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Journal of Chromatography A, 872 (2000) 119–140

JOURNAL OF
CHROMATOGRAPHY A

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Pulsed discharge emission detector: an element-selective detector for gas chromatography

W.E. Wentworth^{a,*}, Kefu Sun^a, De Zhang^a, Janardhan Madabushi^b, Stanley D. Stearns^b

^aChemistry Department, University of Houston, 4800 Calhoun Road, Houston, TX 77204-5641, USA

^bValco Instruments Co., Inc., P.O. Box 55603, Houston, TX 77255, USA

Received 24 June 1999; received in revised form 2 November 1999; accepted 4 November 1999

Abstract

An element-specific pulsed discharge emission detector (PDED) has been coupled directly with a vacuum UV monochromator so that vacuum UV atomic emissions from Cl, Br, I and S can be observed. The observed sensitivities for the elements are in the range of mid to high pg/s, but can be lowered by direct absorption of the radiation using a vacuum UV radiation photomultiplier tube. A helium pulsed discharge photoionization detector (He-PDPID) was run simultaneously in parallel with the PDED. The chromatograms recorded with the two detectors had similar peak shapes, suggesting that there is no peak tailing in the PDED. The ratio of the detector responses PDED/He-PDPID can be used for qualitative identification of the Cl-, Br-, I- or S-containing compounds. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Detection, GC; Pulsed discharge emission detector; Organohalogen compounds; Sulfur compounds

1. Introduction

In earlier publications [1,2] the pulse discharge emission detector (PDED) was described. In this mode of operation the GC effluent is passed directly into the discharge and the resulting emission spectra are observed. The emission spectra from the GC effluent are the result of excitation from excited and ionic species of helium that are formed in the discharge [3]. In the earlier publications on the PDED [1,2] the emission spectra were analyzed using a McPherson Model No. EU-700 monochromator in a conventional manner. The PDED was simply placed as close as possible to the entrance slit and the emission spectra was recorded using an EMI

IP21 photomultiplier. In this publication we describe a completely different configuration whereby we take advantage of the unique shape of the discharge and use it directly as the optical image rather than pass the emission through an entrance slit. This configuration gives sufficient optical resolution and enhances the recorded emission intensity such that the analysis generally falls in the low picogram range. To the best of our knowledge this direct use of the emission source as the optical image has not been described previously.

In the earlier publications using the PDED [1,2] the continual exposure of the discharge to the GC effluent generally caused a carbon deposit to be built up on the discharge electrodes. This resulted in an atomic carbon emission which contributed to the background and reduced the sensitivity of the analysis. This could be overcome by periodic “cleaning”

*Corresponding author. Tel.: +1-713-7432-727; fax: +1-713-7432-709.

by passing oxygen through the discharge for an extended period of time, typically overnight. However, if a continual operation of the PDED were desired, this periodic cleaning of the discharge would interfere with the operation. In this publication we describe a procedure whereby the electrodes are “blanketed” with pure helium which prevents the GC effluent from contacting the discharge electrodes, thus preventing the carbon deposits. With this design the analysis can be performed continuously without interruption.

A third unique feature to this new PDED is to work in the wavelength region starting at 60 nm, typically referred to as the vacuum UV region, but without using a vacuum. The purpose of the vacuum is to make the gaseous medium in the monochromator transparent to this short wavelength radiation.

Since helium is transparent above the resonance line at 58.8 nm, an alternative is to purge the monochromator with pure helium. Of course it is important to have very pure helium since trace impurities could absorb significantly in a pathlength of 0.2 m. In the development of the Helium Ionization Detector it was necessary to develop techniques to highly purify the helium using extremely efficient getters. This technology has been carried over to this work and the highly purified helium appears to be sufficiently transparent. Emission spectra obtained with the helium purged monochromator are similar to those obtained with an evacuated monochromator. One additional advantage of using the helium purged monochromator is that the PDED can be interfaced directly to the monochromator without using a window. This allows spectral measurements below 120 nm, the cut off wavelength for a MgF_2 window. In our work this is important since we can directly observe the Hopfield emission from He_2 which extends from 60 nm to 100 nm.

Purging a monochromator with a transparent gas is commonly carried out using nitrogen to obtain emission measurements down to ~ 180 nm. This is especially important if the sulfur emission is to be detected at 180.7 nm. Highly purified nitrogen, by recirculation through a filter that removes oxygen, water vapor, and other impurities, apparently gives sufficient transmission to observe atomic chlorine emission at 134.7 nm and atomic oxygen at 130.2 nm [4].

In this publication we will demonstrate this new design of the PDED using emission arising from excitation in “pure helium”. Of course there are always trace impurities in the helium, either from the gas source, through leaks into the apparatus, or from the inside surfaces of the PDED. Presumably these impurities are of sufficiently low concentration that they do not play a role in the excitation process and that the excitation of the GC effluent arises from interaction with helium excited species or helium ionic species. We will also describe specific elemental analyses which are based upon excitation when using excited or ionic species from a dopant inert gas which has been intentionally added to the discharge gas. Generally the dopant is excited/ionized by the helium excited/ionized species since the dopant is at a relatively low concentration and the discharge excitation occurs with the host gas, helium. Each of these involve a unique mechanism of excitation which is a subject in itself and will be discussed in future publications.

There are several techniques that have been developed for elemental analysis in chromatography and these are reviewed in a text edited by Uden [5]. Several of these involve elemental analysis of components which are separated by liquid chromatography (LC) or supercritical fluid chromatography (SFC). These mobile phases generally contain polyatomic molecules such as H_2O , CO_2 , CH_3CN and excitation of elements in the presence of these molecules is more difficult than in gas chromatography where monoatomic inert gases, such as helium, can be used. Of the techniques reported in Uden's text [5], only three are focused on elemental analysis in gas chromatography: microwave induced plasma (MIP), the helium discharge detector (HDD), and alternating current plasma (ACP). In all of these techniques helium is the principal discharge gas and in this way they are similar to the PDED. However, the PDED differs from these techniques in four respects: (1) very low power is supplied to the variable-pulsed frequency (typically 4 to 5 W), (2) the low powered discharge has a very narrowly defined discharge, allowing us to use it as the optical image, (3) the PDED is a very “clean” discharge such that there are essentially no walls on which to react or deposit and (4) the PDED is very leak tight and high purity helium gives only trace emissions from impurities such as air and water. Evidence for

the last point is revealed in the emission spectra of helium which gives a propensity of He and He₂ emissions. Helium spectra from other excitation sources contain numerous N₂⁺, N₂ and OH emissions.

2. Experimental

Most of the experimental work was carried out with an Acton Vacuum Monochromator, ARC Model VM-502, which has an optical path of 0.2 m. The grating is a holographic type with 1200 grooves/mm. The dispersion is 4 nm/mm and the spectral range extends from 60 nm to 550 nm. However, the efficiency of the grating is significantly less in the lower wavelengths, less than 100 nm, and higher wavelengths, above 300 nm. Consequently, emission measurements in these extreme wavelength regions will be of lower sensitivity.

Both the entrance and exit slits extend outside the chassis of the monochromator and can be removed readily or altered. In our configuration we removed the entrance slit and built the PDED so that it could be attached to the flange with the discharge located at the position of the entrance slit. Consequently, that fraction of the emission which radiates within the aperture of the monochromator is spectrally analyzed and recorded. The exit is equipped with the conventional variable slit width assembly that can be purchased for this monochromator. The exit slit width was varied and the half width of an atomic emission line was measured. A slit width of 0.1 mm was the highest value that could be used before the atomic emission line was broadened. The spectral band width of the monochromator used in this configuration was ~0.6 nm. Given a dispersion of 4 nm/mm this resolution would suggest that the optical image of the discharge has a width of ~0.15 mm. Visual observation of the discharge confirms this estimation. Spectra recorded using this monochromator will be presented later confirming these values.

A schematic diagram of the PDED attached to the Acton Monochromator is given in Fig. 1. The distance from the face of the monochromator to the entrance slit is specified by the manufacturer to be 1.625 in. (1 in.=2.54 cm). The PDED is constructed so that the discharge is at this distance ±0.5 mm.

The compression of the gold O-rings and precision in the machining of the quartz could make up an error of 0.5 mm.

A more detailed schematic diagram of the PDED is shown in Fig. 2. The quartz is sealed to the metal surfaces by compression of gold O-rings. The compression is accomplished by four bolts passing from the back plate (C), through the heater block (H) and into the section attached to the flange (B). Spring washers are placed on the bolts in order to compensate for the difference in expansion between the quartz and the stainless steel bolts, keeping a constant pressure on the seals. The helium purge gas enters through 1/16 in. stainless steel tubing (T) into section B, as shown in Fig. 2. The helium flow is split, some passing through the monochromator and some through the PDED. The flow through these is adjusted by controlling the pressure in the monochromator and in the PDED. Needle valves are attached to the outlet tubes from the monochromator and the PDED to control the small pressure build up in these components, shown in Fig. 1. The flow-rate through the monochromator is typically 30 ml/min and through the PDED 20 ml/min. The pressure build up is typically 6–8 p.s.i. (1 p.s.i.=6894.76 Pa).

Note in Fig. 2 that the column enters through the exit part of the detector and is located so that its effluent just enters the discharge. The effective volume of the detector is the small volume that the effluent occupies while it resides in this discharge. The volume can be estimated to be a cylinder of 2 mm diameter and 2 mm length, a volume of 6.3 μl. With a helium flow-rate of 20 ml/min, this gives a residence time of only 0.02 s=20 ms. This is sufficiently short that the detector could be used in high speed chromatography where the peaks have half widths as short as 50–100 ms.

Also note in Fig. 2 the manner in which the discharge electrodes are purged with helium. The electrodes are made of 0.25 mm diameter molybdenum wire and protrude through a special tee and through the 0.53 mm I.D. silica tubing approximately 1 mm short of the end. This special Tee is not shown in Fig. 2. A small helium flow of ~2 ml/min is added to the Tee so that the helium blankets the wire throughout the silica tubing and especially at the end in the discharge zone. This small helium flow prevents the GC effluent from reaching the molybdenum electrode. Extended use of the detector

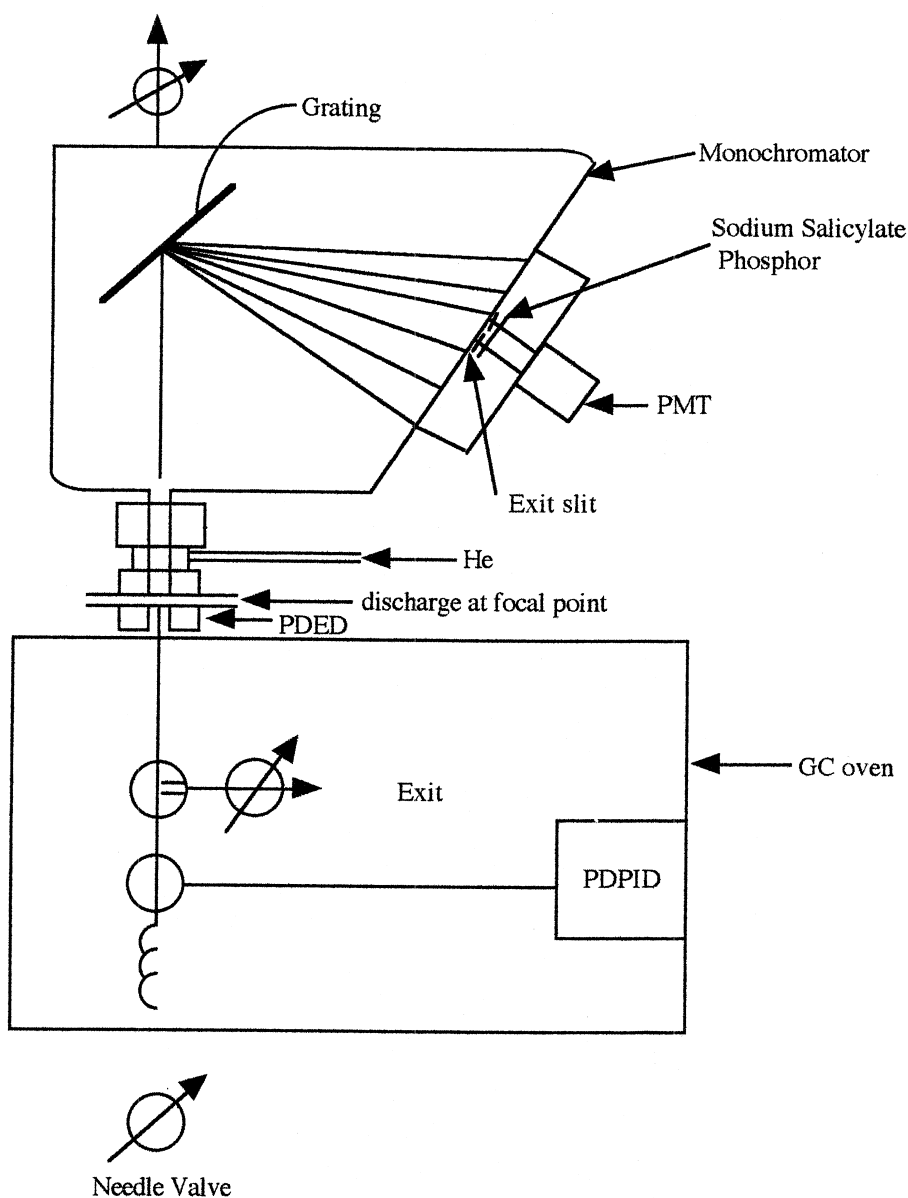


Fig. 1. Schematic diagram showing interfacing of the PDED with the monochromator.

has not given any noticeable carbon deposit on the molybdenum electrodes.

The positioning of the molybdenum wire electrode in the 0.53 mm I.D. silica tubing (~1 mm from the end) is carried out by visual observation. Consequently, the electrode gap is not precisely known and the optimum electrical power necessary to give a

stable pulsed discharge would be difficult to pre-determine. For this reason the power supply used for the pulsed discharge is conveniently adjusted by varying the applied voltage or the time that the voltage is applied to the coil prior to discharge. The electronic circuitry used to supply the pulsed discharge was described in previous publications [6,7].

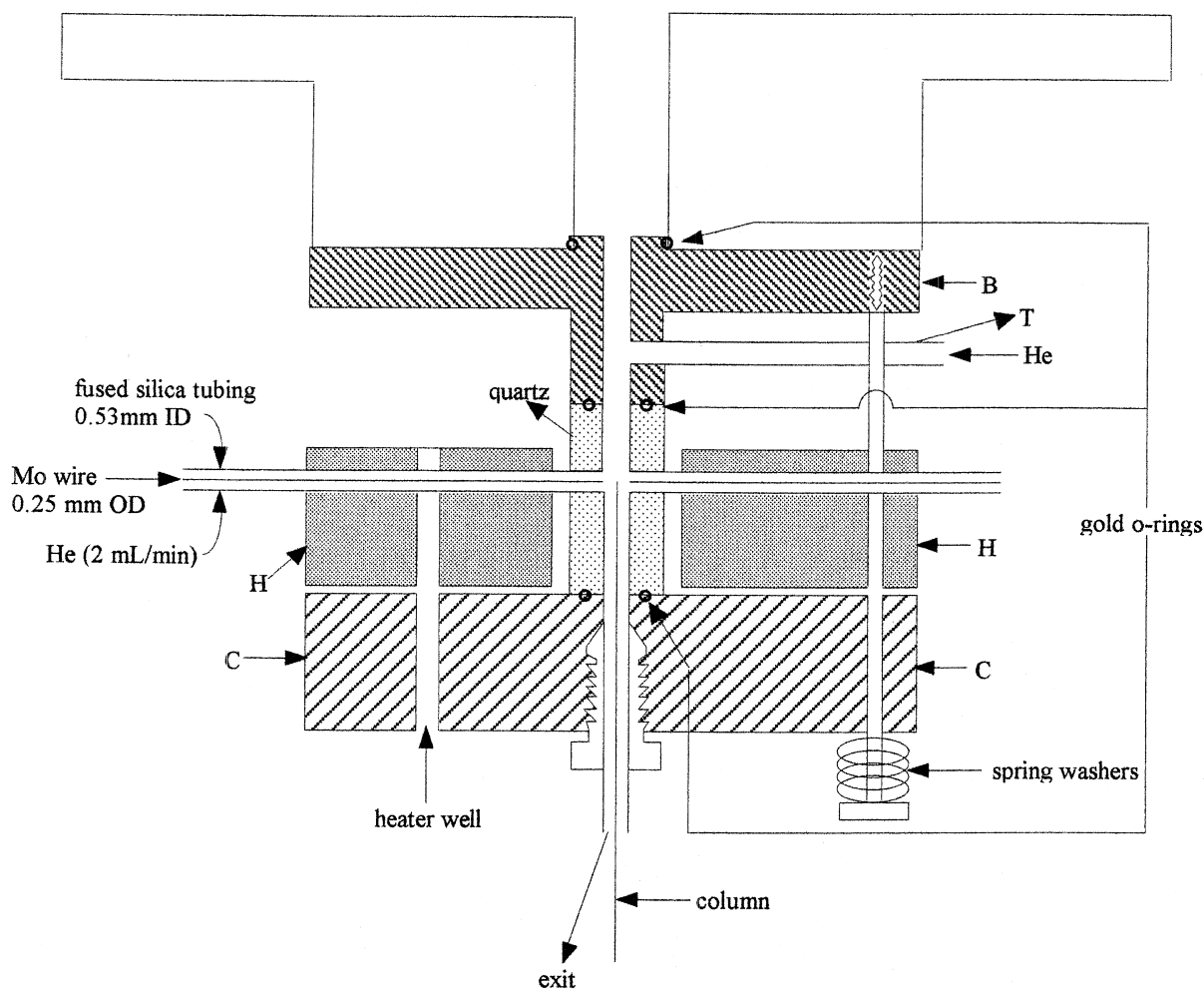


Fig. 2. Schematic diagram of PDED system; C=backplate, H=heater block, B=flange, T=1/16 in. stainless steel tubing soldered to section B.

As mentioned previously, the helium flow-rate through the monochromator is ~ 30 ml/min. Since the volume of the monochromator is so large, the purging must be carried out for ~ 2 weeks before the medium is sufficiently transparent. Helium has no absorption above 60 nm, so this is an ideal purge gas. The purging is never stopped even when the PDED is not in use. The intensity of the emissions generally show a slight increase as the monochromator and PDED are continued to be purged. This improvement in performance is probably due to slow out gassing of the surfaces, especially the large metal surface area of the monochromator. The

hydrogen and oxygen emission in the background diminishes slowly and this probably is due to the decrease in water coming from the metal surfaces.

Other monochromators, as well as other PDED designs, have been used in our laboratory. However, the same concept of using the discharge for the optical image has been retained. When measurements below 120 nm are desired, the monochromators must be purged with helium in a manner similar to that described in this paper. The use of a window for the entrance to the monochromator is optional if emission measurements below 120 nm are not desired. A magnesium fluoride window is used with some of

our monochromators which is transparent above 120 nm. With an entrance window a vacuum can be used to make the monochromator transparent and this is convenient for larger monochromators. Purging of larger monochromators with helium is more difficult due to the larger surface areas and greater volume of the monochromator. For smaller monochromators we purge with helium even if a MgF_2 window is used.

The detector used with the ARC Model VM-502 consisted of a sodium salicylate phosphor in front of a IP28 photomultiplier tube (PMT). The sodium salicylate absorbs radiation from 60–200 nm and fluoresces radiation in the UV which is detected by the PMT. For radiation under 120 nm this is the only way that it can be detected since PMT windows are not transparent below 120 nm. For radiation with wavelengths above 120 nm, a PMT with a MgF_2 windows can be used but they are rather expensive. The use of the sodium salicylate phosphor intermediate is convenient, however, it is much less sensitive than direct absorption by the PMT. Since the phosphor emits radiation in all directions, only a fraction of the radiation reaches the PMT. For this reason we use direct detection by the PMT for radiation with $\lambda > 165$ nm in order to obtain higher sensitivity. The results reported in this paper use the ARC Model VM-502 with the sodium salicylate

phosphor, and are thus less sensitive than direct measurement of the radiation. From our experience the direct measurement of the radiation is 10–20-times more sensitive than the measurement through the phosphor.

A schematic diagram of the entire GC system is shown in Fig. 3. Note that the column effluent is split between the helium pulsed discharge photoionization detector (He-PDPID) and the PDED. The effluent from the column going to the PDED is first mixed with the dopant in a Tee prior to entering the PDED. The dopant gas is selected by the position of a 4-Position Stream Selection Valve (B), similar to the selection of a PDPID [8]. Kr and Ar are continuously passing through Getters and fixed restrictors prior to entering the Stream Selection Valve. In order to have the Kr and Ar available immediately it is necessary to have a continuous flow through the Getters at all times. A small flow of helium is also passed through one of the ports so the transfer line from the valve to the mixing tee is cleared of any Kr and Ar used previously.

The He-PDPID was a research detector that was built prior to the commercialized product. The insulators were constructed of quartz which restricts the upper temperature of operation to $\sim 200^\circ\text{C}$. This was satisfactory for this study since no high boiling

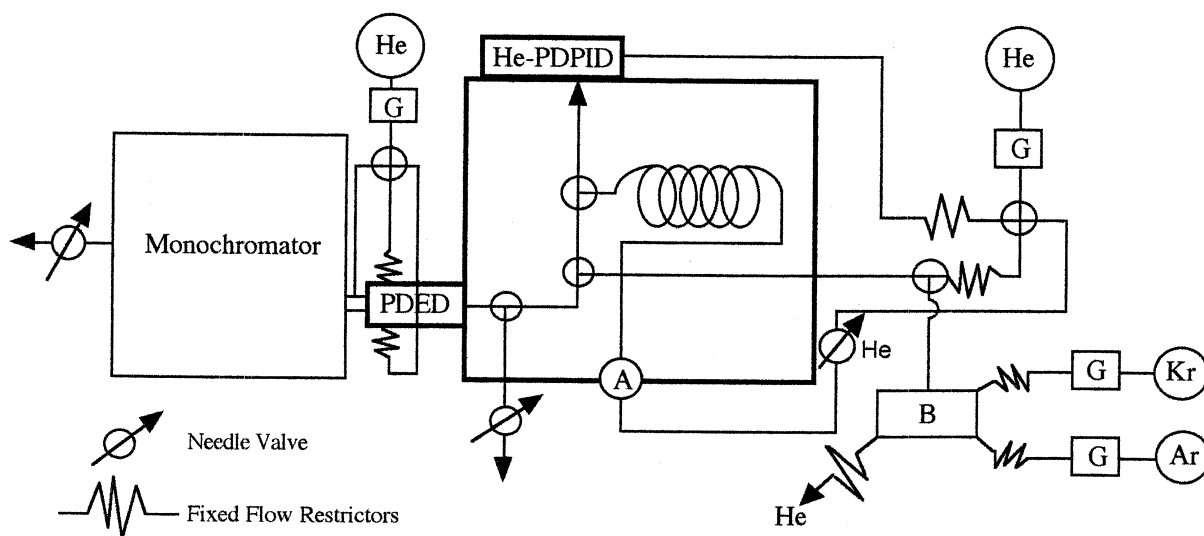


Fig. 3. Schematic diagram of the GC system; A: six-port gas sampling valve, B: four-position stream selection valve, G: gas purifying getter, He: helium cylinder, Kr: krypton cylinder, Ar: argon cylinder.

compounds were included. A schematic diagram of the He-PDPID was given in an earlier publication [8]. The photoionization region consisted of a cylinder of 3 mm diameter and length of 8 mm, thus a volume of 56 μl . A bias voltage of 400 V was applied to the electrode closest to the discharge. The photoionized electrons were collected at the electrode furthest from the discharge and the current was measured with an electrometer conventionally used with a flame ionization detector. The electrode circuitry for the discharge was identical to that for the pulsed discharge electron-capture detector (PDECD) and described in an earlier publication [6,7].

A commercialized version of the PDPID is available from Valco Instruments, which uses sapphire insulators in the ionization region instead of quartz. Sapphire has a lower conductivity than quartz at higher temperatures, allowing operation at $\sim 300^\circ\text{C}$ in the PDPID mode and higher temperatures in the electron-capture mode. A description of the commercial detector and its operation in both the PDPID and the electron-capture modes was described in an earlier publication [9].

Gas samples were introduced through a six-port gas sampling valve (A) with an external loop of 10 μl . Liquid samples were introduced through a four-port liquid sampling valve with an internal loop of $\sim 0.06 \mu\text{l}$. The GC column was a DB-5: 25 m \times 0.32 mm I.D. (J&W Scientific, Folsom, CA, USA). A separate source of helium was used to purge the monochromator and supply the discharge gas for the PDED. These flows are critical and are better regulated using an independent helium supply that can be maintained at an independently set pressure. The small flow of helium for purging the electrodes (~ 2 ml/min) also comes from this helium supply.

3. Results and discussion

3.1. Spectroscopic evaluation of slitless inlet to monochromator

Before examining the element-specific detectors, we should first evaluate the integrity of the spectrometer which uses the discharge itself as the optical image. This is best done by examining atomic

emission lines that are inherently very narrow, much sharper than the resolution of the spectrometer even with an entrance slit. Consequently, the recorded width of the atomic line will reflect the resolution of the optical system.

When the detector is first attached to the monochromator and the system has been purged for only a few days, there is an abundance of residual air in both the detector and the monochromator. Consequently, the emission spectra consists primarily of N atomic lines from N_2 and three unresolved oxygen atomic lines from O_2 at ~ 130 nm. Examination of these atomic emission lines affords an excellent opportunity to evaluate the resolution of the optical system, consisting of the PDED line-like discharge coupled to the slitless inlet of the monochromator.

The emission spectra after purging for a few days are shown in Fig. 4. The most intense line shown is the N line at 149.3 nm. The N lines at 113.5 and 120.0 nm become more intense than the 149.3 nm line after the monochromator has been purged for a longer period of time (1–2 weeks) and the transparency at ~ 120 nm has increased. At this time the He_2 emission at ~ 80 nm will become apparent.

The N line at 149.3 nm has been recorded with an increased recorder chart speed, as shown in Fig. 5. From this expanded wavelength scale the half width of the N 149.3 nm line has been found to be 0.72 nm. This is only slightly greater than the anticipated 0.60 nm, arising from an estimated discharge width of 0.15 mm and an optical dispersion of 4 nm/mm. If a monochromator is used which has a greater path length, the dispersion will be improved and the recorded atomic line width will be reduced. In our future work we intend to use a double monochromator to reduce the stray light and this will automatically improve the dispersion by a factor of 2.

In pure helium at approximately one atmosphere pressure the pulsed discharge initially produces excited atomic helium, which we will represent by He^* , and singly ionized He^+ [3]. The He^* can be in a variety of atomic singlet and triplet states ranging from the lowest triplet state $\text{He}(2^3\text{S})$ at 19.72 eV to the ionization limit at 24.59 eV. From the observed intensities of the atomic transitions in the He emission spectra, it is obvious that there is a much higher population of the lowest states with the excited

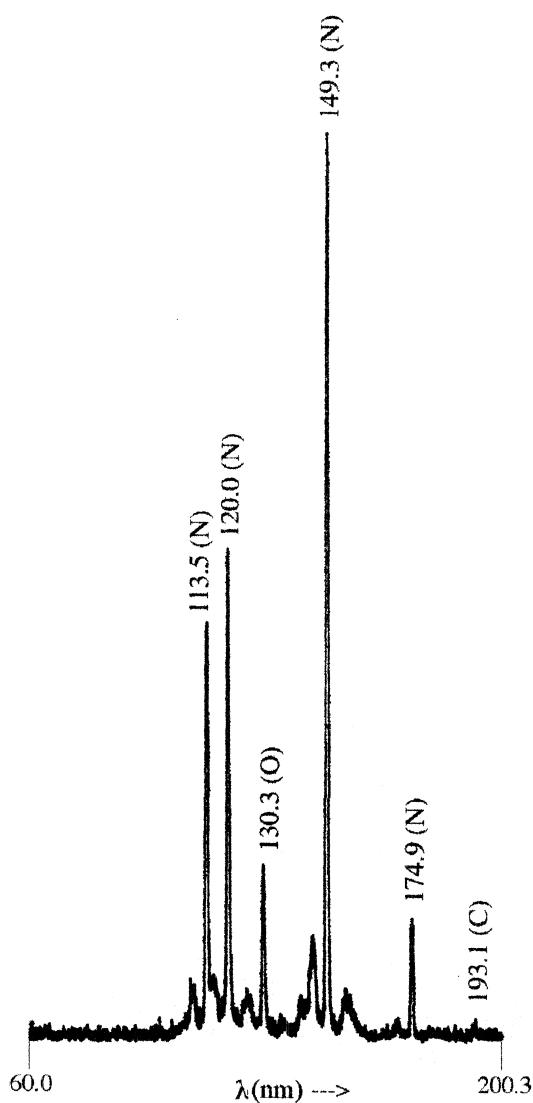


Fig. 4. Emission spectra from atomic N and O.

electron in an orbital with a principal quantum number of 2 to 5. The excited He^* and He^+ are relatively short-lived in that they react with He ground state atoms to give He and He_2^+ , respectively. These species are the longest lived and are probably the species involved in the excitation of GC effluents being detected.

If the helium discharge gas is doped ($\sim 1\text{--}3\%$, v/v) with Ar or Kr, the energy from the helium species is transferred to the argon and krypton. The emission spectra in the VUV region from the doped helium

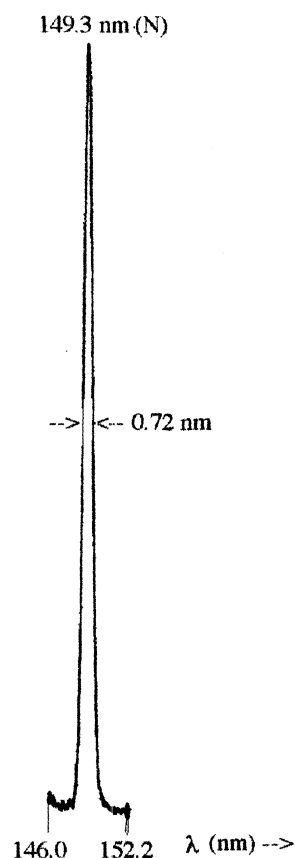


Fig. 5. Expanded emission spectra of N at 149.3 nm.

consists primarily of the resonance lines of Ar or Kr. Presumably the lowest triplet states of Ar (11.5 eV) and Kr (9.9 eV) are also formed by energy transfer from the helium triplet states [10]. Thus in the Ar and Kr doped helium we have these triplet states of Ar and Kr available for excitation of the GC effluents. In addition we have ionized atomic species Ar^+ and Kr^+ and also excited states of the ions $(\text{Ar}^+)^*$ and $(\text{Kr}^+)^*$, as evidenced by the emission spectra in the UV from these excited ions.

3.2. Analysis of Cl, Br, I, S using the PDED

In this paper we will simply present the analytical results using the PDED for specific elemental analysis and refrain from speculating about the mechanism of excitation. A proposed mechanism will be pre-

sented in a later paper after additional spectroscopic measurements have been carried out.

Four elements have been included in this initial investigation: Cl, Br, I and S. These elements are more accessible to excitation since they are more weakly bonded in molecules. The atomic emission of the elements has been observed at various wavelengths that are characteristic of each of the elements with all three discharge gases: pure He, Ar-doped He and Kr-doped He. At each of the wavelengths the intensity of the atomic emission was dependent on the nature of the discharge gas. For each of the elements the most intense emission observed was: chlorine, $\lambda=134.7$ nm in argon–2.65% doped He; bromine, $\lambda=154.1$ nm in krypton–1.88% doped He; iodine, $\lambda=178.3$ nm in krypton–1.88% doped He; sulfur, $\lambda=180.7$ nm in pure He.

As described earlier, the change of discharge gas is readily accomplished using a multiposition Stream Selection Valve. For this monochromator the wavelength was set manually, which could be accomplished with a precision of ± 0.1 nm. This should be quite sufficient considering the band pass of ~ 0.7 nm. Many other monochromators use a computer to select the wavelength and this may be desirable for greater speed and possibly greater reproducibility.

For the three halogens the greatest intensity is with either the Ar- or the Kr-doped helium discharge gas. The exact nature of the intensity enhancement from Ar or Kr is unknown but excited states of Ar and Kr are similar to halogen atoms in that a p electron in the ground state is excited to a higher energy orbital, leaving the lowest energy orbitals with an electronic configuration of the adjacent halogen atom Cl or Br. Also the singly ionized Ar^+ and Kr^+ are formed in the discharge and these have the same electronic configuration as that of $\text{Cl}\cdot$ and $\text{Br}\cdot$, respectively. Very likely the excited Ar^*/Kr^* or the ion Ar^+/Kr^+ are the species leading to the excitation.

The responses to the He-PDPID and the PDED are recorded simultaneously on a dual channel recorder. The recording of the PDPID is displaced above the recording of the He-PDPID. The pens are positioned so that the chromatograms are essentially at the same time. We feel that this type of presentation is the most informative about the element specific detector for the following reasons:

(1) The peak shape of the element-specific detec-

tor can be compared to that from the ionization detector. Any irregularities such as peak tailing, can be readily noted and assessed to the element-specific detector. Without the ionization detector for comparison, one is never certain if peak tailing may be due to the chromatography.

(2) Interferences from numerous other elements can be readily assessed by including other compounds that do not contain the specific element being detected. One chromatogram can evaluate possible interference from other elements. Frequently emphasis is placed on interference from carbon, which is quantified by a term called selectivity, but interference from other elements may be equally important.

(3) The response of the ionization detector serves as a check on the concentrations in the mixture in that the response of the He-PDPID is somewhat uniform on a per gram basis [11]. Large errors in sample preparation, say by an order of magnitude, will be apparent by an inordinate response on the He-PDPID.

(4) Any sample decomposition, which may readily occur with iodine compounds, will be apparent from the shape of peaks from the He-PDPID.

(5) Finally, it is convenient to compare the ratio of the PDED response to that of the He-PDPID in the evaluation of optimum conditions. By taking the ratio of the responses, variations in the amount of sample injected are accounted for by the He-PDPID response and the ratio of responses will be a more precise evaluation of the PDED response under different conditions.

The ratio of the PDED response to the He-PDPID response also is a useful parameter in the qualitative evaluation of a GC peak. This is analogous to the use of the ratio of any two detector responses, as has been reported previously [8,10,12]. This topic will be considered in more detail later in the paper.

In Fig. 6 we show the response to the Cl atomic emission at 134.7 nm in the upper chromatogram and the universal response from the He-PDPID in the lower chromatogram. Note the large response to the air peak from the He-PDPID but no apparent response to the PDED. The response for air from the He-PDPID is so large that it pegs off at the top of the chart and thus transcends the Cl-PDED graph, giving the appearance of a response to the Cl-PDED. However, the baseline for the Cl-PDED does not

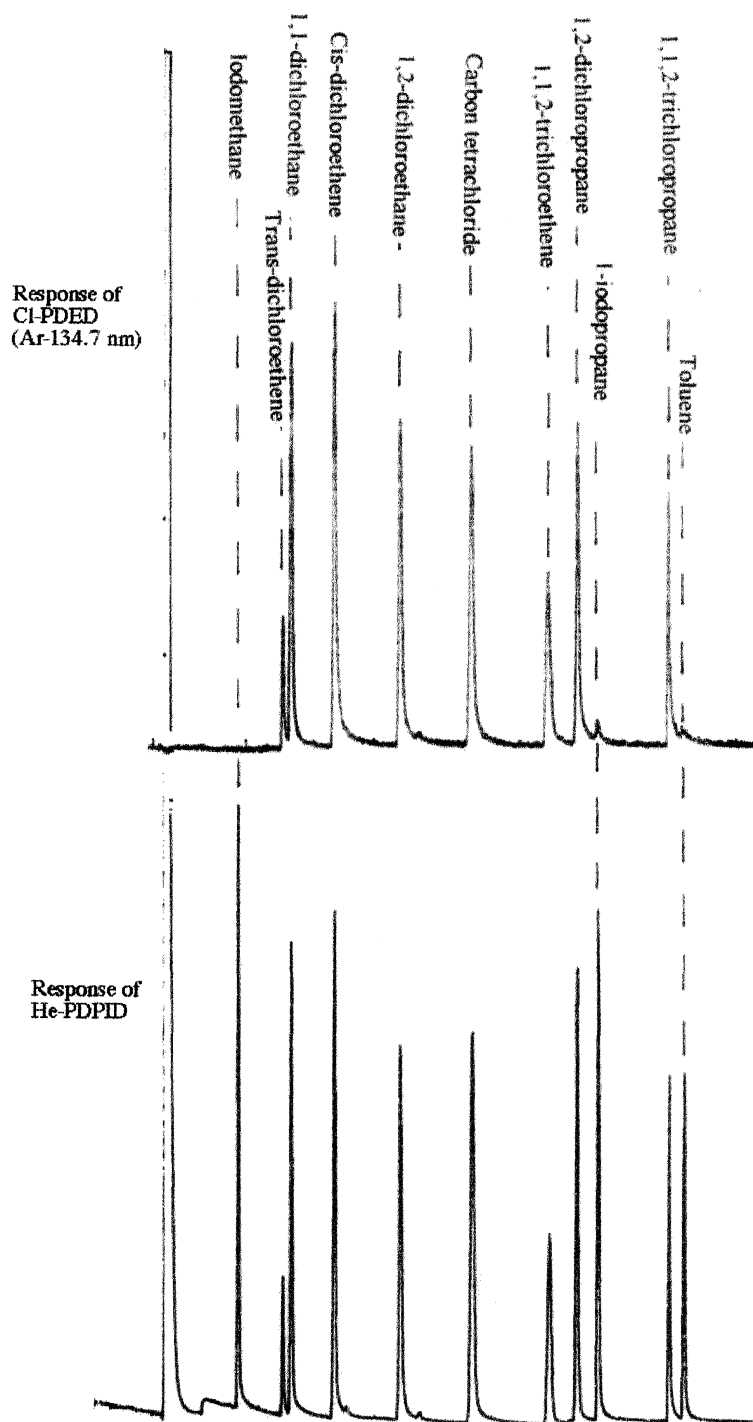


Fig. 6. CI-PDED/He-PDPID responses for Cl and I compounds.

show any response at the time of the air peak, as evidenced by the flat baseline in this area. The high response for air also appears in Figs. 7–10. All chlorine-containing compounds give significant responses to the PDED at 134.7 nm as expected, whereas the non-chlorine containing compounds (iodomethane, 1-iodopropane and toluene) show little or no response to the PDED. The peak shapes for the two detectors are very similar. The ratios of the response to the PDED to that of the He-PDPID vary by a factor of about four for the Cl-containing compounds investigated. This variation is most certainly due to the PDED and not the He-PDPID.

The response of the PDED to atomic bromine emission at 154.1 nm is shown in Fig. 7 along with the He-PDPID response in a manner similar to Fig. 6. The two bromine containing compounds give a good signal to the Br-PDED whereas the other compounds give no significant response with the exception of 1-iodopropane. This is surprising since iodomethane and 2-iodopropane do not respond at this wavelength of 154.1 nm. Possibly there is a bromine containing impurity that happens to co-elute with 1-iodopropane.

The response of the atomic iodine at 178.3 nm in Kr-doped helium is given in Figs. 8 and 9, as before, along with the universal He-PDPID response. In Fig. 8 the I-PDED response is given for three iodine containing compounds in the presence of sulfur- and bromo-containing compounds. There appears to be little or no interference from the sulfur or bromine compounds. In Fig. 9 we show the I-PDED response in the presence of several chlorine-containing compounds and toluene. There does not appear to be any significant response from the chlorine-containing compounds at 178.3 nm in Kr-doped helium, where as the two iodine compounds give a good response.

The response of the PDED to sulfur at 180.7 nm is shown in Fig. 10, but the results are much less satisfactory than those for the halogens. First of all the response to the S-PDED is much lower and the peaks are broader. This is not due to decomposition on the column since the peaks from the He-PDPID are reasonably sharp. The peak for carbon disulfide has a significant tailing and this could be due to decomposition in the PDED or a non-linear response. The second concern is the strong interference from iodine containing compounds. However, samples

containing sulfur frequently do not contain iodine compounds. This interference could be confirmed by observing the I-PDED response, as was shown in Fig. 8 for this mixture. Direct observation of the sulfur atomic emission does appear to give a satisfactory analysis for sulfur. Another reaction mode is being investigated for the analysis of sulfur and this should eliminate the interference and enhance the intensity of the emission.

3.3. Qualitative analysis using the PDED/He-PDPID ratio of responses

As mentioned previously, the ratios of two or more detector responses, can be used to qualitatively identify a GC peak. This has been demonstrated using pulsed discharge photoionization detectors [8,10] and a flame ionization detector [12]. It is convenient to take the ratio with respect to the helium photoionization detector (He-PDPID) since it gives a universal response to all compounds or elements except neon [11,13]. The ratio of the detector responses relative to the He-PDPID will always be positive and finite.

The ratio of the detector responses is independent of the concentration if the detector responses are both linearly related to concentration. If the ratio of the responses is made relative to an internal standard, the ratio will then be independent of the split ratio between the detectors and factors which may influence the overall sensitivity of a detector on a daily basis [12]. In principle the ratio of detector responses should be inherent to a compound relative to the internal standard selected.

In this study several mixtures were run, all under the same chromatographic conditions. In each mixture the compounds were sufficiently separated on the GC column so that the detector responses could be measured without interference from adjacent peaks. The chromatograms shown in Figs. 6–10 are from some of these mixtures. The ratio of the PDED response for a given element to that of the He-PDPID is evaluated relative to an internal standard. For the Cl-, Br-, I- and S-PDED the internal standards are 1,2-dichloropropane, 1-bromobutene, 1-iodopropane and carbon disulfide, respectively. The relative responses for each of the PDED are summarized for all of the mixtures in Tables 1–4. Note that

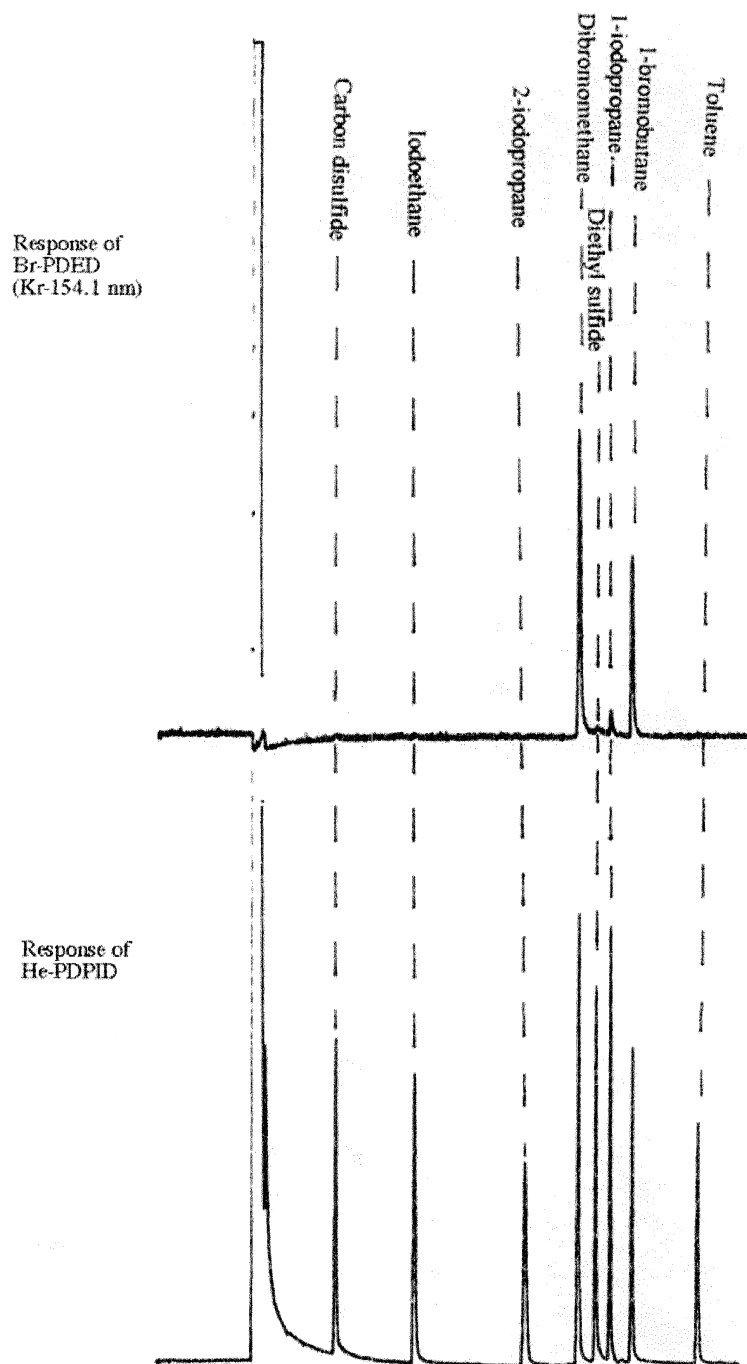


Fig. 7. Br-PDED/He-PDPID responses for S, I, Br compounds.

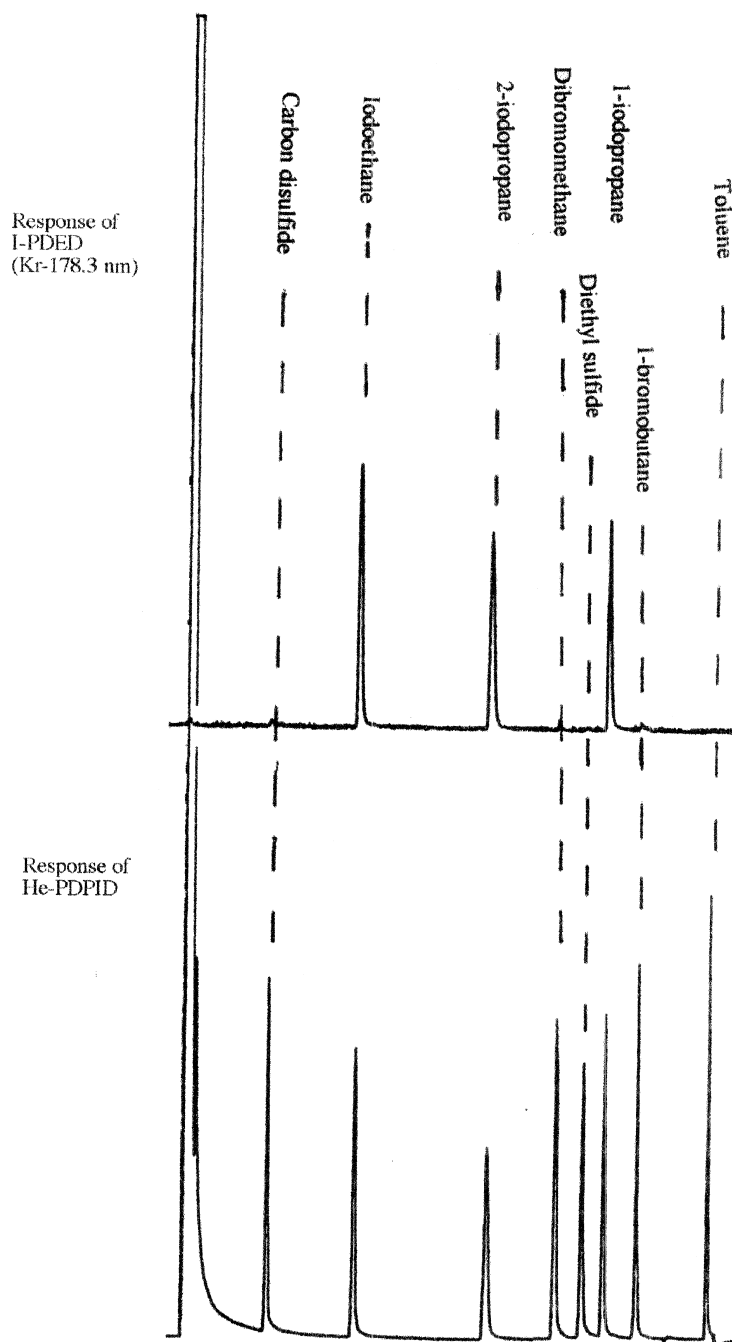


Fig. 8. I-PDED/He-PDPID responses for S, I, Br compounds.

the response ratio of the internal standard is 1.00 since all ratios are relative to the internal standard.

The retention time of a compound can also be

used to qualitatively identify the compound. Since the retention time can vary on a day-to-day basis due to variations in carrier flow-rate and other chromato-

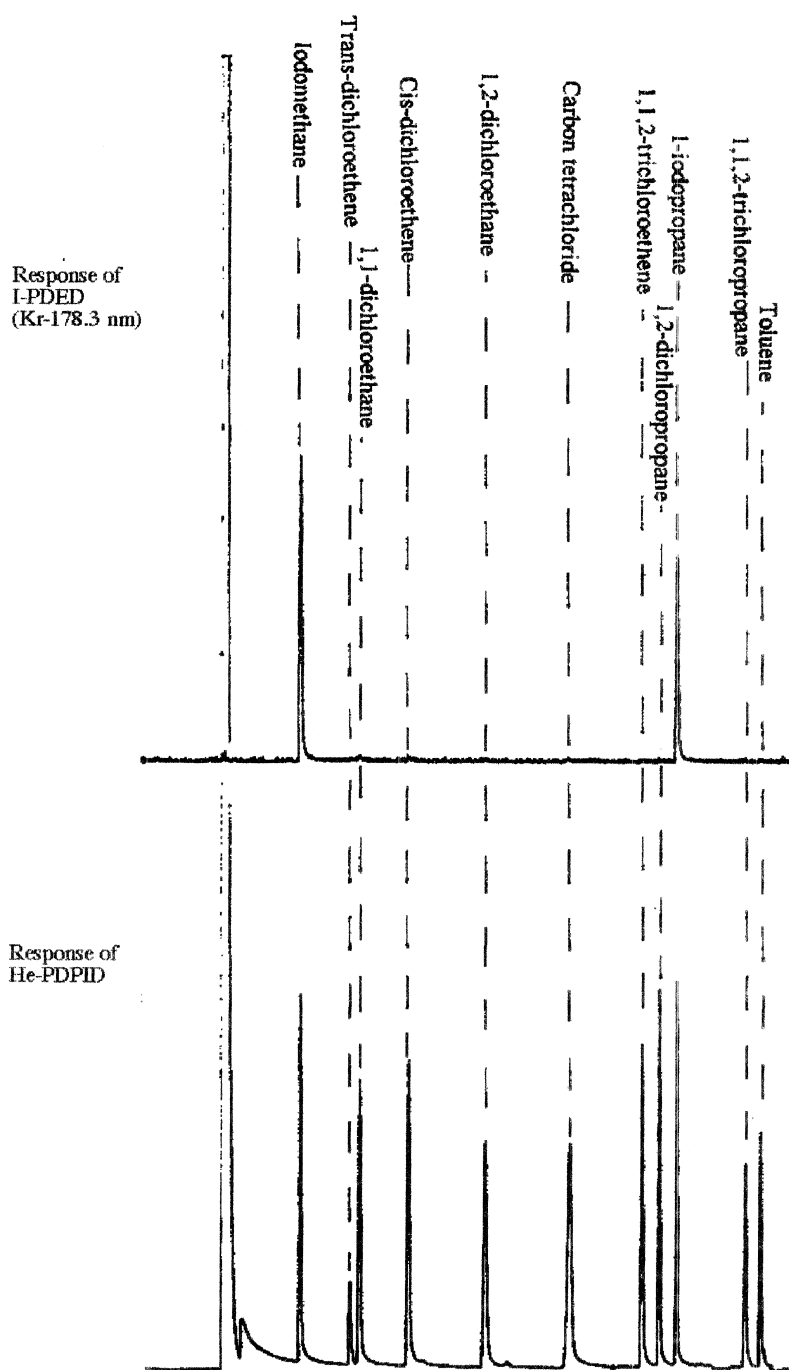


Fig. 9. I-PDED/He-PDPID responses for I, Cl compounds.

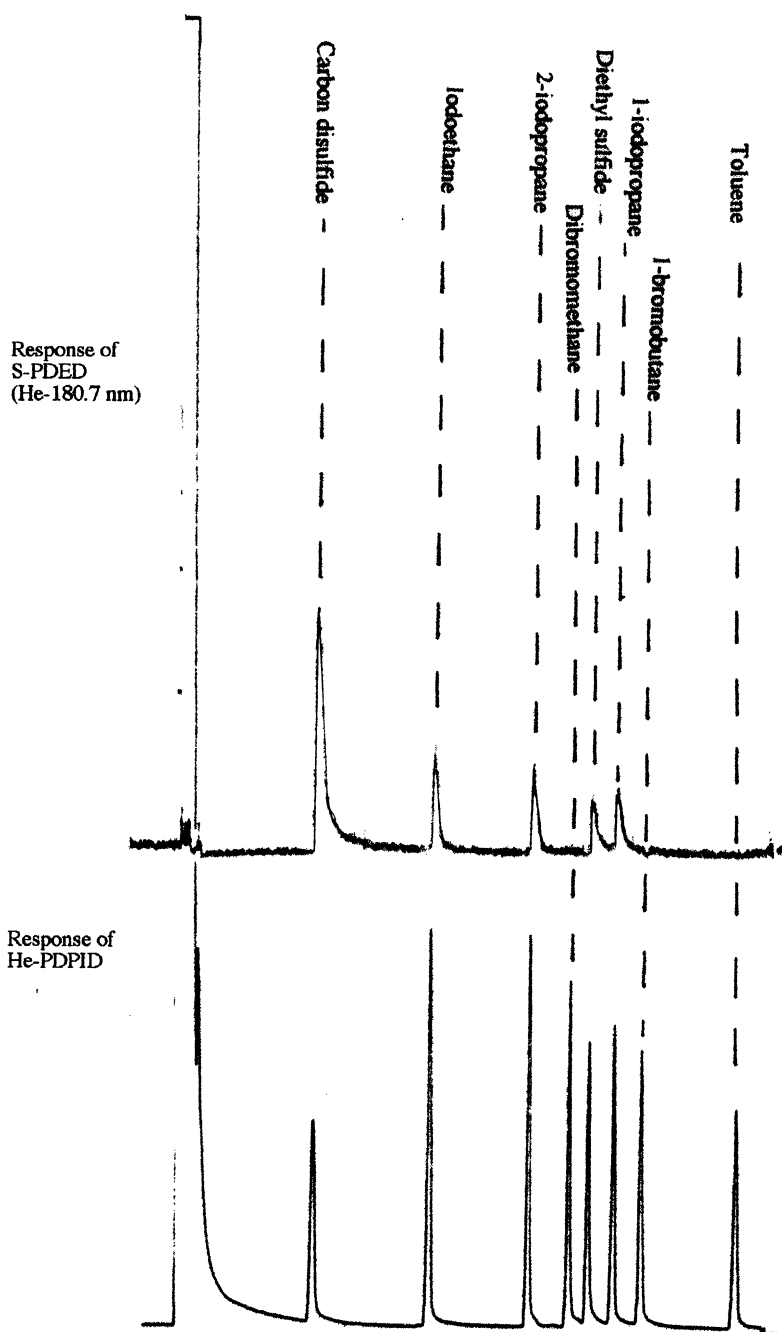


Fig. 10. S-PDED/He-PDPID responses for S, I, Br compounds.

graphic variables, a relative retention time, relative to some internal standard, gives a more precise parameter to identify a compound. The relative retention

times are generally more reproducible than the actual retention time by about an order of magnitude. In this study toluene was used as the internal standard

Table 1
Relative retention times and relative Cl-PDED/He-PDPID responses^a

Compound	Relative retention time	Relative detector response
2-Chloropropane	0.2747±0.0019	0.46±0.07
Dichloromethane	0.3027±0.0018	1.06±0.08
Allyl chloride	0.3178±0.0026	1.52±0.17
1,1,2-Trichloro-trifluoroethane	0.3256±0.0027	1.70±0.03
2-Chloro-2-methylpropane	0.3338±0.0027	0.73±0.08
<i>trans</i> -Dichloroethene	0.3602±0.0051	1.24±0.19
1,1-Dichloroethane	0.3734±0.0047	1.29±0.23
3-Chloro-1-butene	0.4258±0.0029	1.31±0.06
<i>cis</i> -Dichloroethene	0.4403±0.0073	1.25±0.10
Chloroform	0.4730±0.0106	1.09±0.14
2,2-Dichloropropane	0.4854±0.0091	1.26±0.12
1-Chloro-2-methylpropane	0.4930±0.0029	0.87±0.19
3-Chloro-2-methylpropene	0.5271±0.0022	0.97±0.26
1,2-Dichloroethane	0.5439±0.0078	1.12±0.16
1,1,1-Trichloroethane	0.5860±0.0064	1.13±0.19
1-Chlorobutane	0.5908±0.0100	0.49±0.04
Carbon tetrachloride	0.6412±0.0089	0.80±0.05
1-Chloro-2,2-dimethylpropane	0.6445±0.0066	0.48±0.03
2-Chloro-2-methylbutane	0.6482±0.0180	0.45±0.09
<i>trans</i> -1,4-Dichloro-2-butene	0.6476±0.0020	0.77±0.09
1,1,2-Trichloroethene	0.7228±0.0064	0.92±0.06
1,2-Dichloropropane	0.7558±0.0044	1.00 (REF)
1-Chloropentane	0.9539±0.0011	0.66±0.04
1,1,2-Trichloroethane	0.9617±0.0016	0.93±0.09
1,3-Dichloropropane	1.0072±0.0017	1.46±0.10
Cyclopentylchloride	1.0440±0.0005	0.47±0.08
<i>cis</i> -1,4-Dichloro-2-butene	1.0466±0.0014	1.46±0.15
Tetrachloroethene	1.1516±0.0032	1.16±0.12
1,1,1,2-Tetrachloroethane	1.2442±0.0044	0.96±0.06
Chlorobenzene	1.2467±0.0048	0.91±0.08
1,1,2,2-Tetrachloroethane	1.4106±0.0069	0.93±0.03
<i>p</i> -Chlorotoluene	1.6562±0.0077	0.38±0.03

^a Cl-PDED at $\lambda=134.7$ nm and argon-doped discharge; retention time relative to toluene.

for relative retention times for all mixtures. The relative retention times are also shown for all compounds studied in Tables 1–4.

The compounds included in this study were simply those that were available in our laboratory. Obviously there are more Cl-containing compounds and the use of the relative detector responses for qualitative analysis of Cl compounds can be evaluated more critically. In order to examine if the relative retention times can be used to distinguish compounds in a mixture, a graph of relative detector responses versus relative retention time can be examined. Such a graph is shown in Fig. 11 for the Cl-PDED, using an argon-doped discharge gas at $\lambda=134.7$ nm. In Fig. 11 a rectangle is drawn to represent the error bars

about the data point. Complete separation of a rectangle from the others indicates that the compound can be identified by this combination of relative retention time and relative detector response ratio. The actual relative retention time and relative detector response ratio for each of the the compounds is at the center of the rectangle and the size of the rectangle is defined by $\pm 1\sigma$ about this point.

Note the wide range of relative detector responses from 0.4 to 1.7. Generally one would expect a compound with a greater fraction of Cl atoms to have a higher ratio of responses. However, this does not seem to be true in that the compounds with multiple Cl, such as CCl_4 and CHCl_3 , do not show an extremely high ratio compared to those with a

Table 2
Relative retention times and relative Br-PDED/He-PDPID responses^a

Compound	Relative retention time	Relative detector response
Bromoethane	0.2993±0.0028	1.49±0.12
2-Bromopropane	0.3895±0.0051	1.59±0.10
Allyl bromide	0.4764±0.0071	2.03±0.43
1-Bromopropane	0.5024±0.0106	1.29±0.16
3-Bromo-1-propyne	0.5565±0.0085	2.50±0.26
2-Bromo- <i>trans</i> -2-butene	0.6609±0.0056	1.58±0.13
Dibromoethane	0.7278±0.0074	1.27±0.07
1-Bromobutane	0.8524±0.0050	1.00 (REF)
1-Bromo-2-butene	0.9176±0.0011	1.58±0.24
2-Bromopentane	1.0479±0.0021	1.00±0.14
1,2-Dibromoethane	1.0809±0.0027	1.73±0.06
1-Bromopentane	1.2066±0.0043	0.96±0.09
Bromoform	1.3311±0.0067	2.42±0.04
1-Bromo-4-fluorobenzene	1.4592±0.0076	1.52±0.11

^a Br-PDED at $\lambda=154.1$ nm and krypton doped discharge; retention time relative to toluene.

Table 3
Relative retention times and relative I-PDED/He-PDPID responses^a

Compound	Relative retention time	Relative detector response
Iodomethane	0.2909±0.0024	1.59±0.11
Iodoethane	0.4715±0.0099	1.44±0.32
2-Iodopropane	0.6515±0.0083	1.20±0.13
1-Iodopropane	0.7975±0.0041	1.00 (REF)

^a I-PDED at $\lambda=178.3$ nm and krypton doped discharge; retention time relative to toluene.

Table 4
Relative retention times and relative S-PDED/He-PDPID responses^a

Compound	Relative retention time	Relative detector response
Carbon disulfide	0.32334±0.00311	1.00 (REF)
Diethyl sulfide	0.77324±0.00972	0.22±0.03
1-Butanethiol	0.80827±0.00341	0.23±0.02
Allyl sulfide	1.29388±0.00633	0.33±0.03

^a S-PDED at $\lambda=180.7$ nm and pure helium discharge; retention time relative to toluene.

lower fraction of Cl. The variation in the ratio of detector responses probably can be attributed to variations in the PDED, since the He-PDPID response is approximately proportional to the mass of the compound. In any event there is a wide range of response ratios in Table 1 and this is helpful in compound identification.

One can examine Fig. 11 to see if closely eluting peaks can be differentiated based upon the response ratio. There are three pairs of compounds that have similar relative retention times and relative detector response ratios:

	Relative retention time	Relative detector response ratio
Carbon tetrachloride	0.641±0.009	0.80±0.05
<i>trans</i> -1,4-Dichlorobutene	0.648±0.002	0.77±0.09
1-Chloro-2,2-dimethylpropane	0.644±0.007	0.48±0.03
2-Chloro-2-methyl butane	0.648±0.018	0.45±0.09
1,1,1,2-Tetrachloroethane	1.244±0.004	0.96±0.06
Chlorobenzene	1.247±0.005	0.91±0.08

With only two detectors to give a single ratio of responses, it is very likely that two compounds in a mixture will coincidentally have similar relative

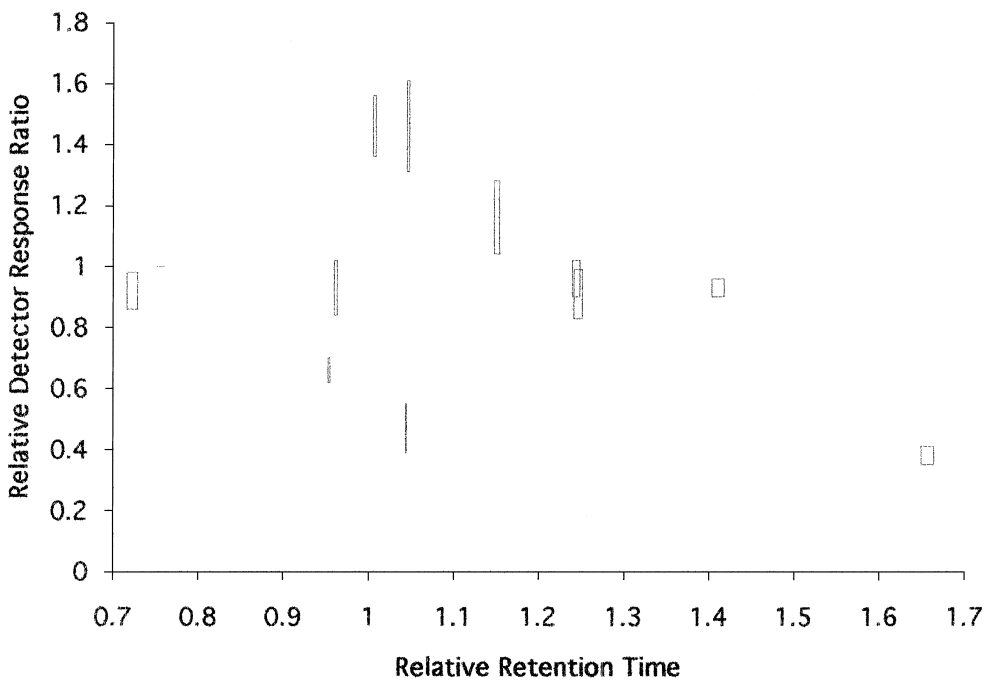
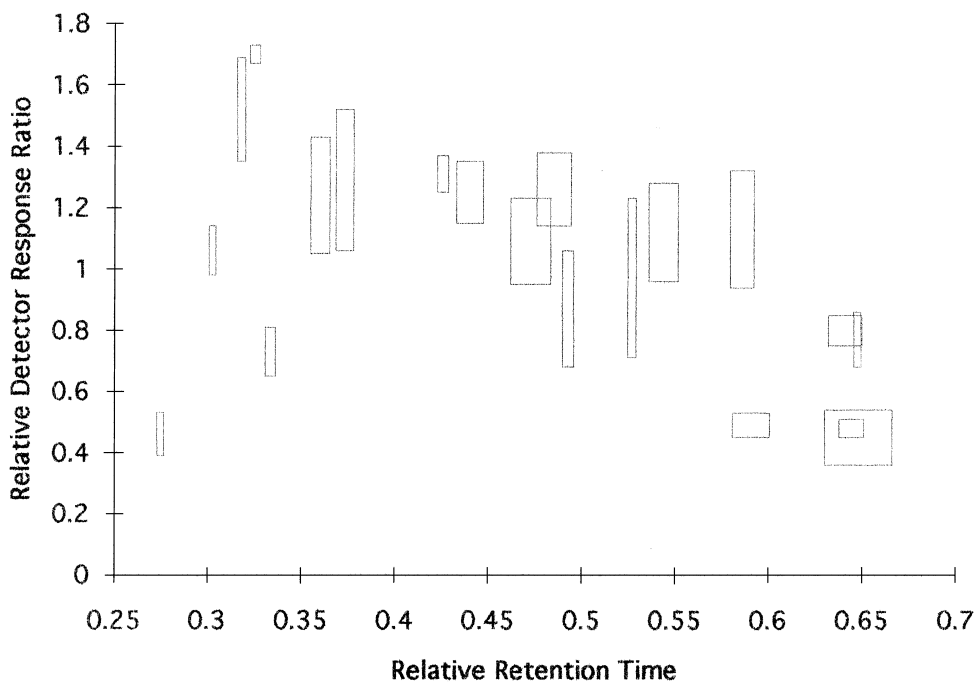


Fig. 11. Graph of relative detector response ratio versus relative retention time for Cl-containing compounds.

retention times and relative detector response ratios. In such a circumstance a third detector can be used such as the Kr-PDPID which will differentiate between compounds based on unsaturation and chain branching [8]. Alternatively, another column can be used which separates the two compounds.

There are 14 Br compounds shown in Table 2 which also includes the internal standard 1-bromobutane. The 13 relative response ratios are graphed in a similar manner in Fig. 12. The relative response ratios range from ~1 to 2.5, a factor of 2.5, which is less than the range for the Cl compounds 0.4 to 1.7, a factor of 4.25. For the Br compounds plotted in Fig. 2, there are no overlaps of adjacent pairs and all 13 compounds could be identified unequivocally. Probably the use of a single relative response ratio in conjunction with the relative retention time would be sufficient to identify a mixture of 20–30 compounds.

There are only a few I and S containing compounds included in this study and these are shown in Tables 3 and 4, respectively. The range of relative response ratios is only 1.0–1.6 for the I compounds but 0.22 to 1.0 for the S compounds. Since there are such few data points, the compounds are readily distinguished on a graph of relative response ratio versus relative retention time.

3.4. Detector sensitivity, selectivity and linearity

There are three quantities which are used commonly to evaluate an element specific detector: sensitivity, selectivity and linearity of the response. As mentioned earlier the sensitivity of the PDED in the present configuration using the sodium salicylate phosphor, would be lower than one in which the vacuum UV radiation (VUV) photons were absorbed directly by the PMT. Nevertheless, it is useful to evaluate the sensitivity in the present configuration to see how it compares with other element-specific detectors and one could then anticipate the improved sensitivity using the direct absorption of radiation.

The sensitivity of the PDED, based upon the mass of element being analyzed, varies somewhat for different compounds. However, the variation is not great, <25% for most of the elements in this study. A more quantitative evaluation of this variation will be included in subsequent publications. For the present we will give the sensitivity for an element

from a specific compound which can be considered typical of that observed from several compounds. In the following table we give the sensitivities measured for the designated compound. The sensitivity is commonly expressed in pg/s which suggests that the detector is mass sensitive, such as the FID. The PDED is most certainly concentration sensitive, but for simplicity of comparison we will also express the sensitivity in pg/s. Also included in the table are the MDQs

Element (compound)	Wavelength/ discharge gas	MDQ (pg/s)			
		PDED	MIP	HDD ^a	ACP
Cl (CH ₂ Cl ₂)	134.7 nm/Ar	56	25	3	1100
Br (CH ₂ Br ₂)	154.1 nm/Kr	267	30	8	-
I (CH ₃ I)	178.3 nm/Kr	163	20	2	-
S (CS ₂)	180.7 nm/He	47	1	5	-

^a Sensitivity is reported as mass in pg rather than mass/time.

obtained with the MIP, the only commercial AED [14]. In all cases the sensitivity for the MIP is greater than that for the PDED. However, with the anticipated increase in sensitivity when the photon emission is measured directly by the PMT, the PDED sensitivity will be on the order of that for the MIP. This result is surprising in that the MIP uses more than 10-times the power of the PDED. Most certainly the rationale for this result is the concentration of the power in the narrow discharge which serves as the optical image.

The sensitivity for these elements using the helium discharge detector [15] are much lower than those from the PDED and the MIP. In fact they are as low as those anticipated using the PDED with direct absorption of the photons by the PMT. The sensitivity for Cl using the ACP technique is considerably less than the other techniques [16]. As the authors point out [16], the C–Cl emission had to be used for Cl analysis and this would necessarily be of lower sensitivity than an atomic emission.

In this initial study we have not evaluated the selectivity quantitatively for each of the element specific detectors, but one can obtain an estimate from the chromatograms since they all contain toluene which is separated from the other com-

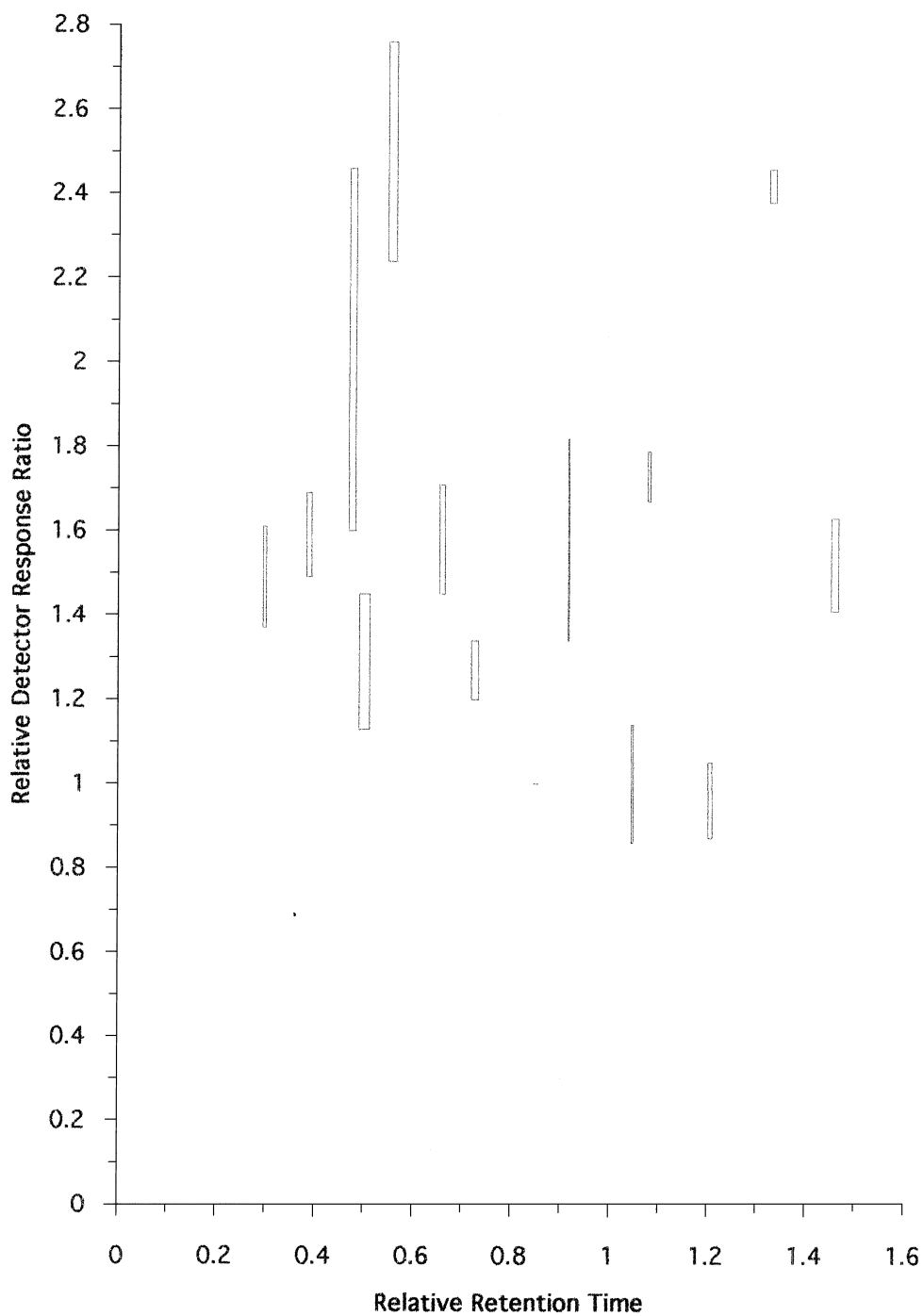


Fig. 12. Graph of relative detector response ratio versus relative retention time for some Br-containing compounds.

pounds. In Fig. 6 one can see a small response to toluene on the Cl-PDED, but in Figs. 7–10 there is no apparent response to toluene on the Br-, I- and S-PDED. If the small response to the Cl-PDED is indeed due to toluene and not a co-eluting impurity, there must be carbon emission overlapping with the Cl at 134.7 nm. This would make the selectivity of the Cl-PDED less than that of the Br-, I- and S-PDED. From the responses observed and the noise level of the baseline we would estimate the selectivity with respect to carbon to be in excess of 100 for the Br-, I- and S-PDED. The use of a monochromator for the isolation of the elemental emission will limit the selectivity due to stray light in the monochromator. Commonly the stray light is on the order of one part in 10^4 and this would limit the selectivity to 10 000 if the carbon emission is comparable to the elemental emission being used in the PDED. The use of the Kr and Ar doped helium most likely diminishes the carbon emission and would tend to increase the selectivity. A later paper in this series evaluates the selectivity quantitatively for another Cl-specific emission detector which uses Kr-doped helium and the selectivity was found to be 1000.

In regards to linearity we would expect linearity up to some maximum concentration which depends upon the concentration of excited species available for excitation. At concentrations higher than this maximum, one would expect a decrease in intensity below the linear relationship simply because there are insufficient excited species available. This maximum concentration for the emission detector is around 1 ng/s which we observe for the Cl-, Br-, I-PDED. This is also the upper limit for the Cl-specific emission detector based upon the Kr^+ reaction, which is discussed in a later paper [17]. The linearity is then dependent on the MDQ for the detector. If the MDQ for Cl is ≈ 50 pg/s as in this study, the linearity range is just over one-order of magnitude. If on the other hand, the MDQ were reduced to say 1 pg/s as anticipated using direct absorption by the PMT, the linearity would be over three-orders of magnitude.

4. Conclusion

A PDED has been constructed and directly cou-

pled with a Vacuum Monochromator (50–550 nm) using highly purified helium as the transparent medium rather than a vacuum. There are no optical components or slits between the PDED and the monochromator. The discharge itself acts as the optical image and experimentally gives a band pass of 0.7 nm. This experimental apparatus allows optical emission measurements from the pulsed discharge above 60 nm to the upper limit of the monochromator.

Argon–2.65% doped helium in the discharge gave the most intense emission from atomic Cl at 134.7 nm with the fewest number of interferences. Krypton–1.88% doped helium in the discharge gave the most intense emission from atomic Br and I at 154.1 nm and 178.3 nm, respectively. These also gave the fewest interferences from other elements. The use of a sodium salicylate phosphor in front of the PMT absorbs radiation in the range 60–200 nm and fluoresces in the UV where the PMT is sensitive. The procedure allows the use of a less expensive PMT which is sensitive in the UV region, but there is a considerable loss of detector sensitivity since the phosphor emits in all directions and only a small fraction is absorbed by the PMT. Direct absorption of the vacuum UV radiation (VUV) using a VUV PMT should improve the sensitivity by over an order of magnitude. Sensitivities observed for the Cl-, Br-, I- and S-PDED are observed in the mid to high picogram level and these should be decreased by an order of magnitude by direct absorption of the VUV radiation.

References

- [1] S.V. Vasin, W.E. Wentworth, S.D. Stearns, C.J. Meyer, *Chromatographia* 34 (1992) 226.
- [2] W.E. Wentworth, H. Cai, J. Madabushi, Y. Qin, S.D. Stearns, C. Myer, *Process Qual.* 5 (1993) 193.
- [3] W.E. Wentworth, Y. Qin, S. Wiedeman, S.D. Stearns, J. Madabushi, *Appl. Spectrosc.* 49 (1993) 1282.
- [4] H. Falk, L. Thissen, US Pat. No. 5 225 681 (1992).
- [5] P. Uden, *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy*, American Chemical Society, Washington, DC, 1992.
- [6] W.E. Wentworth, E. Desai D'Sa, H. Cai, *J. Chromatogr. Sci.* 30 (1992) 478.
- [7] W.E. Wentworth, S.V. Vasin, S.D. Stearns, C.J. Meyer, *Chromatographia* 34 (1992) 219.
- [8] W.E. Wentworth, Y. Li, S.D. Stearns, *J. High Resolut. Chromatogr.* 19 (1996) 85.

- [9] W.E. Wentworth, J. Huang, E.C.M. Chen, S.D. Stearns, *J. Chromatogr. Sci.* 34 (1996) 368.
- [10] G. Gremaud, W.E. Wentworth, A. Zlatkis, R. Swatloski, E.C.M. Chen, S.D. Stearns, *J. Chromatogr. A* 724 (1996) 235.
- [11] S. Mendonca, W.E. Wentworth, E.C.M. Chen, S.D. Stearns, *J. Chromatogr. A* 749 (1996) 131.
- [12] W.E. Wentworth, N. Helias, A. Zlatkis, E.C.M. Chen, S.D. Stearns, *J. Chromatogr. A* 795 (1998) 319.
- [13] W.E. Wentworth, H. Cai, S.D. Stearns, *J. Chromatogr. A* 688 (1994) 135.
- [14] J.J. Sullivan, B.D. Quimby, in: P. Uden (Ed.), *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy*, American Chemical Society, Washington, DC, 1992, Chapter 4.
- [15] G.W. Rice, in: P. Uden (Ed.), *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy*, American Chemical Society, Washington, DC, 1992, Chapter 12.
- [16] E.F. Barry, L.A. Colon, R.B. Constanzo, in: P. Uden (Ed.), *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy*, American Chemical Society, Washington, DC, 1992, Chapter 10.
- [17] K. Sun, W.E. Wentworth, S.D. Stearns, *J. Chromatogr. A* 872 (2000) 141.