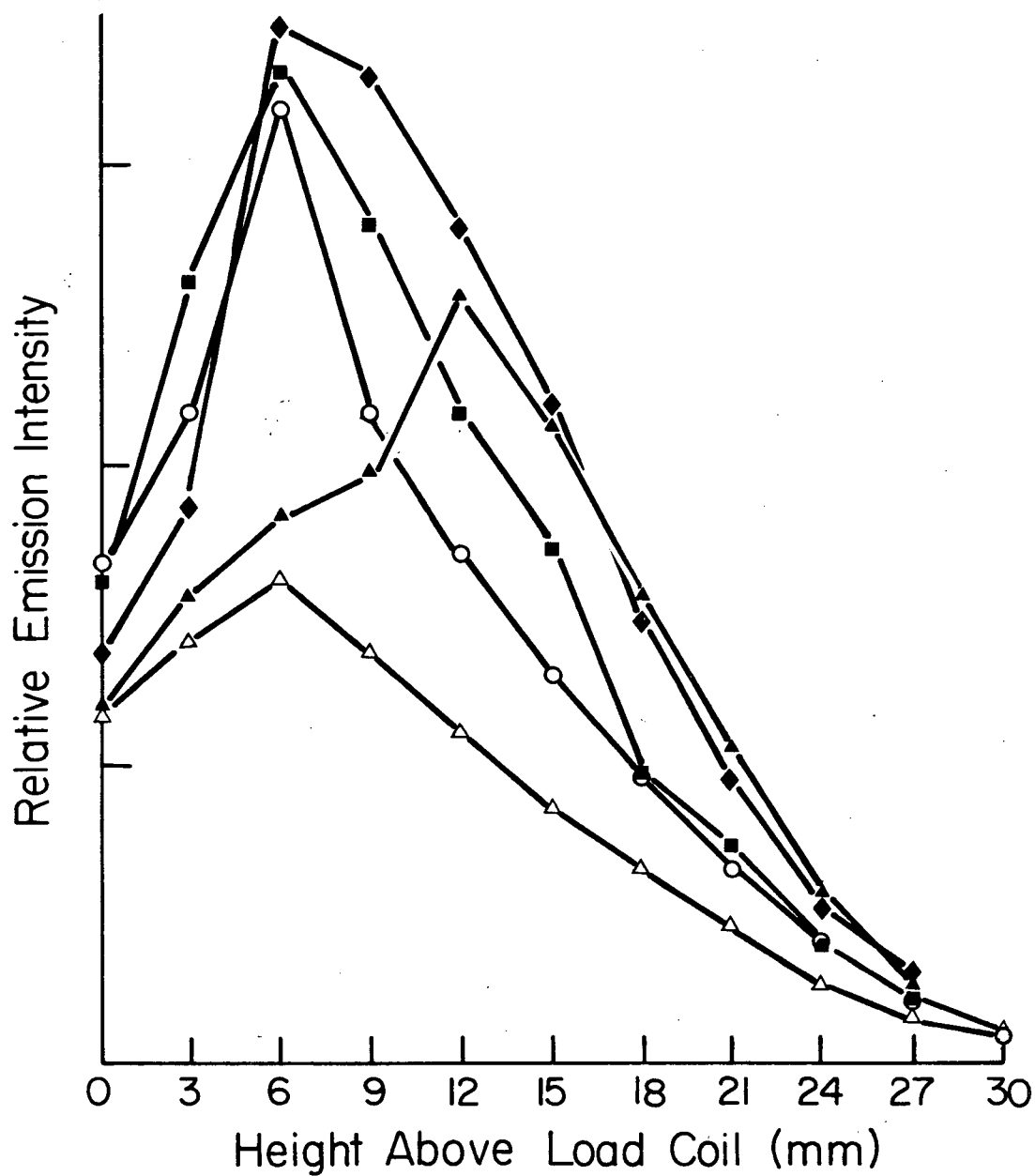


Figure 28. Sulphur emission intensities along the central axis when diphenyldisulfide in xylene (1 % sulphur) aspirated. Five different nebulizer flow rates were employed.

Δ - 0.4 l/min ○ - 0.5 l/min ■ - 0.6 l/min
 ◆ - 0.7 l/min ▲ - 0.8 l/min

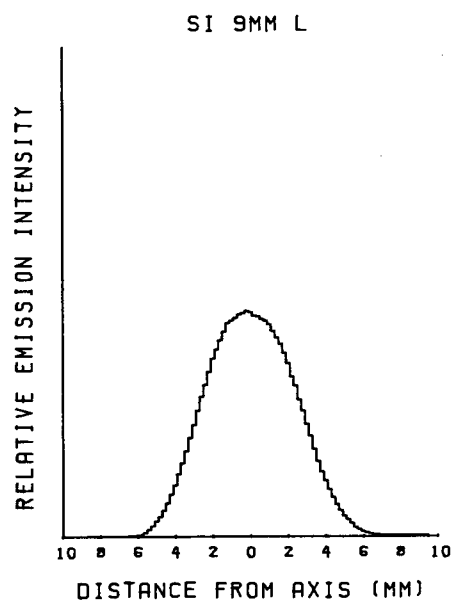
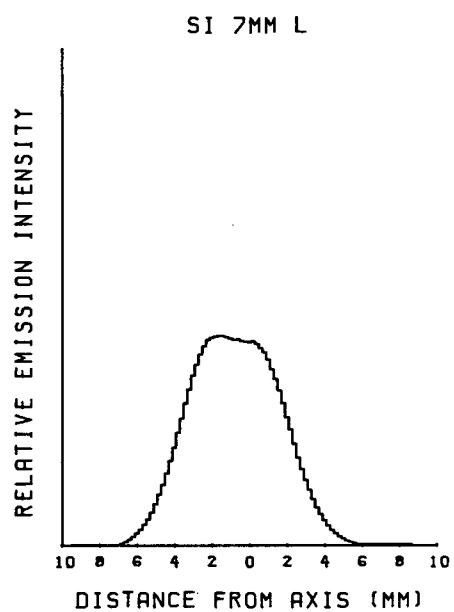
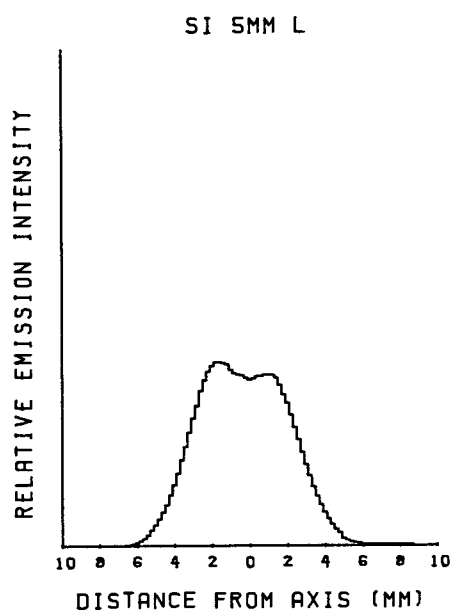


Figure 29. Lateral SI emission profiles.

3.4.5. CONTROLLED SAMPLE DELIVERY

The use of a pump to control sample flow to the nebulizer was attempted. This promises to reduce interference effects due to inconsistent delivery rates because of different physical properties of samples (especially viscosity) and allows an optimization of sample delivery rate (and nebulizer efficiency) independent from the nebulizer gas flow rate. Signal intensities were found to increase strongly with delivery rate. At relatively high delivery rates (up to 3 ml/min) the time to reach a stable signal after changing a sample became very long (approximately 5 min) due to memory effects in the spray chamber. It was also found, that the capillary tips of concentric nebulizers tend to get damaged when force-fed at rates greater than the free uptake rate. For these reasons controlled sample feed was not generally employed.

3.4.6. CONCLUSIONS

The torch extension allowed us to establish an optimal viewing height for oxygen and to evaluate the extent and spatial dependance of entrainment of atmospheric gases and to distinguish ambient oxygen and nitrogen in the solvent and argon supply.

Compromise operating conditions adopted for the

determination of the three elements were: rf input power 2 kW, plasma gas flow rate 12 l/min, and auxiliary gas flow rate 2 l/min. The nebulizer gas flow rate was set to 0.5 l/min. The visible C₂ core extends to about 2 mm above the load coil for this flow rate. The sulphur line was usually measured 6 mm above the load coil and the oxygen and nitrogen lines 3 mm above the loadcoil, which was 2 mm below the torch rim. Determination of oxygen and nitrogen could be done without the torch extension, because the best viewing height for these elements was found below the torch rim, where there is no interference from the atmosphere.

The fact that the peak emission intensities of the two nonmetals were found low in viewing height originating mostly from the toroidal region, as shown in section 3.3.2.2 for sulphur, agrees well with data presented for other neutral high energy emission lines [62]. An explanation is attempted as follows.

Ionization of the nonmetals is unlikely, because of their high ionization energies, and no emission from ionic O, N or S has been detected for the Ar-ICP [21,22,28]. Therefore, the decrease of nonmetal emission intensity with viewing height above the height of peak intensity cannot be caused by gradual ionization, but must be due to a decreasing fraction of the nonmetal being excited. This

agrees with the fact, that in the toroidal region, where most of the nonmetal emission originates, the excitation temperature decreases with height.

The optimal viewing height is probably determined by two mechanisms which counteract each other. With increasing height more and more of the analyte diffuses into the hot toroidal region where it can get excited to the upper state level of the near IR emission line. The temperature in the toroidal region however decreases steadily with height so that the fraction of present analyte species which gets excited decreases as well. This does explain as well, why the best viewing height for sulphur is higher than for oxygen because of the lower upper state level and therefore higher fraction of sulphur which is presumably excited.

3.5 ANALYTICAL PERFORMANCE

3.5.1 RESPONSE FROM DIFFERENT COMPOUNDS

Whether the nonmetal emission intensity was dependent on the sample composition was investigated by comparing the response of a series of solutions all of which contained the same amount of the nonmetal but in form of a different compound. Solutions containing 1 % oxygen, 3 % nitrogen or 1 % sulphur in xylene were thus prepared and the respective nonmetal emission intensity measured. It was found that when the solutes containing the nonmetal, had boiling points lower than 200°C, a dependence on the volatility of these compounds was exhibited. The nonmetal emission intensity was higher, the lower the boiling point of the nonmetal parent compound.

3.5.1.1 VOLATILE SOLUTES

Table IV gives a list of the volatile solutes containing the nonmetals which were tested and their response factors. In Fig. 30 the emission intensities of the nonmetals are plotted as a function of the boiling point of the parent compound. Note, that the intensity scale is logarithmic, therefore this effect is very pronounced, a decrease of 50°C in boiling point causes roughly a

TABLE IV
Volatile Solutes

	<u>Compound</u>	<u>B.P.</u> <u>(°C)</u>	<u>Relative</u> <u>Response</u>
Oxygen containing compounds as 1 % O in xylene			
01	Dimethylsulfoxide	189	1.5
02	2-Octanol	177	1.4
03	2-Octanone	170	1.8
04	Acetic Acid Anhydride	139	3.3
05	Isopropanol	82	36
06	Methyl-ethyl-ketone	80	21
07	Methanol	65	71
08	Acetone	56	43

Nitrogen containing compounds as 3 % N in xylene

N1	Di-n-hexylamine	192	1.5
N2	N,N-Dimethylacetamide	165	1.5
N3	Cyclohexylamine	134	2.8
N4	Pyridine	115	4.6
N5	Isobutyronitrile	107	8.3
N6	Triethylamine	89	9.8

Sulphur containing compounds as 1 % S in xylene

S1	Dimethylsulfoxide	189	1.14
S2	1,3-Propanedithiol	169	1.07
S3	Sulphur-I-chloride	138	1.8
S4	Tetrahydrothiophene	119	2.6

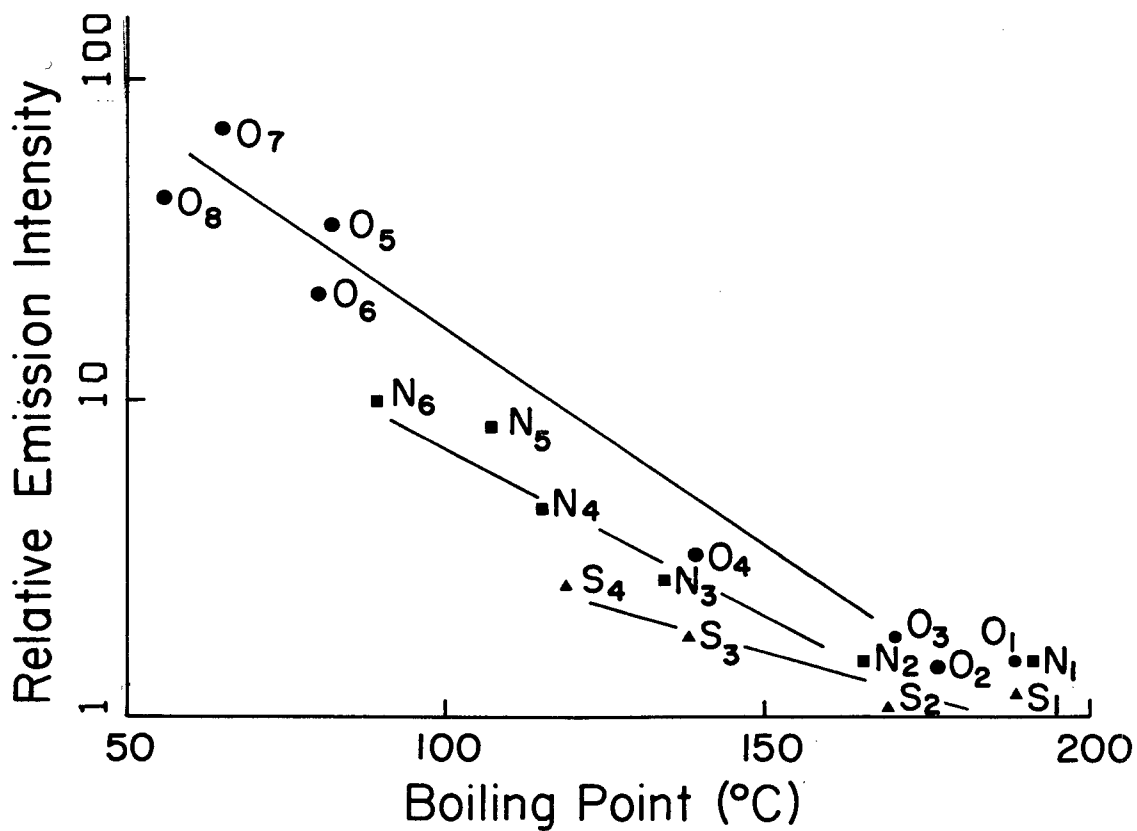


Figure 30. Nonmetal emission intensity as a function of the boiling point of the solutes. Compounds and boiling points see Table IV.

fivefold increase in emission intensity.

Whether this was caused by an effect in the nebulizer chamber, was then tested in the following manner. The waste effluent from the spray chamber was reintroduced into the nebulizer using the pump system. The delivery rate was 3 ml/min and a total volume of about 10 ml was cycled through the assembly. Four compounds with widely differing boiling points (2-octanol - 177 °C, isopropanol - 82 °C, methanol - 65 °C and acetone - 56 °C) were added to xylene to yield 1 % oxygen each. The plots of oxygen emission intensities versus time in Fig 31 show that the lower boiling compounds gave higher intensities at first and then decayed rapidly, whereas the less volatile ones started lower but remained at relatively high levels for longer. Therefore, redistribution is the cause of this interference. The nonmetal parent compound becomes enriched in the aerosol stream to the torch while the waste effluent loses that substance. The most likely explanation for this effect is that the volatile compounds evaporate from the aerosol droplets and reach the plasma as vapour. The amount which evaporates, is of course dependent on the boiling point of the compound. However, the points in Fig. 30 do not fall on smooth curves. Therefore, besides the boiling points of the solutes, other compound properties must exert an influence. Because the standards are of

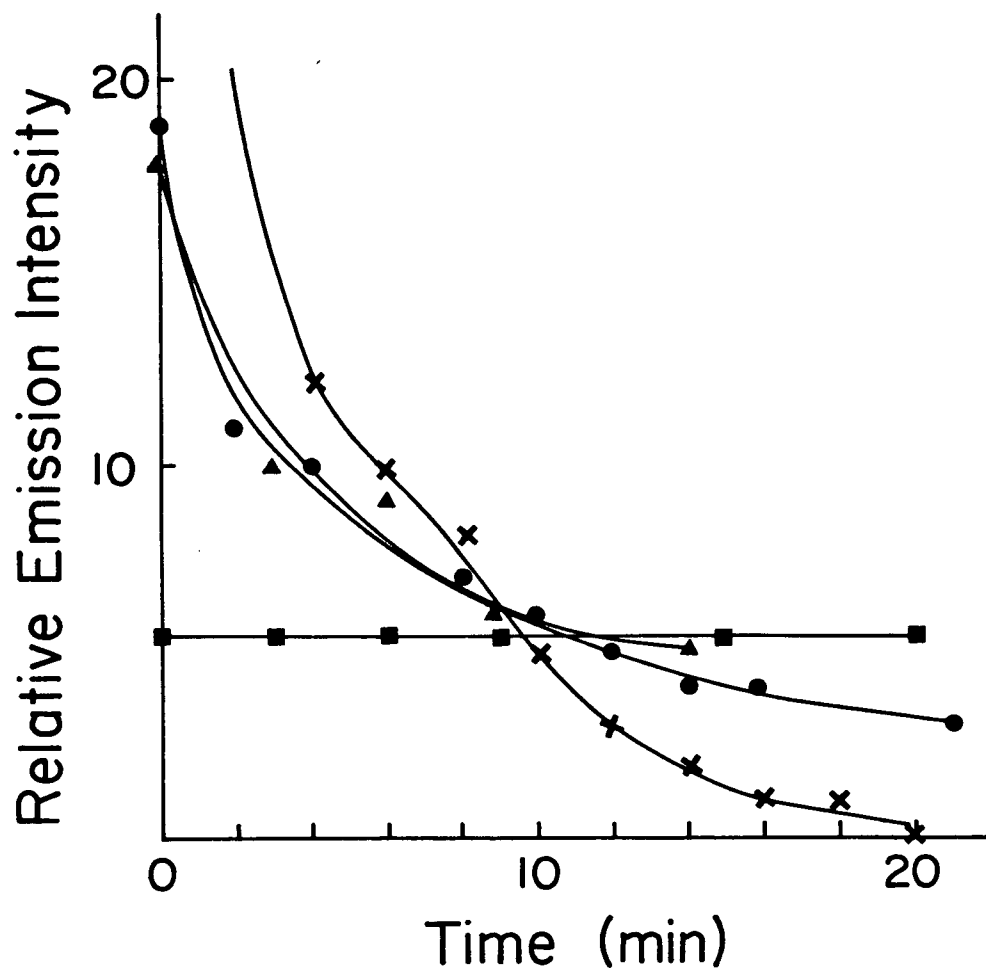


Figure 31. Decay of oxygen emission intensities when sample recycled from the spray chamber drain outlet back through nebulizer. 1 % oxygen in xylene. x- methanol ●-isopropanol ▲ -acetone ■- 2-octanol.

different molecular structure they contain different percentages of the nonmetal element and accordingly different amounts of the substances were added to xylene. The vapour pressure depends not only on the boiling point but also on the concentration and the nature of the volatile species. The amount of sample reaching the plasma as vapour contains varying amounts of the nonmetal again in dependence of the molecular structure.

3.5.1.2 NONVOLATILE SOLUTES

Compounds with boiling points higher than 200°C did not show a detectable volatility enhancement effect. Table V gives a list of nonvolatile compounds which were tested. Again, the solutions contained 1 % oxygen, 3 % nitrogen or 1 % sulphur in xylene. Problems occurred with the solutions of some of the solids, because they tended to clog the capillary of the concentric nebulizer.

TABLE V

Nonvolatile Solutes

<u>Compound</u>	<u>B.P.</u> <u>(°C)</u>	<u>Relative</u> <u>Response</u>
Oxygen containing compounds as 1 % O in xylene		
Nitrobenzene	210	0.96+/-0.07
3-Phenyl-1-propanol	235	0.97+/-0.07
Phenol	solid	0.96+/-0.07
8-Hydroxyquinoline	solid	1.05+/-0.07
N-Methyl-N-nitroso-p- -toluenesulfonamide	solid	1.04+/-0.07
Nitrogen containing compounds as 3 % N in xylene		
Nitrobenzene	210	1.1+/-0.1
Diphenylamine	solid	0.9+/-0.1
Bipyridine	solid	1.0+/-0.1
Azobenzene	solid	0.9+/-0.1
N-Methyl-N-nitroso-p- -toluenesulfonamide	solid	1.0+/-0.1
Sulphur containing compounds as 1 % S in xylene		
Diphenyldisulfide	solid	1.00+/-0.02
Diphenylsulfoxide	solid	0.99+/-0.02
N-Methyl-N-nitroso-p- -toluenesulfonamide	solid	1.01+/-0.02

Note, that in Fig. 30 the nonmetal emission intensities of these nonvolatile standards would appear as unity, i.e. fall on the zero line of the log scale. The intensities of the volatiles therefore are given as multiples of the nonvolatile response.

It was found, that when nonvolatile samples were determined, the time to reach a stable signal after the switchover of samples is much shorter than for volatile samples. This is consistent with the above described volatility effect when one assumes that vapour and small droplets are flushed from the nebulizer less rapidly than droplets. This observation also explains the particularly long switchover times experienced with the pump delivery system, because only volatile compounds had been used for those experiments.

3.5.2 AMOUNTS OF AMBIENT OXYGEN AND NITROGEN

The amounts of ambient oxygen and nitrogen (from the solvent and the argon supply) were typically equivalent to 2.7 % oxygen and 8.1 % nitrogen aspirated as nonvolatiles in xylene.

3.5.3 SIGNAL TO BACKGROUND RATIOS

Signal to background ratios were determined as: 0.064, 0.0057 and 1.4 for oxygen, nitrogen and sulphur respectively, for an analyte concentration of 1 % nonvolatiles. Ambient amounts of oxygen and nitrogen were counted as background.

3.5.4 DRIFTS

Drifts of signal intensities were found to affect the detection of all three elements. In all three cases the uncertainty of the measurements introduced by these drifts exceeded random noise fluctuations of the signal.

A major contribution was a drift of the continuum background intensities. This is not surprising considering the signal to background ratios. Background intensities were found to increase by 1.5 % and 2.8 % in one hour at the oxygen and sulphur lines respectively. This amounts to the

equivalent of the intensities of 0.2 % and 0.02 % measured oxygen and sulphur respectively of nonvolatile solutes. The background at the 820 nm nitrogen line was found to decrease by 0.6 % per hour which is equivalent to about 1 % measured nitrogen. The ambient oxygen intensity (from impurities in xylene and the argon supply) was found to decrease over time to an amount slightly exceeding the increase of the background, whereas no drift of ambient nitrogen was detected.

Intensities due to oxygen and sulphur contained in samples appeared to be rather stable. Corresponding data for nitrogen is not available because limited work was done with this element.

The use of a photodiode array allowed us to monitor and correct for these drifts as far as background was concerned, by measuring the intensity of the background close to the analytical line. A suspected reason for these drifts was insufficient thermal stability of the nebulizer torch assembly. The temperature in the plasma box was found to rise to about 50°C when the ICP was in use. Heating of the nebulizer assembly must change transport efficiencies and the implemented cooling of the spray chamber was not sufficient to overcome this problem. Background intensities decreased in all three spectral regions with sample load compared to the pure argon plasma. Therefore, an increase in

the background points to a decreasing nebulizer efficiency. However, this is not consistent with a decreasing background intensity found at 820 nm.

Drifts are not unusual in ICP emission spectroscopy and pose a problem also when aqueous samples are analyzed. Lorber et al. have reported a drift of metal emission intensities of up to 5 % within 30 minutes [63].

3.5.5 DETECTION LIMITS

OXYGEN:

The emission intensity for 1 % oxygen as nitrobenzene, a nonvolatile standard, was measured. The integration time of the photodiode array was set to 2.5 s which yielded approximately 75 % saturation of the array at the analyte line. The noise of the ambient oxygen concentration was determined as the standard deviation of 20 consecutive readings of the array. The drifts did not influence these readings because of the short time duration of the experiment. The concentration equivalent to three times the noise of the ambient concentration, the detection limit, was determined as: 1.0 g/l oxygen in xylene.

NITROGEN:

The detection limit for nitrogen was determined similarly using the 821 nm line, with 3 % nitrogen as nitrobenzene in xylene and an integration time of 3.0 s. It was found to be 16 g/l nitrogen in xylene. The detection limit for nitrogen in water could not be determined, because it is higher than 50 g/l.

SULPHUR:

The detection limit for sulphur was determined as the emission intensity equivalent to three times the noise of the background. Solutions of 0.125 % sulphur as diphenyldisulfide in xylene and 0.5 % sulphur as sulfosalicylic acid in water were used to measure the line intensities. The detection limits were determined as: 120 mg/l sulphur in xylene and 390 mg/l sulphur in water. The detection limit in water is poorer because the transport efficiency for xylene is better, and the optimization was done for xylene aspiration.

Table VI summarizes the detection limits and gives the reported VUV values for xylene for comparison.

TABLE VI

<u>Nonmetal</u>	<u>Solvent</u>	<u>Detection Limits</u>	
		<u>NIR (PDA)</u>	<u>VUV (PMT)</u>
Oxygen	Xylene	1.0 g/l	
Nitrogen	Xylene	16 g/l	100 mg/l [32]
	Water	>50 g/l	
Sulphur	Xylene	120 mg/l	0.05 mg/l [33]
	Water	390 mg/l	

When comparing the NIR- and VUV detection limits, it has to be considered, that the PMTs are inherently photon amplifiers, while the PDA is not. Depending on the nature of the noise determining the detection limit, the use of a PMT or an intensified PDA for the detection of the NIR lines might improve those detection limits by perhaps three orders of magnitude. However, all PMTs have a sharp drop of sensitivity at 900 nm, so that their sensitivity for the 920 nm sulphur line can be expected to be relatively poor. Detection limits for PMTs could not be determined, because of a lack of necessary equipment.

The measured detection limits provide only a rough guideline. An increase of integration time or signal averaging decreases random noise and improves detection limits. Then, an optimization of working conditions (flow rates, load power and viewing height) for signal to noise

ratio most likely would improve the figures as well. A proper optimization of the working conditions is not trivial because it is not clear how the different parameters interact. Simply changing one parameter at a time does not necessarily lead to an optimum. For this reason, a mathematical aid, the "Simplex Method" is therefore sometimes used to optimize ICP working conditions [64].

Not surprisingly, the detection limits follow the order of the upper state energy levels of the respective lines, which are: 7.9 eV for sulphur, 10.7 eV for oxygen and 11.8 eV for nitrogen [21,22,28]. An estimate of xylene detection limits for other nonmetal lines in the near infrared could be made on this basis.

3.5.6 WORKING CURVES

OXYGEN:

Working curves for two "nonvolatile" (nitrobenzene and 3-phenyl-1-propanol) and two "volatile" (dimethylsulfoxide and acetic acid anhydride) oxygen containing compounds are shown in Fig. 32. The nonvolatile substances gave identical and linear curves, while the volatile compounds still produced linear curves but at higher overall intensities.

NITROGEN:

Working curves for nitrogen were not acquired because of the relatively low sensitivity.

SULPHUR:

Working curves for both diphenyldisulfide and dimethylsulfoxide were found to be linear and are presented in Figure 33.

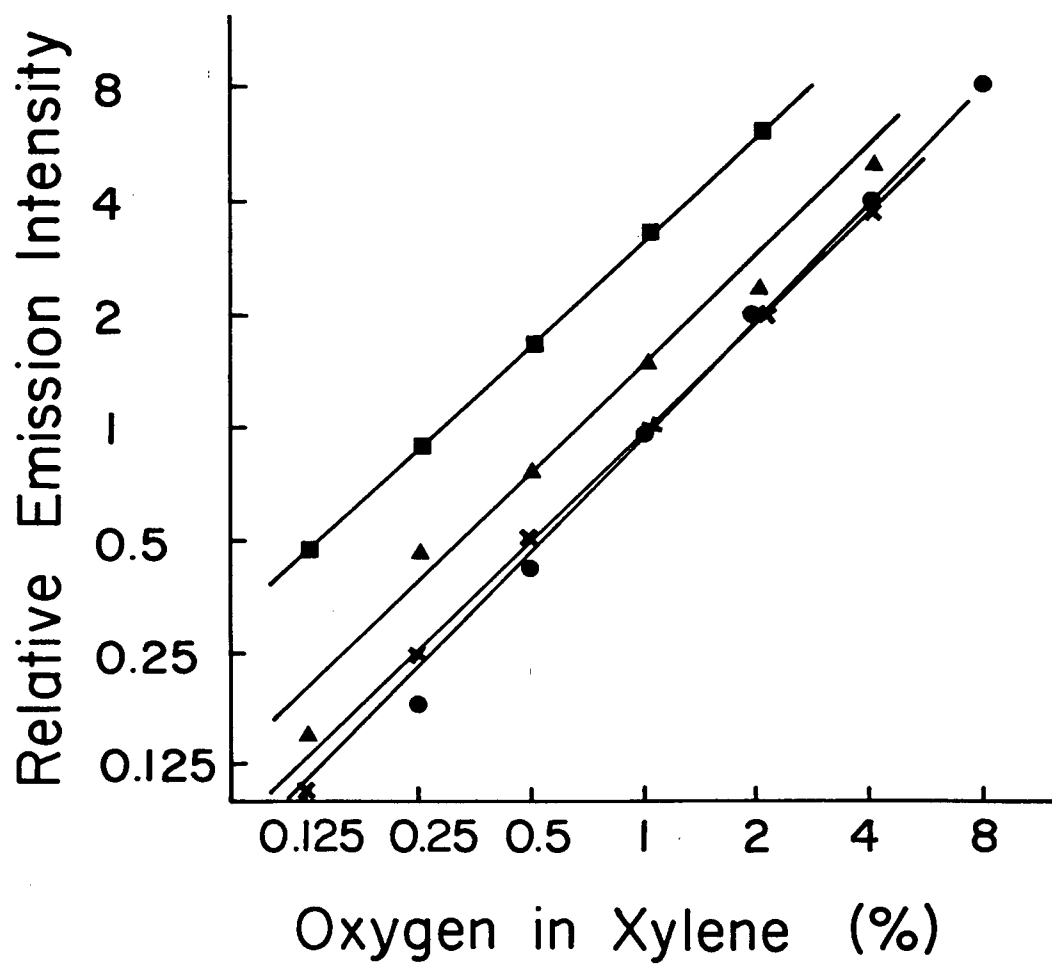


Figure 32. Working curves of oxygen in xylene.
 ● - Nitrobenzene, ✱ - 3-Phenyl-1-propanol
 ▲ - Dimethylsulfoxide, ■ - Acetic acid anhydride

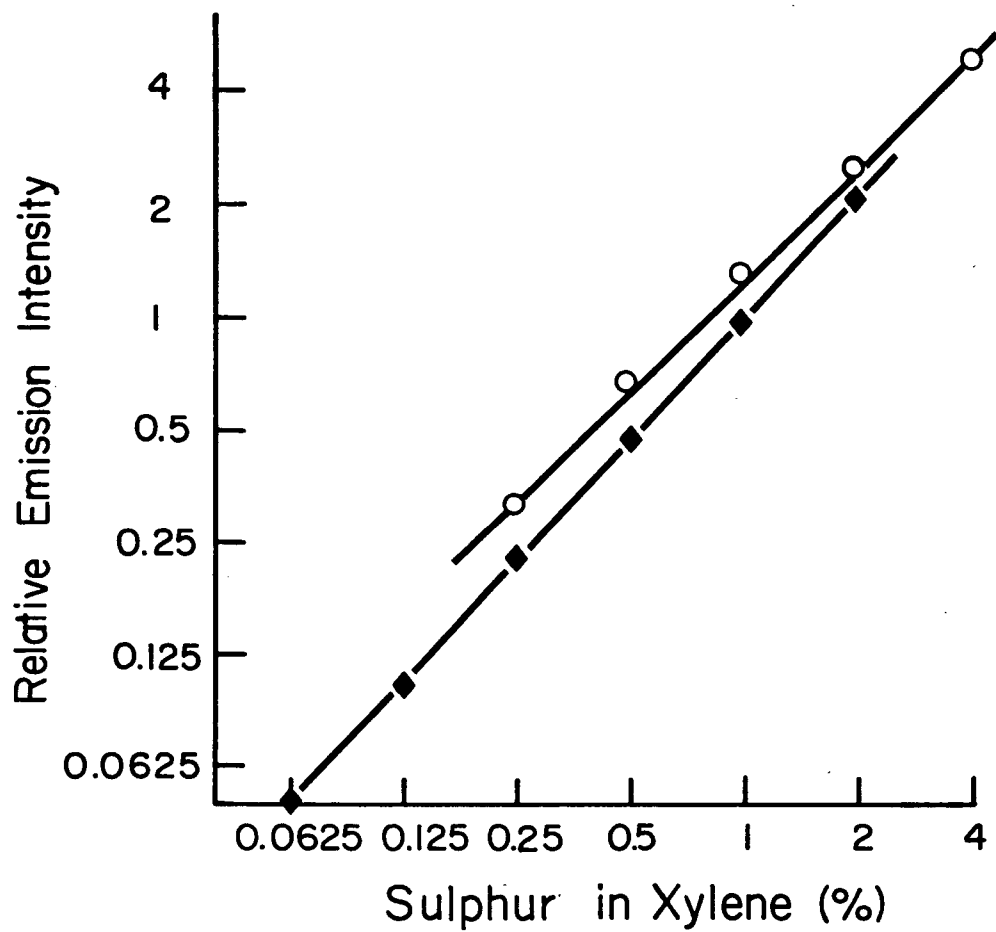


Figure 33. Working curves for sulphur in xylene.
◆ - Diphenyldisulfide, ○ - Dimethylsulfoxide

3.5.7 CERTIFIED OIL STANDARDS FOR SULPHUR

As a final check of the usefulness of the method for the determination of sulphur in oil samples, five certified standards from the US National Bureau of Standards (NBS) were tested.

The standards were diluted in xylene to minimize matrix effects due to different physical properties. However, the extent of this dilution was limited by the detection limit. A working curve from 0.0625 to 2 % sulphur as diphenyldisulfide in xylene was employed. The results are listed in Table VII.

TABLE VII

<u>Standard</u>	<u>Dilution</u> (g/50ml)	<u>NBS Samples</u>		<u>Accuracy</u>
		<u>% S found</u>	<u>% S certified</u>	
1620a	5	4.1+/-0.1	4.504+/-0.010	91 %
1621b	10	0.80+/-0.02	0.950+/-0.005	84 %
1622b	5	1.9+/-0.1	1.982+/-0.018	96 %
1623a	20	0.15+/-0.02	0.240+/-0.001	63 %
1624a	neat	0.065+/-0.02	0.141+/-0.002	46 %

As a comparison of the determined and the certified concentrations shows, the results were more accurate the more the standards were diluted (see last column in Table VII, accuracy = determined concentration in % of certified concentration). This strongly points to reduced transport efficiencies, i.e. reduced amounts of the samples reaching the plasma because of reduced delivery rates and / or nebulizer efficiency. Whether this was true was investigated in two ways.

Three of the samples were diluted by a higher factor to check whether a decrease in viscosity would increase the accuracy. The results are given below in Table VIII.

TABLE VIII

<u>Dilutions</u>				
<u>Standard</u>	<u>Dilution</u>	<u>% S found</u>	<u>% S certified</u>	<u>Accuracy</u>
1620a	5 g/50ml	4.1	4.504	91 %
	2 g/50ml	4.5		100 %
1621b	10 g/50ml	0.80	0.950	84 %
	5 g/50ml	0.88		93 %
1622b	5 g/50ml	1.9	1.982	96 %
	2.5 g/50ml	2.1		106 %

The accuracy improved in two cases and in one case it increased to above 100 %.

A second check was done by making a standard addition of sulphur as diphenyldisulfide. If all of the added sulphur is recovered, then the transport efficiency is the same as for the solutions used for the acquisition of the working curve and another matrix effect must take place. The results are given in Table IX.

TABLE IX
Standard Additions

<u>Standard</u>	<u>Dilution</u>	<u>Addition</u>	<u>Recovery of added Sulphur</u>	<u>Corrected accuracy (see text)</u>
1620a	5 g/50ml	0.50 %	94 %	97 %
	2 g/50ml	0.20 %	95 %	105 %
1621b	10 g/50ml	0.10 %	86 %	98 %
1623a	20 g/50ml	0.10 %	69 %	91 %

Comparing the accuracy of the sulphur determination in the certified samples (Table VII) with the recovery of the added sulphur (Table IX) shows that these match quite closely. When the recovery of the added sulphur is taken into account when calculating the sulphur concentrations in the standards, the errors become much smaller (see Table IX, corrected accuracy).

An other indication for a transport efficiency interference is the fact that the background intensities were higher when the diluted NBS samples were measured than when pure xylene was aspirated. Table X gives a list of these shifts.

TABLE X

Background Shifts at 920 nm when NBS standards in xylene are aspirated

<u>Standard</u>	<u>Dilution</u>	<u>Background</u> <u>(% BG)</u>	<u>Increase</u> <u>(as % S)</u>
1620a	5 g/50ml	4.6	0.033
	5 g/50ml+0.5 % S	4.5	0.032
	2 g/50ml	2.4	0.017
	2 g/50ml	1.0	0.007
1621b	10 g/50ml	3.1	0.022
	10 g/50ml+0.1 % S	2.8	0.020
	5 g/50ml	1.4	0.010
1622b	5 g/50ml	2.8	0.020
	2.5 g/50ml	1.7	0.012
1623a	20 g/50ml	3.8	0.027
	20 g/50ml+0.1 % S	4.6	0.033

Generally background intensities were found to decrease with aspiration rate when organic solvents were introduced.

Therefore, the higher the background intensity, the smaller the sample load in the plasma and the smaller the transport efficiency. Higher background intensities were indeed found for the less diluted NBS-samples. These shifts did not affect the measured quantities because the background was subtracted. This effect shows again the importance of monitoring the background intensity to obtain accurate results.

Generally, the results obtained compare well with the ones of Wallace [32] for similar NBS standards when diluted 1:100 with xylene using a VUV line at 180 nm. The accuracies for four standards were 97, 102, 85 and 102 % (Wallace did not compare the NBS samples with a working curve, but took the accuracy of the standard with the highest sulphur concentration as 100 % and measured the the response of the other standards on that particular sample).

The fact that the experimentally determined concentrations of sulphur in the NBS-samples did not exceed the certified values (except in one case) means that no volatility redistribution occurred. Therefore, the sulphur containing compounds in the oil samples must be of low volatility.

CHAPTER IV

CONCLUSION

Oxygen in an organic liquid was determined for the first time with ICP-OES. Near-infrared emission lines were used for the determination of that element as well as nitrogen and sulphur. The detection limits were determined as 1.0 g/l, 16 g/l and 120 mg/l in xylene for oxygen, nitrogen and sulphur respectively. These nonresonant emission lines proved therefore to be much less sensitive than the respective vacuum-ultraviolet lines. However, the detection of the near-infrared lines does not require a purging or evacuation of the light path.

Working curves for oxygen and sulphur were found to be linear. A working curve for nitrogen was not acquired because of the relatively low sensitivity for that element. Sulphur in certified oil standards (National Bureau of Standard) was determined successfully, even though the relatively low sensitivity caused some limitations. Not all of the samples could be diluted sufficiently to eliminate interference effects. Therefore the standard addition method had to be used. A dilution factor of about 10 is deemed to be necessary to eliminate interference effects with the NBS oil samples.

The entrainment of air into the plasma did not interfere with the determination of oxygen and nitrogen, because the highest emission intensities for these elements were found low in the plasma, where that effect is not significant.

Atomization of the organic samples in the plasma regions where atomic nonmetal emission originates was shown to be complete, so that an interference effect due to incomplete atomization is unlikely.

A comparison of a series of standards, disclosed a redistribution effect in the spray chamber when compounds with boiling points below 200 °C were used. This limits the use of the method to nonvolatile species or well defined systems such as element selective detection in liquid chromatography. The elimination of the spray chamber by nebulizing the samples directly into the plasma could overcome this limitation. Such a system was reported recently by Lawrence et al. [65]. Direct forced sample introduction into the plasma would also eliminate the need for matrix matching imposed by the various interference effects at the aerosol production step and very likely would improve the detection limits somewhat because the aspiration rate for xylene can be higher than the natural one. Detection limits probably could also be improved by assuring better diffusion of the sample into the low toroidal region

of the plasma by a low nebulizer gas flow rate in combination with forced sample feed.

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