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# Optimization and evaluation of atomic emission gas chromatographic detection for nitrogen using the 388 nm molecular emission spectral band

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## Abstract

Nitrogen determination by gas chromatography with atomic emission (microwave-induced plasma) detection (GC–AED) has been accomplished using the 174 nm atomic emission line, but with very limited selectivity and sensitivity. Nitrogen can also be detected using the cyanogen (CN) molecular band at 388 nm. A commercial GC–AED system was modified to allow the use of the 388 nm line for nitrogen detection, giving an improvement of 100-fold in sensitivity and selectivity, when compared with the 174 nm mode. Limits of detection of 10 pg/s were common, representing a 10-fold improvement. Compound-independent behavior was found for the system, working with optimum operating conditions, while instrumental problems were clearly reflected by a drastic compound dependent behavior. Response factors showed an important dependency upon the concentration of the element present. This dependency affected the accuracy of the determination of empirical formulae using GC–AED. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Detection, GC; Atomic emission detection; Response factors; Calibration, compound-independent; Empirical formula; Nitrogen

## 1. Introduction

Throughout the development of atomic emission detection (AED) for gas chromatography (GC), high performance has been attained for many elements but nitrogen detection has been characterized by low selectivity, sensitivity and high background levels, limiting its application to samples with high nitrogen content in simple matrices [1–5].

This lack of sensitivity and selectivity has been

attributed to air leaks in the system, severe carbon interference and inefficiency of the excitation process. Nitrogen needs high temperatures to reach its excited state [6], therefore a lower response from its atomic line is expected, while formation of molecules, such as CN, N<sub>2</sub> and N<sub>2</sub><sup>+</sup>, is preferred when carbon is available [1,7,8]. Approaches to overcome those problems ranged from changing reagent gases and plasma conditions to injection of larger sample volumes [9].

The Hewlett-Packard 5921A GC–AED system introduced in 1989 showed some usable selectivity and sensitivity of nitrogen using the 174 nm atomic emission line, but did not produce the high selectivity

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over carbon found for other elements [10]. The later (Hewlett-Packard 2350, 1996) version of the commercial instrument enabled nitrogen using the CN molecular band at 388 nm instead of the atomic emission line at 174 nm affording operational improvements [11].

The use of spectral molecular emission bands to determine some elements using microwave-induced plasmas (MIPs) was common in the early development of these instruments. McCormack et al. first demonstrated the MIP as a gas chromatographic detector, using argon as carrier gas [12]. Argon plasmas are less energetic than helium, producing conditions under which eluted compounds are incompletely atomized, and elements such as nitrogen, fluorine and chlorine are not efficiently excited [1,13]. McCormack et al. [12] reported the suitability of the C<sub>2</sub> band (385.2 nm) for determination of carbon, the CS (257.6 nm) band for sulfur detection and the CCl diatomic emission band (278.8 nm) for chlorine detection. Additionally, the OH band at 300 nm and the CN band at 388.3 nm were proposed for the detection of oxygenated and nitrogen-containing species, provided that oxygen and nitrogen were rigorously excluded from the instrument.

The determination of carbon-containing compounds using an argon plasma was also proposed by monitoring the CN emission band at 388 nm, while nitrogen gas was detected using the NH band emission at 336 nm. However, limits of detection were poorer than expected [14,15] due to a high complex molecular spectral background [13]. This problem was addressed by using helium as the plasma gas, although a very efficient vacuum system was needed. The much higher electronic energy available in the low-pressure helium MIP improved atomization and excitation of organic compounds, but problems for nitrogen detection remained, although reduced.

The utilization of the CN band in the Hewlett-Packard 2350 instrument requires pure methane as auxiliary gas instead of the more common mixture of N<sub>2</sub>–methane (90:10); higher hydrogen flows are also required. The Hewlett-Packard 5921A, available for the present study, was converted to determine nitrogen similarly by installation of a new operational recipe and a new auxiliary gas flow restrictor.

Now presented is the optimization of the modified

5921A system for the determination of nitrogen at 388 nm, and its evaluation and comparison with 174 nm line emission under these new conditions. A study of compound independent behavior for the modified system and its application for the determination of empirical formulas is also presented.

## 2. Experimental

### 2.1. Reagents

Undecane (Aldrich, Milwaukee, WI, USA), nitrobenzene, 2,6-dimethylaniline, 2,4-dimethylaniline, triethylamine, *n*-hexylamine, benzonitrile, aniline, pyridine, methylaniline, *N,N*-dimethylaniline (Eastman Kodak, Rochester, NY, USA), and *N,N*-dimethyl formamide (Fisher Scientific, Fair Lawn, NJ, USA), were used without any purification, and solutions were prepared by dilution in hexane (HPLC grade, Fisher Scientific, St. Louis, MO, USA).

The following compounds, 2,4-dichloroaniline, 4-chloroaniline, 3,4-dichloroaniline and 3,5-dichloroaniline (Eastman Kodak) were purified by sublimation before use. Solutions were prepared in hexane. The pesticides used were isazofos 97% purity (Ciba-Geigy, Greensboro, NC, USA) and chlorpyrifos 99.2% purity (Dow, Midland, MI, USA) and were dissolved in acetone (HPLC grade, Fisher Scientific) without any purification.

### 2.2. Gases

Helium (Merriam Graves 99.995% purity or better) was used as carrier gas and detector gas. Hydrogen, oxygen and nitrogen were technical grade (Associated Gases Products or Merriam Graves). High-purity methane (Associated Gas Products 99.999%) was used as auxiliary gas.

### 2.3. Instrumentation

A Hewlett-Packard HP 5921A atomic emission detector (Agilent Technologies, Little Falls, DE, USA) interfaced with a HP 5890 II gas chromatograph was used. A HP 7673A automatic injector and a split/splitless capillary injector operated in the split

mode were used. A new restrictor for hydrogen auxiliary gas flow was installed in the system that allowed the use of higher hydrogen reagent gas flows. Reagent gas pressures were controlled manually using the manometers on each cylinder. After any pressure was changed, the plasma conditions were allowed to stabilize for at least 60 min before each injection. Detector and gas chromatograph control and data processing were done using a Pascal-based operational system and a Hewlett-Packard 300 computer.

GC employed a 25 m fused-silica SE-54 capillary column (Supelco, Bellefonte, PA, USA) of 0.32 mm internal diameter and 0.17  $\mu\text{m}$  film thickness. The injection port, cavity and transfer line were held at 300°C. The helium carrier gas flow-rate was 1 ml/min. A 1- $\mu\text{l}$  volume was injected at a split ratio of 10:1 unless otherwise specified. A solvent vent was set during the first 3 min of each run to avoid introducing excess solvent into the plasma. GC oven conditions were optimized for each set of samples to produce the best resolution and peak shape.

### 3. Results and discussion

#### 3.1. Optimization of reagent gases

Reagent gases such as hydrogen, oxygen and air are added to the MIP to alter the chemistry of the plasma. Some elements react with the reagent gases to give products that may emit, as in the case of the CN band, or to reduce the interaction of the analyte with the discharge tube walls, thereby improving the detection and reducing carbon deposition in the discharge tube [8,10,13,16–20].

For nitrogen detection using the 388 nm CN molecular band, a reagent gas mixture of oxygen, hydrogen and methane was recommended by Quimby et al., along with high make-up flows to avoid excess carbon deposition in the discharge tube [11]. Therefore, these operational features were optimized for the modified GC–AED system.

The presence of reagent gases was characterized by changes of color in the plasma, ranging from off-white when no reagent gases were used, to

intense blue when methane was present. These observations are similar to those reported by Estes et al., when chlorobenzene was used to dope the plasma [8].

The nitrogen response at 388 nm was optimized using a simplex experimental design to produce the largest gas chromatographic peak area for a 100  $\mu\text{g/ml}$  nitrobenzene solution. A summary of the fixed step simplex experiment used is shown in Table 1. The initial conditions were taken randomly and the conditions for the next vertex were calculated according to Miller and Miller [21]. Calculation of new conditions that correspond to a vertex were repeated to obtain duplicate experimental conditions that produced the maximum response, for example, vertex 8e corresponded to same conditions as vertex 6e. Some calculated conditions were not always used because the recommended gas pressures could not be set at the regulators (such as vertex 6 or 8), or because those conditions produce a very unstable plasma, such as at vertex 5. A fine tune was done to get a better understanding of the effect of each reagent gas with the conditions optimized from the simplex.

Fig. 1 shows that the methane pressure has a substantial effect on the nitrogen response (peak area) at 388 nm for 1  $\mu\text{l}$  of 100  $\mu\text{g/ml}$  nitrobenzene solution (10:1 split) injected,  $\text{O}_2$  pressure being kept at 50 p.s.i. (and  $\text{H}_2$  pressure at 40 p.s.i.). (1 p.s.i. =  $6.894757 \cdot 10^3$  Pa) There was an increase in the signal with increase of methane up to 55 p.s.i.; further increases did not affect the signal. The almost constant section of the response plot was probably because all the nitrogen reacted with the excess of carbon to form CN. A pressure of 50 p.s.i. was chosen as optimum to avoid excess of carbon in the plasma that could increase the carbon deposition and thereby reduce the performance and the discharge tube lifetime. Oxygen and hydrogen pressure changes did not appreciably alter the N 388 response when the other gases were kept at the optimum conditions [22].

The best conditions corresponded to a methane pressure of 60 p.s.i., hydrogen 20 p.s.i. and oxygen 50 p.s.i. Although, a low hydrogen pressure was found as optimum (20 p.s.i.), a higher pressure was actually used (40 p.s.i.) to reduce carbon deposits on the discharge tube [23]. Under these conditions a

Table 1  
Simplex optimization of the reagent gases

Simplex	Vertex	Methane pressure (p.s.i.)	Hydrogen pressure (p.s.i.)	Oxygen pressure (p.s.i.)	N 388 response <sup>a</sup> (peak area) (area units)	Rejected when <sup>b</sup>
1	1	20	20	20	7709	Third
	2	60	20	20	11 012	
	3	20	50	20	6864	Second
	4	20	20	50	1355	First
2	5c	46	40	10	10 759	Fourth
	5e	60	50	20		
3	6c	100	10	40	12 043	
	6e	60	20	50		
4	7c	60	40	40	11 248	
	7e	60	40	40		
5	8c	60	4	54	12 036	
	8e	60	20	50		

<sup>a</sup> N 388 response (peak area): average of five injections of same solution.

<sup>b</sup> Rejected when=indicates in which simplex combination this vertex was rejected.

c=Calculated value.

e=Experimental value used.

discharge tube could last for more than 2 months of daily use, however, it was necessary to clean the cavity and the spectrometer window at least once a

month, to maintain the performance of the instrument.

### 3.2. Optimization of make-up flow

Nitrogen determination by CN band emission requires a high level of methane in the plasma, and therefore high helium make-up is desirable to stabilize the plasma and avoid carbon deposition. Fig. 2 shows the effect of the helium make-up flow on the peak area for a 1- $\mu$ l (inlet split 10:1) 100  $\mu$ g ml nitrobenzene sample. This standard sample of nitrobenzene was employed also for the calculation of figures or merit shown in Table 2, three replicate injections being typically made.

A steady decrease in the signal occurs at higher make up flows, due to the decrease in residence time of the analyte in the plasma. Since the main purpose of using make-up flow is to avoid carbon deposition, the largest flow-rate that did not affect the signal significantly was chosen as optimum, namely 160 ml/min. Decrease of background counts was also noticeable as flow-rate was increased. This effect

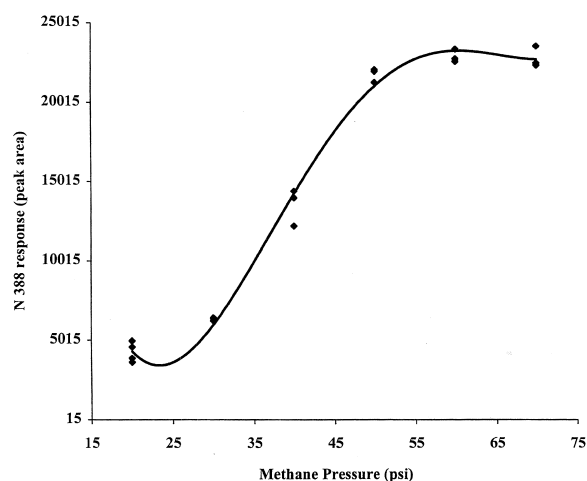


Fig. 1. Nitrogen signal (388 nm) dependence upon methane pressure in the plasma.

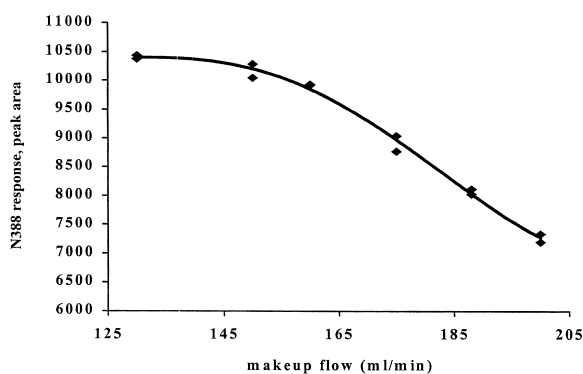


Fig. 2. Nitrogen signal (388 nm) dependence upon make-up helium flows.

could have been due to increased gas mixture purity as a higher flow of high-purity helium was introduced into the plasma [22].

### 3.3. Evaluation of nitrogen detection performance and comparison with carbon at 193 nm and nitrogen at 174 nm detection

The modified 5921A atomic emission detector performance was evaluated for the optimized conditions by determining analytical figures of merit for the 388 nm nitrogen detection mode and comparing it with the former nitrogen detection (174 nm) mode and with carbon detection at 193 nm. The general qualitative performance of the system for a catalytically cracked gasoline sample is shown in Fig. 3. It is clearly seen that the nitrogen chromatogram at 174 nm follows closely the profile for carbon,

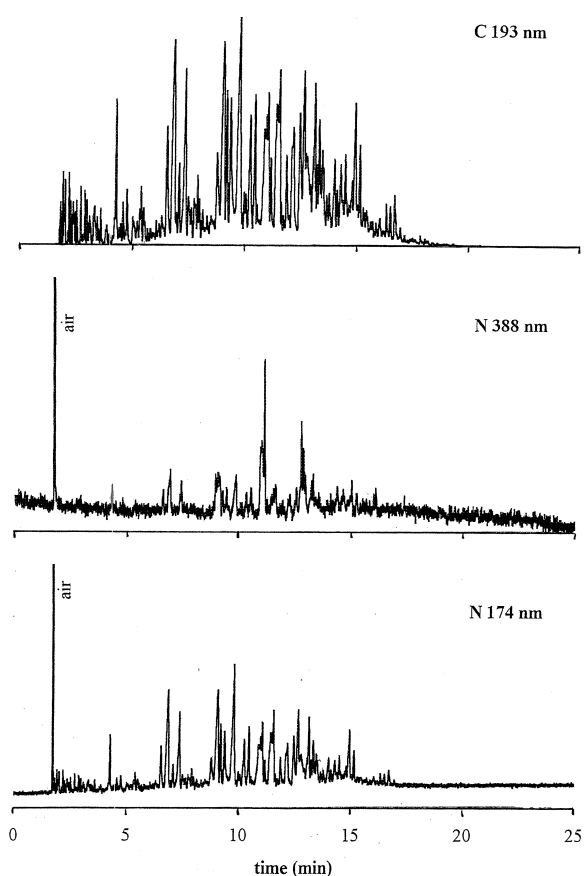


Fig. 3. Carbon (193 nm), nitrogen (388 nm) and nitrogen (164 nm) profiles for a catalytically cracked gasoline.

suggesting that N/C selectivity is minimal. However a substantially different profile is seen at 388 nm indicating a completely different selectivity ratio.

Table 2

Figures of merit for the determination of N using 388 nm and 174 nm emission lines, and C using 193 nm emission line<sup>a</sup>

	N 388 nm	C 193 nm	N 174 nm
Precision (RSD, %)	1–5%	1–5%	5–20%
Selectivity vs. C	5000 (800 000) <sup>b</sup>	1	50 (7 K) <sup>b</sup>
MDL	10 pg/s (18.1) <sup>c</sup>	1 pg/s (0.6) <sup>c</sup>	25 pg/s (4.6) <sup>c</sup>
DL	160 pg N	200 pg C	1100 pg N
LDR	>3 orders of magnitude	>3 orders of magnitude	>3 orders of magnitude
Sensitivity	~4 ct/pg N	~0.5 ct/pg C	~0.015 ct/pg N

<sup>a</sup> Values in parentheses are reported for the new commercial instrument.

<sup>b</sup> Ref. [11].

<sup>c</sup> Ref. [28].

### 3.3.1. Precision

The reproducibility of the measurements was evaluated by comparing the peak areas obtained from replicate injections of a nitrobenzene standard solution. The autosampler was used and all the replicates were done on the same day while maintaining the plasma lit. Table 2 presents the results for the three lines and it is noteworthy that the 174 nm nitrogen detection was always accompanied by lower reproducibility, when compared with the other lines used, at least in the range of concentrations used in this study (50 pg–50 ng of N).

When data obtained on different days and following reignition after turning off the plasma were compared, a considerable decrease in precision was noted. Therefore, any quantitative analysis required calibration and measurement while maintaining the plasma lit.

### 3.3.2. Selectivity

The selectivity of the atomic emission detector for nitrogen is defined as the ratio of the peak response per mole of nitrogen to the peak response per mole of carbon [10]. *n*-Undecane was used as the carbon source, since, under defined GC conditions, it co-eluted with the nitrobenzene peak. It is important that selectivity over carbon be measured against reference peaks eluting with retention close to the analyte, thereby ensuring that linear response regions of both are similar. The selectivities obtained for the 388 nm and 174 nm lines are shown in Table 2.

Comparison of nitrogen detection for the 174 nm and 388 nm lines showed an improvement approaching two orders of magnitude for the latter, paralleling that reported (Table 2) for the HP G2350A instrument [11]. However, the selectivities in our study were lower than those obtained with the G2350A. The difference in selectivity may result from different gas purities and/or different spectrometer resolution. The improved accuracy in the wavelength tuning in the G2350A helps reduce interferences from carbon molecular emission in the same spectral region, thereby improving selectivity of the nitrogen emission at 388 nm.

### 3.3.3. Linear dynamic range

The linear dynamic range (LDR) was taken as the range of sample concentrations over which the

response factor varied by less than 20%. Linearity of at least three orders of magnitude was observed for the three lines (Table 2).

### 3.3.4. Sensitivity

The sensitivity of the GC–AED measures its ability to discriminate between small differences in the analyte concentration. The sensitivity was determined for the modified system as the slope of the calibration curve. Table 2 shows important differences among the sensitivities of the three lines measured. The 388 nm nitrogen line was over two orders of magnitude more sensitive than the 174 nm line, and 10 times better than the 193 nm carbon line most frequently measured. This represents an important advantage in the use of the modified system for nitrogen determinations.

### 3.3.5. Detection limits

The minimum amount of analyte that could be detected at a known confidence level was calculated using two definitions: the minimum detectable level and the absolute detection limit. Results are presented in Table 2.

The minimum detectable level (MDL) is defined as the amount of element 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 [10]. The results of the MDL for the modified system were comparable with the results reported for the new commercial system (Table 2, values in parentheses).

Absolute detection limits (DLs) were calculated as the response that produced a signal-to-noise ratio of three. The 388 nm line shows an order of magnitude improvement over the 174 nm line and it is comparable with the carbon detection limit. Reproducibility of the DL was approximately 5%.

## 3.4. Compound-independent calibration by GC–AED

The ideal element selective detector for GC responds to that element in any compound injected, and its response is independent of the molecular structure of the analyte. This structure-independent response allows the use of just one or a few standards to quantify any sample, using what is

called “compound-independent calibration”. This facility has very important advantages for analytical chemistry in reducing costs of analysis, since many of the required standards are expensive, toxic or extremely difficult to obtain. It reduces analysis time, since preparation of multicomponent standard mixtures is not necessary.

In theory, the helium MIP has enough energy to atomize and excite all elements of compounds eluting from the gas chromatographic column. Consequently, the response should depend on the element concentration in the plasma and not be influenced by the molecular structure of the analyte. Thus, compound-independent calibrations could be carried out using standards that contain the elements of interest. In high-resolution GC, the resolved analytes reaching the detector have high purity, and thus elements in the compound can be detected with high selectivity and in some cases simultaneously, reducing the amount of sample required for analysis. However, compound independent calibration and determination of empirical formulas using GC–AED

have shown some conflicting results, probably due to residual elemental response dependence on molecular structure [24–26].

Using the optimum conditions, a series of calibration curves for nitrogen-containing standard analytes were prepared to compare their sensitivity with that of nitrobenzene. Standards were chosen to include different molecular structures and also to evaluate the effect of chlorine atoms in the molecule. Nitrobenzene was used as a standard since it did not react with any of the compounds used and its chromatographic peak shows good symmetry. The standard solutions were prepared in hexane and the appropriate concentration of nitrobenzene added. Each calibration curve was obtained using the autosampler, with duplicate injections for two or more aliquots of each solution. Carbon 193 nm and nitrogen 174 nm could be monitored simultaneously, while a separate injection was needed for nitrogen 388 nm.

Table 3 presents the ratios of the slope of the calibration curve for each analyte to the slope for

Table 3  
Compound-independent studies compared with nitrobenzene<sup>a</sup>

Compound	Slope ratio (compound/nitrobenzene)		
	N 388 nm	C 193 nm	N 174 nm
<i>Water vapor present in plasma</i>			
2,6-Dimethylaniline	1.56±0.04	ND	ND
Benzonitrile	1.23±0.03	ND	ND
Isazophos	0.70±0.02	0.35±0.06	0.63±0.04
Chlorpyrifos	0.70±0.02	0.69±0.01	0.61±0.04
Pyridine	0.65±0.01	0.75±0.03	0.88±0.07
Aniline	1.07±0.02	1.09±0.03	1.51±0.08
<i>No water vapor in plasma – new internal seals in waveguide</i>			
Aniline	1.08±0.04	1.05±0.02	1.07±0.04
Methylaniline	0.99±0.03	0.98±0.02	0.98±0.04
<i>N,N</i> -Dimethylaniline	1.05±0.04	1.05±0.03	1.09±0.04
2,6-Dimethylaniline	0.98±0.04	1.00±0.02	1.03±0.04
2,4-Dichloroaniline	0.97±0.07	0.97±0.06	1.00±0.07
4-Chloroaniline	0.96±0.07	0.96±0.06	0.96±0.09
3,4-Dichloroaniline	0.96±0.08	0.99±0.07	1.12±0.09
3,5-Dichloroaniline	0.96±0.12	0.99±0.07	1.00±0.09
Pyridine	1.03±0.04	1.03±0.02	1.06±0.10
Isazophos	1.02±0.09	ND	1.24±0.13
Chlorpyrifos	1.08±0.01	ND	0.91±0.05

<sup>a</sup> Slopes of calibration curves of compound in the table are divided by the slope of the calibration curve of nitrobenzene used as internal standard.

ND=Not determined.

nitrobenzene. Since compound independent behavior is the goal, the ratio of slopes for standard/nitrobenzene should be very close to unity.

An important observation was made during this study, whose further implications are discussed later. During the initial stages, it was difficult to keep the plasma ignited for lengthy periods and all emission lines showed high background noise. Investigation showed the waveguide to contain water (liquid and vapor), arising from leaking seals in coolant lines. As shown in Table 3, under these circumstances the ratios of sensitivities deviated significantly from unity, suggesting that the sensitivity was strongly dependent on the compound to be analyzed.

After the seals were replaced and water vapor rigorously excluded, the system was optimized again and compound dependency was reevaluated. As shown in Table 3, the ratios of sensitivities were now close to unity for all the compounds determined. A combined calibration curve, using the data from calibration curves of different compounds and that for nitrobenzene, showed correlation coefficients ( $r^2$ ) between 0.99 and 0.9999 for nitrogen determined at 388 nm or 174 nm and for carbon at 193 nm. This good linearity, coupled with compound independent behavior in the range of concentration used was encouraging, even when complex molecules such as the pesticides isazophos and chlorphyrifos were examined, or when chlorine was present in the molecule.

### 3.5. Response factors

Considering the fact that the AED response was compound independent for the compounds studied the response factors for each element should also reflect this. Elemental response factors were calculated by dividing the AED response at each concentration by the corresponding amount of the element determined. It was found that elemental response factors were similar for all the compounds when they had similar concentrations of nitrogen as would be expected from compound independent behavior. However, response factors were significantly different when compared at different concentrations. Fig. 4 shows the considerable increase in response factors observed when nitrogen atom levels below 2000 pg were introduced to the plasma. This

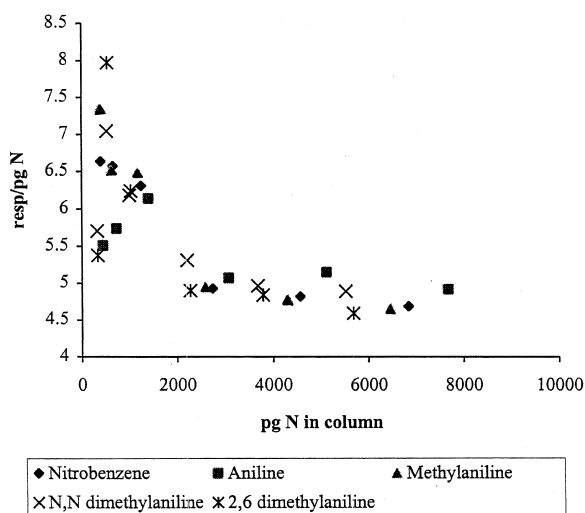


Fig. 4. Dependence of nitrogen response factor (388 nm) upon the mass of analyte in the column.

larger relative emission occurring when there is less analyte in the plasma was observed for all wavelengths monitored during this work (N 388 nm, N 174 nm, C 193 nm, S 181 nm, P 178 nm and Cl 479 nm), and for all compounds examined. This effect was seen both before and after the waveguide seals were replaced, thus eliminating the possibility that the altered plasma conditions caused this behavior. A similar dependence has been reported by Janák et al. for carbon detection of acridine compounds [27].

### 3.6. Empirical formulae calculations

One of the applications of the compound-independent response of the GC–AED system is in the determination of empirical formulae. Therefore, the modified GC–AED system was evaluated for the determination of carbon-to-nitrogen ratios of known compounds. Carbon-to-nitrogen ( $C/N$ ) ratios were calculated for different compounds using nitrobenzene as known standard. It was found that the carbon-to-nitrogen ratio accuracy was affected by the concentrations of the known standard and the unknown compound. Table 4 shows that when determining  $C/N$  for methylaniline using nitrobenzene as standard, different  $C/N$  ratios were found when different concentrations were used even when the



Table 4

Calculated carbon-to-nitrogen ratios for methylaniline, using nitrobenzene as standard, and different concentrations of each

		Nitrobenzene				Average C/N	Standard deviation	Absolute error
		6844 pg N	2737 pg N	651 pg N	398 pg N			
Methylaniline C/N=7	6461 pg N	6.87	7.33	8.36	10.16	8.18	1.46	1.18
	2584 pg N	6.48	6.92	7.89	9.59	7.72	1.38	0.72
	615 pg N	5.71	6.09	6.94	8.45	6.80	1.21	0.20
	376 pg N	4.62	4.93	5.62	6.84	5.50	0.98	1.50
Average calculated C/N		5.92	6.32	7.20	8.76			
Standard deviation		0.99	1.06	1.21	1.47			
Absolute error		-1.08	-0.68	+0.20	1.76			

sensitivity of the instrument was similar for both compounds. To determine whether this behavior was reduced for similar molecular structures, *N*-methylaniline was used to determine the C/N for *N,N*-dimethylaniline, as shown in Table 5. Poorer accuracy was observed when low reference concentrations were used, and low reproducibility was observed, even for a difference in molecular structure of one carbon atom. Similar results were obtained for the compounds listed in Table 3, using different compounds as standards [22]. In general, it was found that the accuracy of measured ratios was not improved by the use of similar molecular structures, but it appears that when low concentrations of either the standard or the unknown were used, larger deviations of the expected carbon-to-nitrogen ratio were found. The previously noted concentration dependency of response ratios again mitigates against accurate measurements for unknown compounds.

#### 4. Conclusions

Nitrogen detection has been an important challenge when using the commercially available GC–AED system, however, after some modifications, the GC–AED system prove to be very promising system. Examination of response for the CN 388 nm line showed it to be more than one hundred times more sensitive than for the atomic 174 nm line and 100 times more selective; this represents a promising characteristic for its application in real samples analysis.

The AED response was also independent of the molecular structure, for the compounds evaluated and in the concentration ranges used. This suggested the possibility of using a single standard, such as nitrobenzene, as a internal standard for the quantitative determination of the nitrogen compounds studied, even for the pesticides, thereby reducing time and cost of analysis.

Table 5

Calculated carbon-to-nitrogen ratios for *N,N*-dimethylaniline, using *N*-methylaniline as standard, and different concentrations of each

		<i>N</i> -Methylaniline				Average C/N	Standard deviation	Absolute error
		6461 pg N	2584 pg N	615 pg N	376 pg N			
<i>N,N</i> -Dimethylaniline C/N=8	5510 pg N	8.13	8.61	9.78	12.08	9.66	1.76	+1.66
	2208 pg N	7.52	7.97	9.05	11.18	8.93	1.63	+0.93
	526 pg N	7.17	7.60	8.63	10.67	8.51	1.55	+0.51
	321 pg N	6.79	7.20	8.17	10.10	8.06	1.47	+0.06
Average calculated C/N		7.40	7.85	8.91	11.00			
Standard deviation		0.57	0.60	0.68	0.84			
Absolute error		-0.60	-0.15	+0.91	+3.00			

The use of GC–AED for the determination of empirical formulae was promising, but must be considered carefully. Even when AED showed compound-independent behavior, dependency of the response factors with the concentration was found, affecting the accuracy in the empirical formulae determination. Therefore, before using the GC–AED system for empirical formulae determinations more studies must be done.

Nitrogen detection using GC–AED has been widely improved by the use of the molecular band at 388 nm, instead of the atomic line at 174 nm. This improvement should be more widely evaluated along with effect of the modification of the instrument on other detection modes and if possible comparing it with a non-modified instrument.

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