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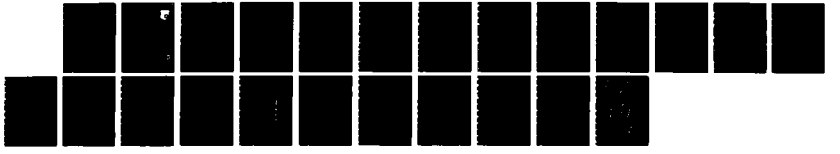

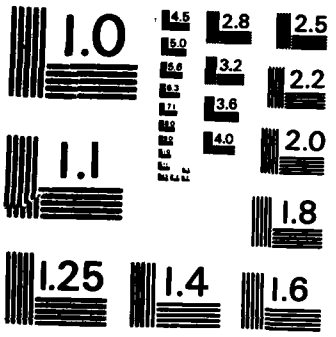

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THE USE OF A PYROCHEMILUMINESCENT NITROGEN ANALYZER AS A CAPILLARY G.C. DETECTOR

Edward W. Pitzer

Experimental Support Branch
Aero Propulsion Laboratory

February 1986

Final Report for Period March 1985 - May 1985

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This technical report has been reviewed and is approved for publication.

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A study was conducted to determine the feasibility of interfacing a pyrochemiluminescent nitrogen analyzer to a high resolution glass capillary gas chromatograph. The instruments used were a Varian Model 3700 gas chromatograph and an Antek Model 703C pyrochemiluminescent nitrogen analyzer.

Known standards of nitrogen containing compounds were prepared in shale derived jet propulsion fuel that had been previously determined to have no nitrogen containing species. These solutions were then chromatographed on the GC/CLD system. The resulting data were reduced using relative response factors with an internal standard. The nitrogen content of the standard solutions were validated by analyses on a separate Antek nitrogen analyzer used to determine total nitrogen content.

The method of GC/CLD was deemed feasible. However, it is recommended that appropriate design changes be made to the Antek Model 703C nitrogen analyzer to accommodate the type of flows common with capillary gas chromatographs. Keywords:)

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FOREWORD

This research was conducted in the Experimental Support Branch, Fuels and Lubrication Division, Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio under Project No. 3048, Task No. 304805, Project No. 30480591 by Edward W. Pitzer as Project Scientist.

This research was conducted during the period March 1985 - May 1985.

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LIST OF ABBREVIATIONS

GC	Gas Chromatograph
CLD	Chemiluminescent Detector
FID	Flame Ionization Detector
ppm-N	Parts per million Nitrogen
RRF	Relative Response Factor
C	Degrees Celsius
RT	Retention Time
Kb	Base Dissociation Constant
ng-N	nanograms Nitrogen
nm	nanometers

SECTION I

INTRODUCTION

The Antek Model 703C nitrogen analyzer is a very reliable, and highly quantitative method for determining the total bound nitrogen content in a wide variety of sample matrices (References 1,2,3). The excellent quantitative capability is attributable to the high temperature (1000+ Deg. C) and abundant oxygen supply in the quartz combustion tube which allows for total oxidation of the sample. Figure 1 shows a typical combustion tube used with Antek nitrogen analyzers.

Nitrogen containing organic species introduced to the combustion tube are converted, via oxidative pyrolysis, to carbon dioxide, water, and nitric oxide as shown below (Reference 2).

$$R\text{-}N + O2 \rightarrow CO2 + H2O + NO$$

The resultant nitric oxide is then routed to a reaction chamber which is supplied with ozone from an internal ozone generator. In this reaction chamber the nitric oxide reacts with the ozone to form a metastable nitrogen dioxide, which upon relaxation to its stable state, emits a photon of light in the wavelength range of 700-900 nm (Reference 2).

$$NO + O3 \rightarrow NO2^* + O2$$
$$NO2^* \rightarrow NO2 + \text{photon}$$

The Antek Model 703C measures these photons of light with a photomultiplier tube and bandpass filter. Figure 2 shows a block diagram of the nitrogen analyzer system used in this study.

The objective of this study was to determine if the eluents of a capillary gas chromatograph could be detected by a nitrogen analyzer to take advantage of its nitrogen specificity and excellent quantitative capability of the analyzer.

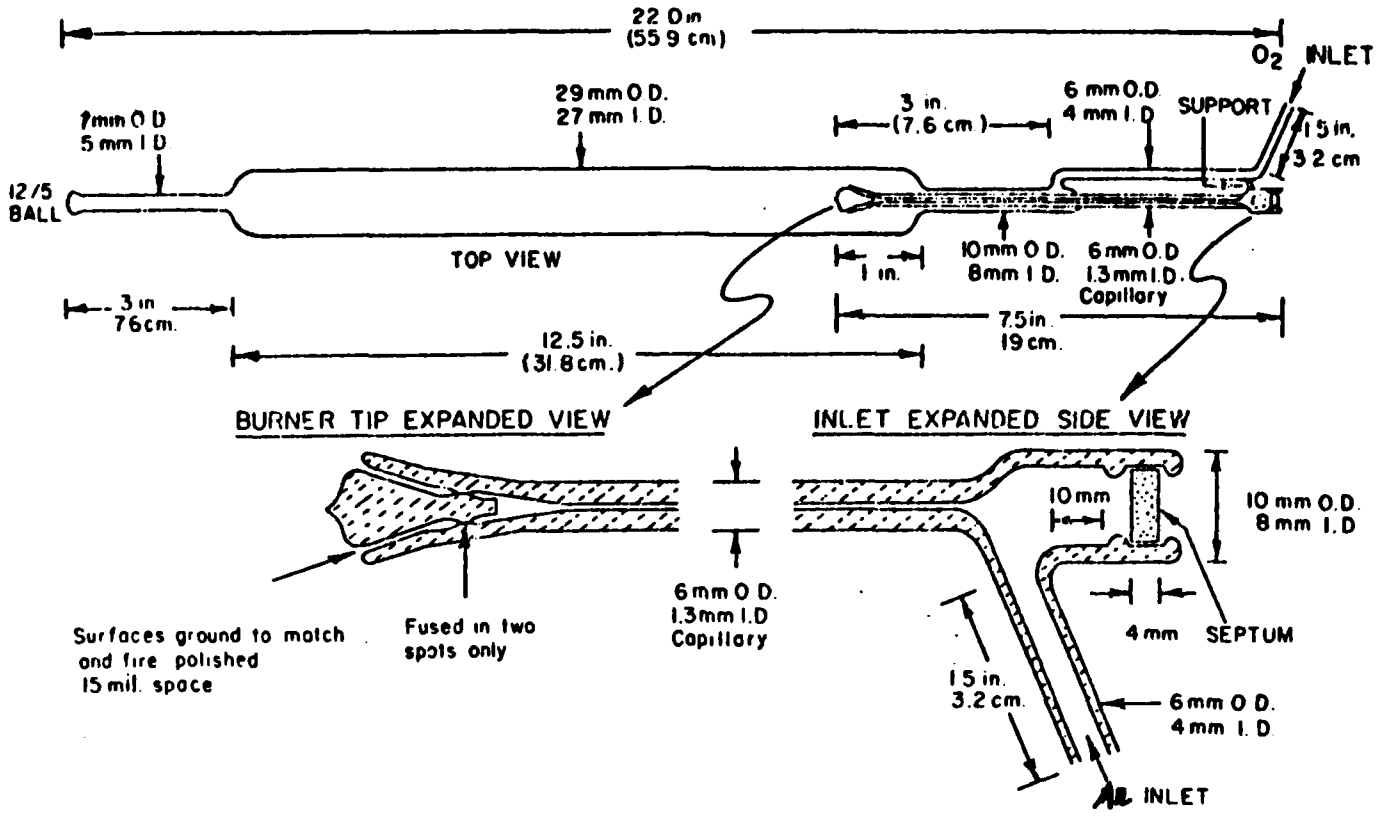

Figure 1. Quartz Combustion Tube

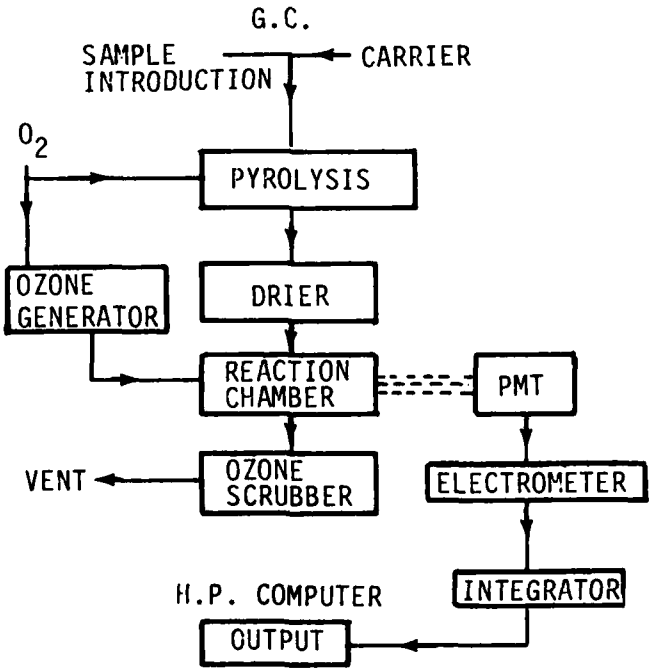

Figure 2. Block Diagram of the Nitrogen Analyzer

SECTION II

EXPERIMENTAL

1. OVERVIEW

A Varian 3700 gas chromatograph, equipped with a split/splitless injector was interfaced with an Antek Model 703C nitrogen analyzer via a heated transfer line. The fused silica column used for the chromatography was routed through the transfer line, through a high temperature septum, and inserted into the quartz combustion tube of the nitrogen analyzer. Initially, the column end extended four inches into the combustion tube (Figure 1). Inspection of the column end after initial operations revealed that the polyimide coating of the column had been totally oxidized along a section of the column end from 1.25 to 3.5 inches. This made it apparent that the column eluents were being released downstream of the optimum oxidation zone of the combustion tube. Accordingly, the column end was inserted only 1.25 inches into the combustion tube which resulted in increased response. Table 1 lists the operating conditions and parts of the GC/CLD system.

2. SAMPLE PREPARATION

Two solutions of nitrogen containing compounds were prepared, gravimetrically, in shale derived jet propulsion fuel that had been previously determined to have no nitrogen containing species. These solutions contained a total of 19 different compounds. Each solution contained approximately the same amount of 2,5-dimethylpyrrole used as an internal standard. The solutions were then gravimetrically diluted in the same shale fuel to concentrations in the 5 to 10 ppm-N range. Table 2 lists the compounds used, their concentrations, and the resultant chromatographic data from this study.

3. METHODOLOGY

A previous study (in this laboratory) on the column chosen for this research, revealed that the minimum operating pressure for the column was 46 PSIG (Reference 4). The column was operated at this minimum pressure to avoid introducing the sample to the combustion tube too quickly.

TABLE 1

CHROMATOGRAPHIC OPERATING CONDITIONS

Detector	Pyrochemiluminescent (Antek Model 703C)
Detector Temp.	1050 Deg. C
Gas Chromatograph	Varian Model 3700 with Split/Splitless Injector
Injector	Split Mode, Fritted Glass Liner
Injector Temp.	270 Deg. C
Liquid Sample	5 uL (Manual Injection), Split 1:2
Detector Make-up	100 ml/min Argon
Det. Pyrolysis 02	260 ml/min
Det. Ozonolysis 02	120 ml/min
Column	DB-1 (Fused Silica Bonded Phase MeSi) WCOT, 60 M, 0.32 mm ID, 1.0 uM Film Thickness, 80,000 Effective Theoretical Plates
Column Flow Rate	8.8 ml/min Argon at 46 PSIG and 40 Deg. C
Column Temp. Profile	40 to 240 Deg. C at 5 Deg. C/min
Data Processing	Antek Attenuation 5 to a Hewlett Packard 3357 Computer via an HP18652A A/D Converter

TABLE 2

C.L.D. CHROMATOGRAPHIC DATA

Compound	R.T. (min)	[ppm-N]	R.R.F. (mean)	Std.Dev.	95%CL
Pyrrolidine	5.46	13.07	1.85333	0.20	0.50
1-Methyl-pyrrolidine	5.50	9.88	1.04798	0.03	0.06
Piperidine	7.40	8.36	1.29789	0.00	0.01
1-Methyl-piperidine	7.60	6.59	1.03673	0.02	0.04
2-Methyl-piperidine	8.55	4.63	1.09290	0.02	0.06
2-Methyl-pyridine	8.69	5.35	0.98190	0.06	0.15
3-Methyl-piperidine	9.37	6.64	1.79694	0.14	0.36
2,6-Dimethyl-pyridine	9.65	6.03	1.01336	0.01	0.01
4-Methyl-pyridine	10.13	11.50	1.02576	0.04	0.10
2,6-Dimethyl-pyridine	11.16	4.82	1.01336	0.01	0.01
2,5-Dimethyl-pyrrole	12.15	8.96/9.17	1.00000	(Internal Standard)	
2,2,6,6-Tetra-methylpiperidine	14.14	6.76	1.48471	0.30	0.75
3,5-Dimethyl-pyridine	14.32	9.54	1.03570	0.03	0.07
3,4-Dimethyl-pyridine	15.19	9.72	1.05710	0.03	0.09
2,3,6-Tri-methylpyridine	15.66	6.27	1.06642	0.05	0.13
2,4-Dimethyl-3-Ethylpyrrole	18.83	4.81	1.30819	0.01	0.01
1-Methylindole	24.36	4.22	1.06968	0.04	0.10
2-Methylindole	27.37	5.91	1.13143	0.10	0.25
5-Methylindole	27.56	4.57	1.00503	0.02	0.06

Figure 3 is a GC/CLD chromatogram of one of the dilute standard solutions analyzed. When compared to Figure 4, a GC/FID chromatogram of the same solution, the selectivity of the GC/CLD detector for nitrogen compounds is readily apparent.

A separate Antek nitrogen analyzer was used to validate the nitrogen content of the dilute standard solutions. The analyzer had been previously calibrated with series of dilutions of 2-methylpiperidine in toluene. Table 3 lists the results of four different calibration curves investigated for the concentration range of the dilute solutions. The data in this table are listed as the back-calculated amount of the standard solution over the relative percent error. For example, the 20.33 ng-N standard was predicted by the first order curve to be 19.95 ng-N which is a relative error of 2.13%. The results were compared by each curve's relative ability to predict its own calibration points. The obviously superior third order curve (Figure 5) was used to analyze the dilute standard solutions with the following results.

	ppm-N(known)	ppm-N(pred.)	Rel % Error
Solution 1	74.57	74.28	0.38
Solution 2	72.23	71.61	0.86

The GC/CLD response of each compound analyzed, relative to the internal standard 2,5-dimethylpyrrole, is listed in Table 2.

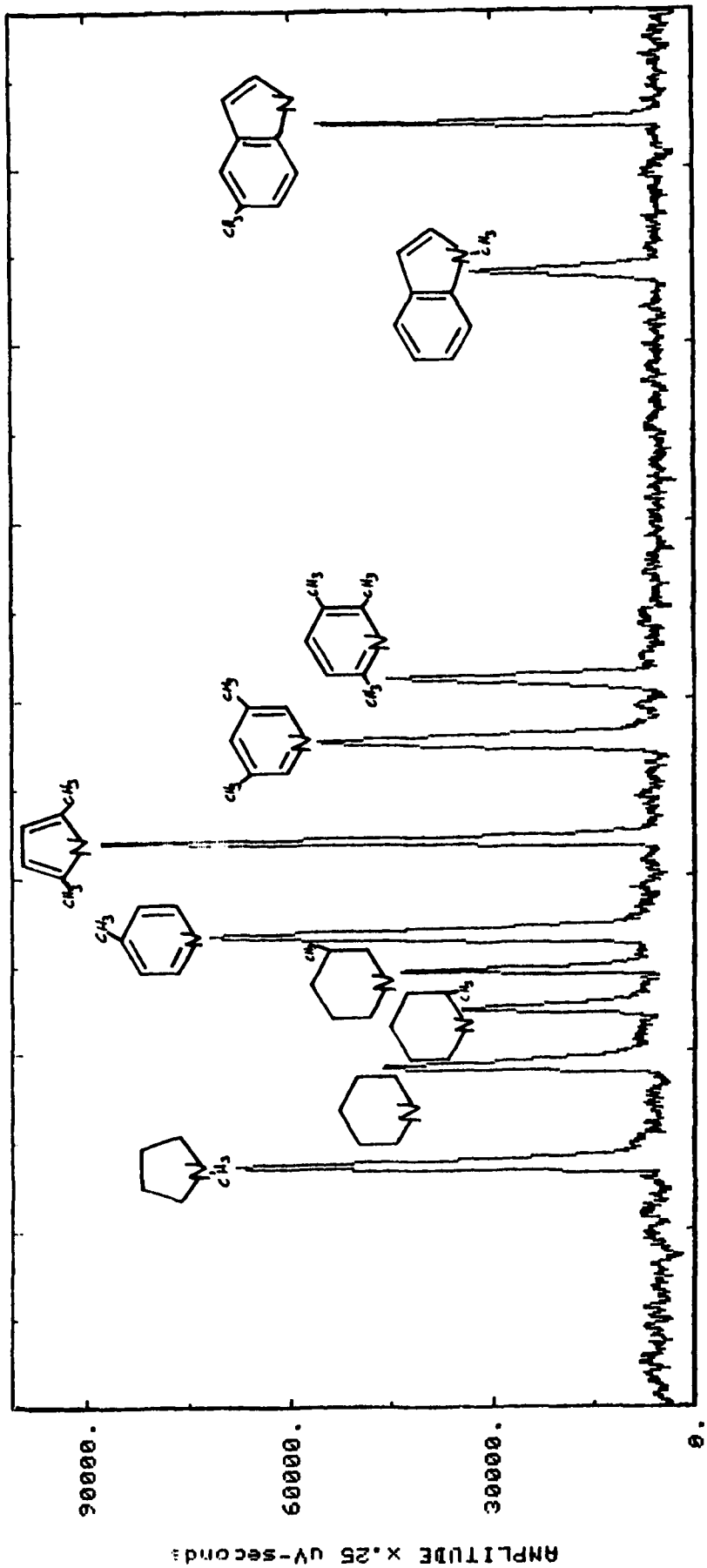

Figure 3. GC/CLD Chromatogram

TABLE 3

ANTEK CALIBRATION CURVES

ng-N	Area Counts	PREDICTED ng-N / RELATIVE % ERROR			
		Exponential	First Order	Second Order	Third Order
8.75	1091	7.86 / 10.20	9.95 / 13.73	9.85 / 12.57	8.81 / 0.69
16.01	2073	14.93 / 6.74	16.13 / 0.73	16.07 / 0.69	15.99 / 0.12
20.33	2680	19.30 / 5.29	19.95 / 2.13	19.91 / 2.31	20.31 / 0.34
38.20	5342	38.48 / 0.72	36.69 / 3.96	36.75 / 3.80	38.25 / 0.13
78.35	12065	86.90 / 10.91	78.97 / 0.79	79.18 / 1.06	78.34 / 0.01
212.48	33293	239.72 / 12.85	212.49 / 0.00	212.41 / 0.03	212.48 / 0.00

Exponential: ng-N = Area Counts exp(a); a=ln(ng-n/Area Counts)
a=-4.93333

First Order: Coefficient of Correlation = 0.999928

Second Order: Coefficient of Correlation = 0.999930

Third Order: Coefficient of Correlation = 1.000000

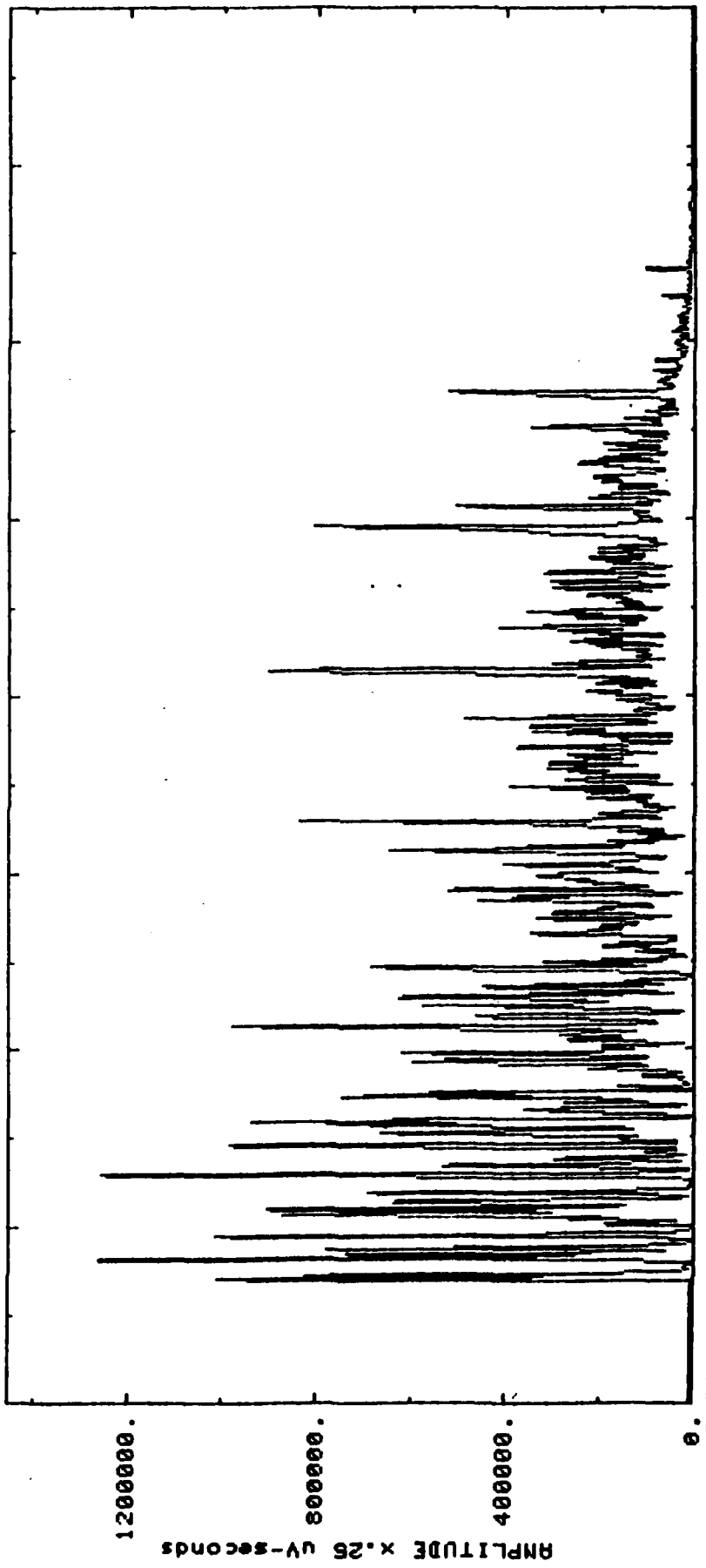

Figure 4. GC/FID Chromatogram

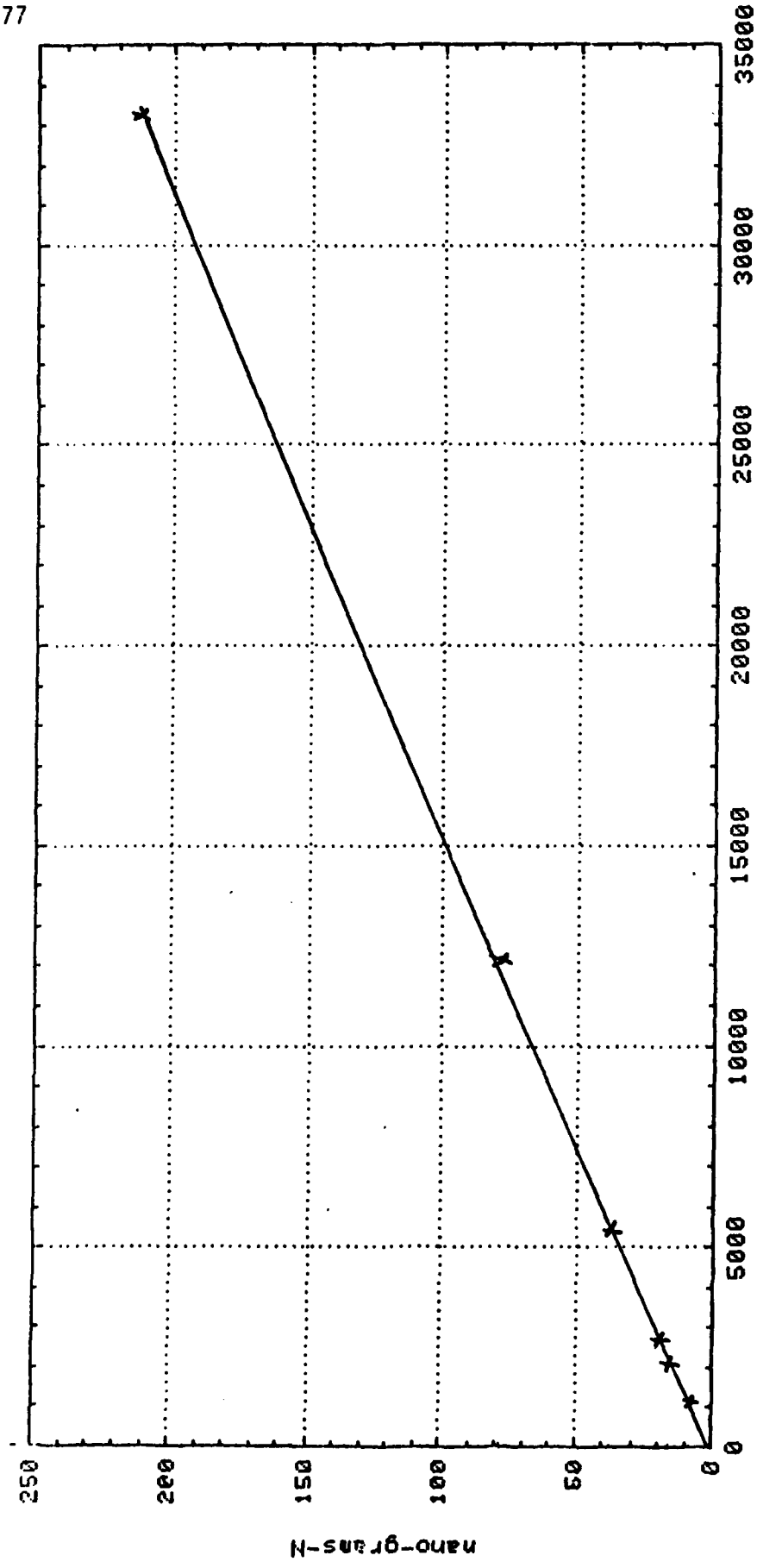

Figure 5. Third Order Calibration Curve

SECTION III

RESULTS AND RECOMMENDATIONS

The nitrogen concentrations listed in Table 2 by no means indicate that nitrogen compounds do not exist at levels much lower than these in shale derived jet fuels. The Antek 703C nitrogen analyzer was not designed to receive eluents from capillary GC columns. Only packed column GC/CLD work has been published to date (Reference 2). Accordingly, a wide bore column, large injection volume, and relatively concentrated samples were used in order to judge the merit of the particular GC/CLD system reported herein.

The minimum detectable limit was investigated by preparing a solution containing a 1.43 ppm-N concentration of one of the higher boiling compounds studied (2-methylindole). Figure 6 shows the measurements of the signal and noise levels which resulted in a signal-to-noise ratio of approximately 6. This indicates that the minimum detectable limit for 2-methylindole, on the system described in this research, is in the range of 0.5 ppm-N.

It would seem obvious that a much smaller combustion tube, and slower flow rates of both pyrolysis and ozonolysis oxygen would result in a much lower minimum detectable limit.

If the Antek nitrogen analyzer totally oxidizes the sample molecules, any relative response factors generated, other than unity response factors, must be due to injection or column effects. The response factors listed in Table 2 show two definite trends: relative response factors greater than one for non-aromatic nitrogen compounds, and relative response factors of near one for aromatic nitrogen compounds.

Although the activity of the column was not determined as a part of this study, it is safe to assume that basic nitrogen compounds would preferentially adhere to any acidic sites on the column, injector, or syringe. Furthermore, it is known that aromatic nitrogen compounds are weaker bases than non-aromatic nitrogen compounds due to a resonance effect (Reference 5). Table 4 lists some of the compounds studied, their relative response factors, and their base dissociation constants in

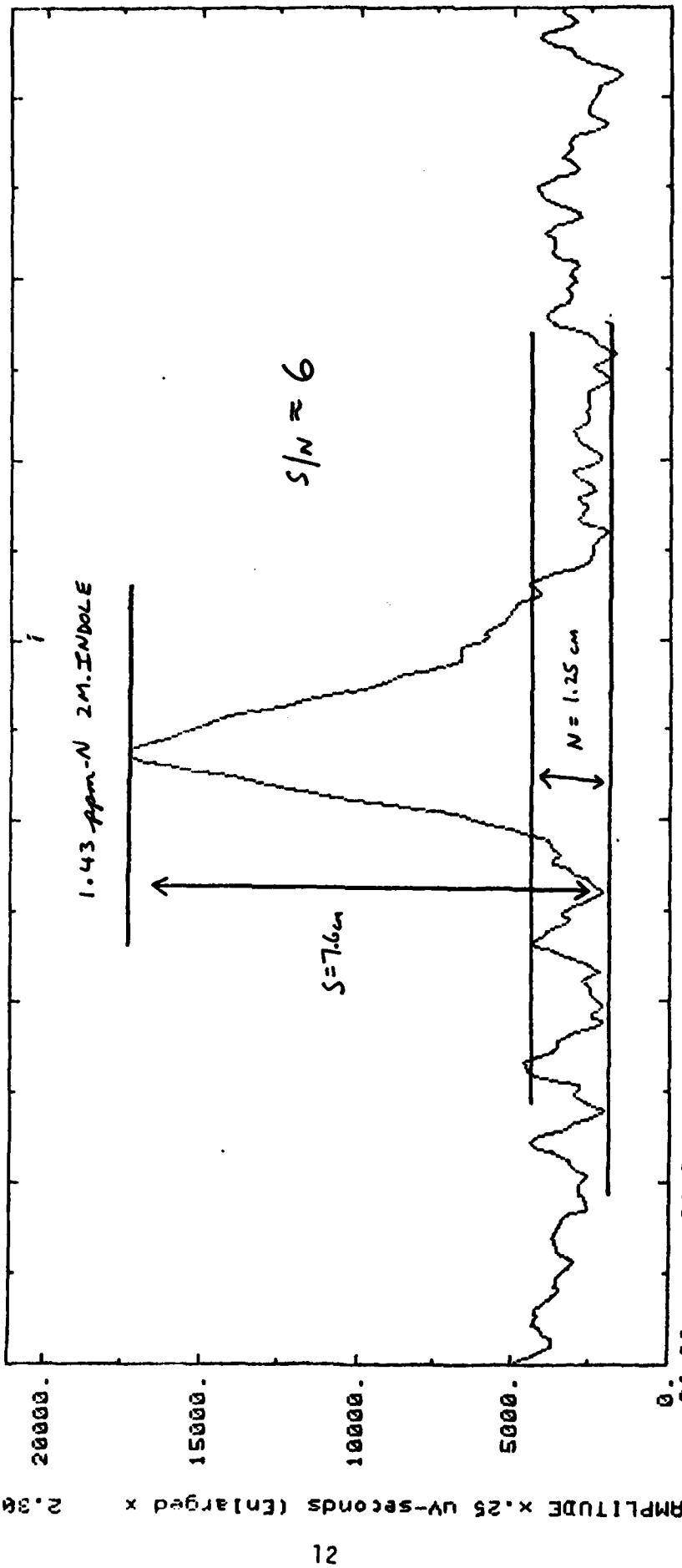

Figure 6. Measurement of Signal-to-Noise Ratio

water (Reference 6). Even though the compounds were not analyzed in water, the comparison of basicities to relative response factors show strong evidence that the non-aromatic compounds were being preferentially adsorbed.

The GC/CLD system investigated in this study appears to have considerable potential as a totally specific, highly quantitative GC nitrogen detector system.

It is recommended that the combustion tube be drastically reduced in size, and and the flow rates be reduced accordingly. The combination of these design changes, the use of on-column injection, and proper deactivation techniques for the injection system and the column should yield a very sensitive, highly quantitative nitrogen specific detector for use with capillary gas chromatographs.

TABLE 4

EFFECT OF BASICITIES ON RESPONSE FACTORS

Compound Name	Response Factor	Kb
Pyrrolidine	1.85333	1.86×10^{-3}
Piperidine	1.29789	1.33×10^{-3}
2,2,6,6-Tetra-methylpiperidine	1.48471	1.18×10^{-3}
3,5 Dimethyl-pyridine	1.03570	1.41×10^{-8}
4-Methyl-pyridine	1.02576	1.05×10^{-8}
2-Methyl-pyridine	0.98190	4.78×10^{-9}

REFERENCES

1. H. V. Drushel, "Analytical Chemistry", Vol. 49, No. 7, 932-938, June 1977.

2. H. A. Hernandez, "American Laboratory", 72-76, June 1981.

3. R. C. Striebich, Nitrogen Analysis by Chemiluminescence, Aero Propulsion Laboratory, WPAFB, Ohio 45433, Report No. AFWAL-TR-84-2089, 1984.

4. Dues/Steward, RD Report Book, AFSC Form 79, No. 60016, AFWAL/POSF, WPAFB, OH 1984.

5. T. W. G. Solomons, "Organic Chemistry", 2nd Ed., 1980, Wiley and Sons.

6. R. C. Weast (Editor), C.R.C. Handbook of Chemistry and Physics, 60th Ed., 1979, CRC Press Inc.

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