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N-, O- and P-selective on-column atomic emission detection in capillary gas chromatography

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Abstract

A 350-kHz He plasma sustained on-column was evaluated for N-, O- and P-selective atomic emission detection in capillary gas chromatography. As the plasma caused peak tailing when sustained in 2.0 ml/min of carrier gas, 15 ml/min of auxiliary helium was added to the discharge. For N- and O-selective detection, CH_4 mixed with O_2 or N_2, respectively, were used as plasma dopant. Even with this extensive plasma doping, non-specific responses arose from eluting hydrocarbons due to temporary changes in the background level of atomic N and O. Without background correction, element-to-carbon selectivities for N and O were limited to 100:1 and 40:1, respectively. For both elements, detection limits at the 50 pg/s level and linearities of $5 \cdot 10^2$ were obtained. P-selective detection was carried out with H_2–CH_4 as plasma dopant, and provided a 39 pg/s detection limit for P. The phosphorus-to-carbon selectivity was 2300:1 and the linearity was $2 \cdot 10^2$. With background correction, both selectivities and detection limits are expected to improve significantly.

1. Introduction

Even though the first papers combining gas chromatography (GC) and atomic emission spectroscopy (AES) were published in 1965 [1,2], the development and applications of this promising technique were until recently restricted to a relatively small number of research laboratories. In 1989, however, the first completely automated atomic emission detector for capillary GC became commercially available [3]. This new accessibility combined with the great versatility of GC–AES suggests that atomic emission detectors may replace a range of universal and element-selective GC detectors within the near future.

In both commercial and non-commercial atomic emission detector systems, the plasma is sustained inside a 1–6 mm I.D. silica discharge tube placed in continuation of the capillary GC column. In order to stabilize the plasma within this tube, typically 50–150 ml/min of make-up gas (helium) are added. Recently, however, two publications [4,5] demonstrated on-column atomic emission detection where a 350-kHz plasma was sustained inside the end of the GC capillary column (0.32 mm I.D.). Owing to the small volume of the detector cell, introduction of make-up gas was unnecessary, and the plasma was sustained in only 2 ml/min of GC carrier gas (helium). Because dilution of the GC effluent was avoided, detection limits were improved significantly and the consumption of high-purity helium was reduced. In addition, no ferrules

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were used to connect the GC column and the plasma tube as the plasma was sustained inside the column. This eliminated air leaks at the inlet of the discharge region which are commonly observed with GC–AES systems. The 350-kHz on-column plasma was combined with a single 0.2-m focal length low-resolution monochromator, which resulted in a sensitive and inexpensive GC–AES system for C-, H-, S-, F-, Cl-, Br- and I-selective detection.

This system was utilized in the present work for the first study of on-column N-, O- and P-selective atomic emission detection in capillary GC. Optimization of the plasma conditions and wavelength selection were emphasized in order to maximize both the signal-to-noise ratios and elemental selectivities and to suppress interactions between analyte constituents and the GC capillary containing the discharge. The aim of the work was to evaluate the on-column plasma in a simple, inexpensive GC–AES system. For this reason, more complicated technical solutions, such as real-time spectral background correction or extensive purification of the GC carrier gas, were not included.

2. Experimental

2.1. Equipment

GC was carried out with a Model 4200 gas chromatograph from Carlo Erba (Milan, Italy) equipped with a capillary split/splitless injection port and a 20 m × 0.32 mm I.D. HP-1 (0.17 μm) fused-silica GC column from Hewlett-Packard (Avondale, PA, USA). Helium at 2.0 ml/min (41 cm/s) was used as the carrier gas.

The on-column detector cell which was placed in the flame ionization detection (FID) block on the top of the gas chromatograph was the same as used in two recent studies [4,5] (Fig. 1). A 5 cm length of stationary phase and polyimide coating was burned off the end of the GC column. The last 2 cm of this uncoated capillary (0.38 mm O.D. × 0.32 mm I.D.) serving as the plasma tube was placed inside a 2-cm piece of silica tube (1/8 in. O.D. × 0.5 mm I.D.) for mechanical protection. The protecting silica tube was fitted into the top of a 1/16–1/8 in.-reducing union from Swagelok (Solon, OH, USA) by a 1/8-in. (1 in. = 2.54 cm) graphitized vespel ferrule. The GC column was extended through this reducing union and through a 4.5-cm piece of 1/16-in. steel tubing (transfer line) to the GC oven. The reducing union and the transfer line were mounted in the heated FID block of the gas chromatograph in order to prevent condensation of high-boiling analytes. A 350-kHz plasma was generated inside the GC column between a 1 mm diameter steel wire at the outlet (top electrode) and the grounded FID block by an HPG-2 radiofrequency power supply from ENI Power Systems (Rochester, NY, USA).

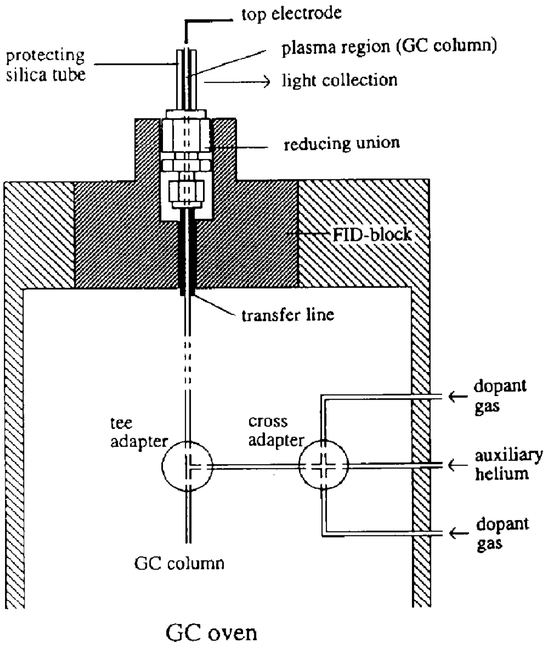

Fig. 1. Detector cell and gas flow system.

The introduction of dopant gases was modified compared with the previous papers reporting on-column atomic emission detection [4,5]. In this work, the dopants were introduced close to the outlet of the GC column. In addition, a third inlet was established at this point for introduction of auxiliary helium. The pressure drop across two 1.4 m × 20 μm I.D. fused-silica capillaries was utilized to restrict the flow of dopant gases, whereas the auxiliary helium was introduced through a 1.4 m × 100 μm I.D. restrictor. All three capillaries were connected to a ZX1C 1/16-in. cross (0.25 mm bore) from Valco (Houston, TX, USA) with Valco FS1-.4 high-temperature polyimide adapters for fused silica. This cross, which was placed inside the GC oven (Fig. 1), served to mix the dopant gases and the auxiliary helium. These were subsequently guided by a 10-cm piece of 0.32 mm I.D. fused-silica capillary to a ZT1C 1/16-in. Valco tee (0.25 mm bore) placed in-line with the capillary GC column 40–70 cm from the outlet. This tee, which also was fitted with Valco FS1-.4 high-temperature polyimide adapters, served to mix the dopants and auxiliary helium with the GC carrier gas.

The optical part of the system has been described in detail elsewhere [4–9]. The plasma was viewed side-on through the wall of the uncoated fused-silica GC column and the protecting silica tube. Atomic emission was measured in the 600–1000-nm region by a Model H-20 IR monochromator from Instruments SA (Metuchen, NJ, USA) equipped with either 50- or 500-μm entrance and exit slits. The optical resolution was 0.4 nm with 50-μm slits. A long-pass filter with a 595-nm cut-off from Melles Griot (Irvine, CA, USA) was used to reject second and third-order radiation, and a pair of achromatic lenses ($f = 58$ mm, 12.7 mm diameter) from Newport (Fountain Valley, CA, USA) were used to image the emission on the monochromator. Light-to-current conversion was performed by an R2658 photomultiplier tube from Hamamatsu (Shizuoka-ken, Japan). This was operated at 1050 V with a Hamamatsu C665 d.c. power supply. Signals from the photomultiplier tube were collected by a Model 428 current amplifier from Keithly Instruments (Cleveland, OH, USA), and recorded on an SR 6335 strip-chart recorder from Graphtec (Yokohama, Japan).

2.2. Gases

Helium (99.9999%) from Hydro (Oslo, Norway) was used both as the GC carrier gas and as the auxiliary plasma gas. This was passed through an OMI-1 indicating purifier from Supelco (Bellefonte, PA, USA) placed in-line between the pressurized cylinder and the gas chromatograph. Traces of 99.998% oxygen, 99.9997% hydrogen, 99.99% nitrogen or 99.95% methane (all from AGA, Oslo, Norway) were added as dopant gases to the on-column plasma.

2.3. Chemicals

For the optimization and performance studies, the following model compounds of analytical-reagent grade were used unless stated otherwise: nitrobenzene (N, O), triethyl phosphate (P), *n*-tetradecane (C), 1-fluoronaphthalene (F), 1,2-dichlorobenzene (Cl) and 1,1,2,2-tetrabromoethane (Br).

2.4. Calculation of elemental selectivities, detection limits and dynamic ranges

The X_{element}-to-Y_{element} selectivity was defined as the ratio of the peak response per gram of element X to the peak response per gram of element Y. In cases where the response for Y was negative or bipolar, the total span of the vertical excursion was used. The detection limit for element X was defined as the amount of X required to produce a peak twice the height of the peak-to-peak noise, divided by the full width at half-height of the peak in seconds. The peak-to-peak noise measurement was taken over a time period of 30 s. The dynamic range for element X was defined as the range of sample concentration over which the response factor for X (area per unit mass) varied by less than 10%.

3. Results and discussion

In two recent papers [4,5], a 350-kHz He plasma sustained inside the end of the capillary GC column (0.32 mm I.D.) was utilized for C-, H-, S-, F-, Cl-, Br- and I-selective atomic emission detection. Owing to the small volume of the detector cell, the plasma was maintained in only 2 ml/min of GC carrier gas (helium) without dilution of the effluent by make-up gas. This resulted in significantly improved detection limits and reduced consumption of high-purity helium. The on-column plasma was combined with a 0.2-m focal length low-resolution monochromator in order to build an inexpensive single-channel GC–AES system. In the present work, this simple technology was evaluated for N-, O- and P-selective atomic emission detection. Optimization of both plasma conditions and wavelength selection were emphasized in order to maximize the performance and to understand both the advantages and limitations of the concept.

3.1. Technical aspects of dopant gas introduction

In the first two papers concerned with on-column atomic emission detection [4,5], GC was accomplished using helium as the carrier gas premixed with traces of O_2 and H_2. The latter served as dopant gases for the plasma in order to suppress non-specific responses and to eliminate distortion of chromatographic peaks in the discharge. However, two problems were inherently connected with this premixing of GC carrier gas and dopant gases: (a) the system required a relatively long period for stabilization following any changes regarding the dopant gases, and (b) polar stationary phases and sample constituents could be degraded owing to the presence of O_2 in the GC column. In this work, both problems were eliminated by introducing the dopant gases close to the outlet of the GC column through two 20 μm I.D. fused-silica restrictors. In addition, a third inlet was established at this point for introduction of auxiliary helium, whereby the flow of plasma gas could be varied independently of the GC carrier gas. The dopants and the auxiliary helium were introduced by a tee placed in the GC column 40–70 cm from the plasma region at the outlet (Fig. 1). With this piece of GC column behind the mixing point, old plasma cells could be replaced several times without disconnecting the tee union. Thus, replacement was easily performed within 5 min by cutting off the used uncoated end of the GC column followed by burning off a new 5-cm length of polyimide coating and stationary phase in a lighter flame. Careful inspection of the uncoated region was carried out in order to ensure that no stationary phase remained in the uncoated end of the GC column.

In this work, a piece of the HP-1 column (containing stationary phase) was used between the tee for gas introduction and the plasma. This was done because the HP-1 capillary was easily available by cutting 40–70 cm off the main column. As the capillary was short compared with the main column, it was found not to cause any problems regarding separation and detection. Alternatively, a well deactivated fused-silica capillary with the same dimensions can be used. This, however, was not tested in this work.

3.2. Atmospheric contamination of the plasma

Several publications have demonstrated that nitrogen and oxygen are among the most difficult elements to determine succesfully by GC–AES owing to the practical problems of excluding air from the plasma [6,10–20]. Air leaks in the GC–AES system and atmospheric impurities in the plasma gases contribute to elevated background levels of atomic nitrogen and oxygen in the discharge. For both elements, this results in deterioration of the signal-to-noise ratios and in temporary baseline fluctuations (non-specific responses) during elution of hydrocarbons.

In this work, plasma contamination was reduced by utilizing high-purity helium (99.9999%), which was passed through a purifier tube to decrease further the levels of oxygen and moisture. In addition, ferrules used in the system were frequently checked for leaks or replaced, and connections involving steel tubing were welded. However, air leaks inside the components of the gas chromatograph (e.g., split/splitless injection port, regulators and gauges) and back-diffusion of air into the discharge were not considered owing to the technological problems of their elimination.

3.3. Nitrogen-selective detection

Initial experiments with N-selective detection utilizing the on-column plasma sustained in pure helium suffered from a low nitrogen-to-carbon selectivity (ca. 20:1) and from tailing or splitting of chromatographic peaks within the discharge. In order to suppress these problems, the plasma composition was optimized by the introduction of dopant gases. From earlier studies, either O_2 [10–12,15,16] or $H_2 + O_2$ [13,14] have been used as plasma dopants for N-selective detection. With the on-column plasma, however, superior results were obtained with a mixture of CH_4 and O_2. CH_4 served to suppress peak tailing and enhanced the nitrogen-to-carbon selectivity by a factor of 5. O_2 was added as a co-dopant in order to avoid deposition of carbon formed from CH_4 and from eluting components. The levels of CH_4 and O_2 were controlled by the intensities of the 656.3-nm H line and the 777.2-nm O line, both relative to the 706.5-nm He line. The optimum values corresponded to $I_H/I_{He} \approx 5$ and $I_O/I_{He} \approx 1$, providing a total concentration of plasma dopants below 1%. Above these levels the signal-to-noise ratios decreased significantly whereas the peak shapes and the nitrogen-to-carbon selectivity were not further improved. With optimum levels of CH_4 and O_2, non-specific responses from hydrocarbons were negative. If the concentration of O_2 in the plasma was increased, however, they changed polarity. Unfortunately, negative and positive interferences were not balanced at moderate O_2 levels, but a dipolar response occurred.

In addition to the plasma composition, signal-to-noise ratios and elemental selectivities were also affected by the intensity and the background characteristics of the emission line used. As background correction was not applied in the present system, the near-infrared portion of the spectrum was considered to be most convenient owing to the low abundance of interfering molecular emission. Within this region, 746.8 nm was found to be superior for N-selective detection. Besides providing lower signal-to-noise ratios and nitrogen-to-carbon selectivities, most of the other strong N-emission lines in the near-infrared region suffered from spectral interferences caused by adjacent emission lines for C, Cl or Br when the low-resolution monochromator was used. For this reason, N-selective detection was carried out at 746.8 nm.

The excitation conditions of the discharge not only were determined by the chemical composition of the plasma, but also were affected by the power level supplied by the plasma generator. With the present system, the applied power was varied between 10 and 20 W. Below 10 W the plasma became unstable and above 25–30 W the GC column melted. As expected, both the signals and signal-to-noise ratios for N increased when the applied power was increased (Fig. 2). A similar relationship has previously been observed for on-column detection of carbon, hydrogen, sulfur and the halogens [4,5]. As the nitrogen-to-carbon selectivity and chromatographic peak shapes did not deteriorate when the applied power was increased, 20 W was selected as the operating level in order to maximize both the detector sensitivity and signal-to-noise ratios. At this power level, the wall of the fused-silica GC column was only slightly affected by the plasma after 1 week of continuous operation. Hence plasma capillaries were used for 4–7 days before replacement.

In two recent papers reporting on-column atomic emission detection [4,5], the plasma was sustained in the GC carrier gas only. With this configuration, the flow of helium provided for the discharge could not be varied independently of the GC carrier gas flow. In the present work, however, this was possible as an inlet for auxiliary helium was established close to the on-column plasma (Fig. 1). This enabled the conditions for the chromatography and the plasma to be optimized separately. A flow-rate of the GC carrier gas of 2.0 ml/min was selected, which

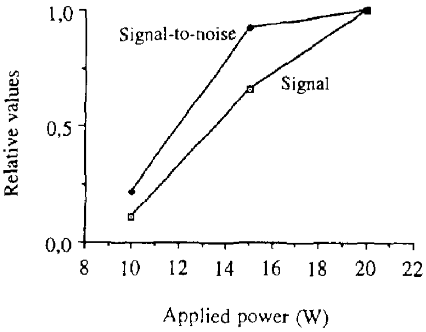

Fig. 2. Effect of applied power on signals and signal-to-noise ratios for N-selective detection.

Table 1
Effect of auxiliary helium on on-column nitrogen-selective detection

Auxiliary He flow-rate (ml/min)	Signal	Signal-to-noise ratio	Nitrogen-to-carbon selectivity	$t_{0.1w}$ [b] (s)
0	1.00[a]	1.00[a]	32:1	4.4
15	0.27	1.86	100:1	4.4

[a] Value defined as 1.00.

[b] Peak width at one tenth of peak maximum.

was a compromise between speed of analysis and chromatographic resolution. Initial work demonstrated almost no peak tailing in the N mode when the plasma was sustained in the GC carrier gas only. However, both the signal-to-noise ratios and the nitrogen-to-carbon selectivity were improved when 15 ml/min of auxiliary helium were added to the on-column plasma (Table 1). In addition, auxiliary helium was found to suppress the release of background nitrogen during the elution of fluorinated compounds. These effects probably arose since the analyte residence time was shortened, and as analyte interactions involving the wall of the plasma capillary were suppressed by the auxiliary helium. Therefore, even though the signals decreased and the operating costs increased, auxiliary helium was used throughout this work for N-selective detection.

When the on-column detector was operated at 746.8 nm with plasma conditions optimized for N-selective detection, a 50 pg/s detection limit of N and a $5 \cdot 10^2$ linearity were obtained (Table 2). With "conventional operation" of the 350-kHz plasma utilizing the same optical system and with the plasma sustained inside a 1 mm I.D. discharge tube in 60 ml/min of helium, a 1 ng/s detection limit of N was obtained. Hence on-column detection improved the signal-to-noise ratios by a factor of approximately 20, even without extensive special precautions to exclude air from the plasma. The on-column detection limit of N was among the lowest reported in the literature [10–16,21], and was significantly lower than those obtained using other GC–AES systems without extensive plasma gas purification [10–12].

Even though the nitrogen-to-carbon selectivity was only 100:1, the present system possessed considerable practical utility since non-specific responses were negative. For the determination of N-containing compounds in complicated matrices, however, a higher nitrogen-to-carbon selectivity is required. Because this value was not enhanced by further plasma doping, either extensive purification of the plasma gas (reduction of the nitrogen background level) or real-time spectral background correction has to be ap-

Table 2
System performance characteristics[a] for N-selective detection compared with literature values

Parameter	This work: on-column r.f. plasma	Microwave plasma [12]	Commercial instrument (HP) [21]
Wavelength	746.8 nm	746.8 nm	174.2 nm
Dopant gas	O_2–CH_4	O_2	O_2–H_2
N detection limit	50 pg/s	4000 pg/s	50 pg/s
Nitrogen-to-carbon selectivity	100:1	–	2000:1
Linearity	$5 \cdot 10^2$	$1 \cdot 10^5$	$2 \cdot 10^4$

[a] All results were obtained with a monochromator equipped with 500-μm slits.

plied. Further purification of the plasma gas may improve both the nitrogen-to-carbon selectivity and signal-to-noise ratios. However, as discussed above, this is technologically difficult because atmospheric contamination probably occurs at several points both in the gas chromatograph and in the small detector cell. With real-time spectral background correction, however, carbon interferences may be subtracted from the N signal by monitoring the N and C channels simultaneously. Even though both the complexity and the cost of the system will be increased, real-time spectral background correction probably is the best choice in order to realize the full advantage of the high-sensitivity performance provided by on-column N-selective atomic emission detection.

3.4. Oxygen-selective detection

O-selective detection with the on-column plasma sustained in pure helium was of no practical value owing both to large non-specific responses from hydrocarbons (oxygen-to-carbon selectivity $\approx$ 10:1) and to extensive tailing of chromatographic peaks. As the first step to improve the system performance, the composition of the plasma was optimized. From the literature, H_2 [18,19], N_2 [10,11,17], CH_4 [6] and N_2–CH_4 [13,14] have been used as plasma dopants for O-selective detection. Among these, N_2–CH_4 was found to be superior with the on-column plasma. CH_4 served to suppress peak tailing and enhanced the oxygen-to-carbon selectivity by a factor of 4. N_2 was added as co-dopant to the on-column plasma in order to eliminate deposition of carbon formed from CH_4 and from eluting components. The amounts of CH_4 and N_2 were controlled by the intensities of the 653.3-nm H line and the 868.0-nm N line, both relative to the 706.5-nm He line. The optimum levels corresponded to $I_H/I_{He} \approx 3$ and $I_N/I_{He} \approx 1$, providing a total concentration of plasma dopants below 1%. Further plasma doping reduced the signal-to-noise ratios without any improvement of the oxygen-to-carbon selectivity.

In contrast to nitrogen, only a few intense emission lines are available for atomic oxygen in the near-infrared region of the spectrum. Among these, 777.2 nm provided the best results regarding both the oxygen-to-carbon selectivity and signal-to-noise ratios. For this reason, 777.2 nm was used throughout this work for O-selective detection.

The signals and signal-to-noise ratios for O increased in a similar way to those observed for N when the power supplied by the plasma generator was increased from 10 to 20 W. Because the peak shapes and the oxygen-to-carbon selectivity were unaffected by the power level, O-selective detection was carried out at the upper limit of the potential working range (20 W) in order to maximize both the signals and signal-to-noise ratios.

Similarity between O and N was also observed regarding the effect of introducing auxiliary helium. With 2.0 ml/min of GC carrier gas, the peak shapes, signal-to-noise ratios and oxygen-to-carbon selectivity were improved when 15 ml/min of auxiliary helium was added to the plasma (Table 3). In addition, auxiliary helium served to suppress serious interferences caused by the release of background oxygen during the elution of fluorinated or chlorinated compounds [22]. Consequently, auxiliary helium was added to the

Table 3
Effect of auxiliary helium on on-column oxygen-selective detection

Auxiliary He flow-rate (ml/min)	Signal	Signal-to-noise ratio	Oxygen-to-carbon selectivity	$t_{0.1w}$ [b] (s)
0	1.00[a]	1.00[a]	26:1	6.8
15	0.21	3.16	40:1	4.8

[a] Value defined as 1.00.
[b] Peak width at one tenth of peak maximum.

on-column plasma throughout this work also for O-selective detection.

When the present system was operated at 777.2 nm with plasma conditions optimized for O-selective detection, a 51 pg/s detection limit of O and a $5 \cdot 10^2$ linearity were obtained (Table 4). Also, the detection limit of O was improved by a factor of ca. 20 when the 350-kHz plasma was sustained on-column. The on-column detection limit of O was among the lowest reported in the literature [6,10–14,17–21], even though no extensive precautions were considered to exclude air from the plasma. As for N, the practical applicability of the system for O-selective detection was higher than predicted by the low selectivity reported relative to carbon (40:1) because non-specific responses were negative. For some applications, however, a higher oxygen-to-carbon selectivity is required. As this value was not further improved by plasma doping, the most convenient solution to suppress non-specific responses is through real-time spectral background correction.

3.5. Phosphorus-selective detection

Besides N and O, P is among the most difficult non-metallic elements to determine by GC–AES owing to the formation of non-volatile compounds with O_2 that adhere to the silica discharge tube. This results in tailing of chromatographic peaks and in degradation of the linearity for the phosphorus response [14]. The high affinity of P towards hot silica surfaces was also evidenced in this work. Initial attempts at P-selective detection with the on-column plasma sustained in pure helium suffered from extensive peak tailing and from poor repeatability and linearity. As a first step to improve the system performance, optimization of the plasma composition was carried out. From earlier studies, either H_2 [13,14,23,24] or N_2 [25] have been used as plasma dopants for P-selective detection. With the on-column plasma, however, H_2–CH_4 was found to be superior. H_2 served to reduce peak tailing and CH_4 enhanced the phosphorus-to-carbon selectivity by a factor of 2–3. The levels of H_2 and CH_4 were controlled by the intensities of the 656.3-nm H line and the 940.5-nm C line, both relative to the 706.5-nm He line. Even with relatively high levels of H_2 and CH_4 in the plasma ($I_H/I_{He} \approx 8$ and $I_C/I_{He} \approx 0.02$), peak tailing was observed in the P chromatograms. This was eliminated, however, and the linearity for the phosphorus response was improved when 15 ml/min of auxiliary helium was added to the on-column plasma (Table 5). In addition, both the signal-to-noise ratios and the phosphorus-to-carbon selectivity were enhanced. Consequently, auxiliary helium was used throughout this work also for P-selective detection.

Among the most intense emission lines for phosphorus in the near-infrared region of the spectrum, 979.7 nm was found to provide the highest phosphorus-to-carbon selectivity and signal-to-noise ratios. Unfortunately, the adjacent 979.3-nm Br line caused a positive spectral interference from brominated compounds owing to the low resolving power of the mono-

Table 4
System performance characteristics[a] for O-selective detection compared with literature values

Parameter	This work: on-column r.f. plasma	Microwave plasma [12]	Commercial instrument (HP) [21]
Wavelength	777.2 nm	777.2 nm	777.2 nm
Dopant gas	N_2–CH_4	–	H_2–N_2–CH_4
O detection limit	51 pg/s	3000 pg/s	120 pg/s
Oxygen-to-carbon selectivity	40:1	80:1	1000:1
Linearity	$5 \cdot 10^2$	$1 \cdot 10^3$	$5 \cdot 10^3$

[a] All results were obtained with a monochromator equipped with 500-μm slits.

Table 5
Effect of auxiliary helium on on-column phosphorus-selective detection

Auxiliary He flow-rate (ml/min)	Signal	Signal-to-noise ratio	Phosphorus-to-carbon selectivity	$t_{0.1w}$ [b] (s)
0	1.00[a]	1.00[a]	818:1	17.6
15	0.38	1.41	2313:1	6.4

[a] Value defined as 1.00.

[b] Peak width at one tenth of peak maximum.

chromator used. With 500-μm slits, the phosphorus-to-bromine selectivity was limited to 10:1. This value was improved by a factor of 2 when the slit widths were reduced from 500 to 50 μm. Although the 979.7-nm line was used in this work, the detection wavelength may be changed to the 975.0-nm P line in order to suppress interferences caused by brominated compounds.

As for N and O, the signals and signal-to-noise ratios increased when the power level supplied by the plasma generator was increased from 10 to 20 W, whereas the selectivity relative to carbon and chromatographic peak shapes remained unaffected. Therefore, 20 W was selected as the operating level also for P-selective detection.

With the on-column detector optimized for P-selective detection, a 39 pg/s detection limit of P was obtained (Table 6). This value was high compared with the 1.5–3 pg/s limits reported utilizing either the 177.5-nm line [13,14,21] or the 253.6-nm line [23,25]. This difference probably arose because the phosphorus emission lines in the ultraviolet region of the spectrum have better signal-to-background characteristics than those in the near-infrared portion. The $2 \cdot 10^2$ linearity of the on-column detector was relatively low compared with most other elements detected on-column [4,5]. However, linearity problems for P-selective detection are general in GC–AES, and may occur even in conventional atomic emission detectors utilizing both high flow-rates of make-up gas and water-cooled discharge tubes [13,14]. The 2300:1 phosphorus-to-carbon selectivity obtained with the present single-channel spectrometer was acceptable for most practical applications. As mentioned above, however, care must be taken when utilizing the 979.7-nm P line owing to the possibility of cross-over interferences from brominated compounds.

3.6. *Text mixture*

In Fig. 3, C-, N-, O- and P-selective chromatograms from four subsequent injections of a multi-element test mixture are shown. Comparison of the C-selective chromatogram with the

Table 6
System performance characteristics[a] for P-selective detection compared with literature values

Parameter	This work: on-column r.f. plasma	Microwave plasma [12]	Commercial instrument (HP) [21]
Wavelength	979.7 nm	253.6 nm	177.5 nm
Dopant gas	H_2–CH_4	H_2	H_2
P detection limit	39 pg/s	3 pg/s	1 pg/s
Phosphorus-to-carbon selectivity	2300:1	10600:1	5000:1
Linearity	$2 \cdot 10^2$	$5 \cdot 10^2$	$1 \cdot 10^3$

[a] All results were obtained with a monochromator equipped with 500-μm slits.

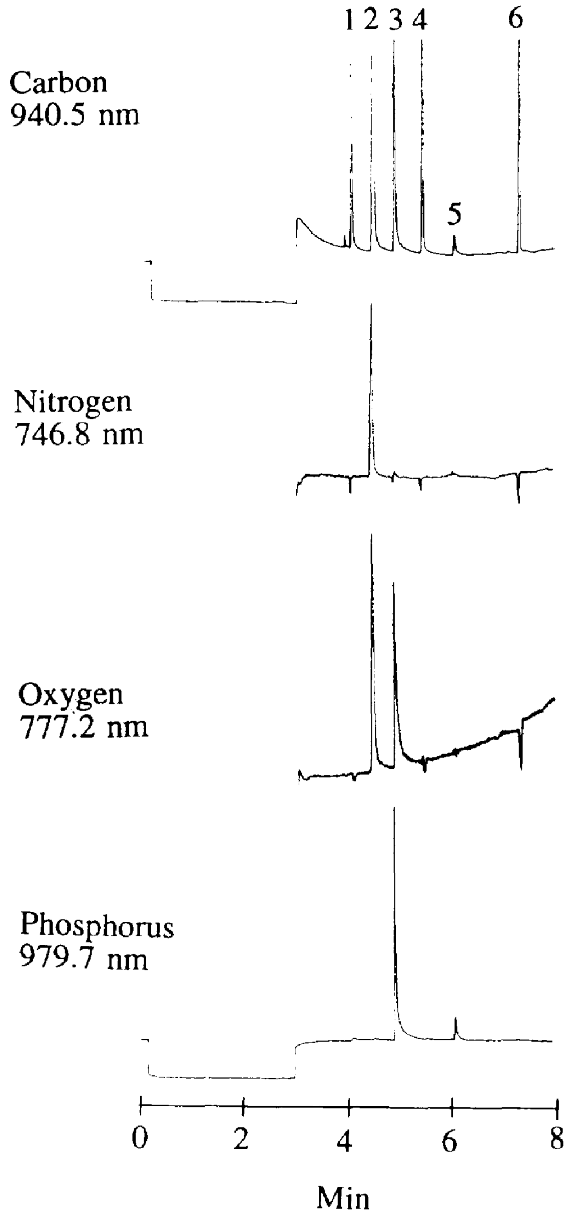

Fig. 3. C-, N-, O- and P-selective chromatograms for a test mixture. Peaks: 1 = 1,2-dichlorobenzene; 2 = nitrobenzene; 3 = triethyl phosphate; 4 = 1-fluoronaphthalene; 5 = 1,1,2,2-tetrabromoethane; 6 = *n*-tetradecane.

traces for N, O and P confirms the absence of peak tailing in the on-column plasma. In addition, the chromatograms support the practical utility of the present single-channel high-sensitivity system for on-column atomic emission detection, even though some of the selectivity values obtained for N and O remained low even after optimization of the experimental conditions. The practical utility of the system was further supported by preliminary experiments indicating that elemental response factors for N, O and P varied by less than 25%. Hence the on-column detector was probably relatively insensitive to positional variations of the atoms within eluting analyte molecules.

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