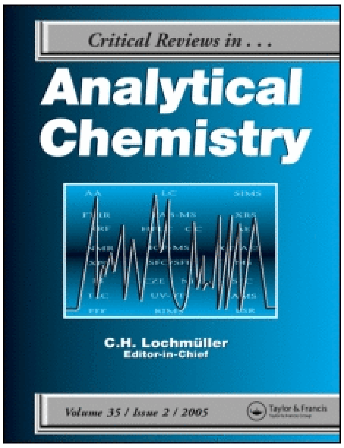

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THE NITROGEN DETECTOR IN GAS CHROMATOGRAPHY

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I. INTRODUCTION

The enhanced interest in determination of trace quantities of nitrogen-containing compounds has resulted in significant improvements in gas chromatographic instrumentation and analytical methodology for the selective detection of nitrogen compounds. Although there have been few recent reports of new detection techniques, most of the nitrogen-selective detectors have been greatly improved and characterized in detail.

There are four basic classes of nitrogen-selective detectors: thermionic, electrochemical, photoemission, and infrared. The alkali flame ionization detector (AFID) and the "flameless" alkali-sensitized detector (often referred to as the N-P detector) are the main variants of the thermionic detector. The electrolytic conductivity detector (ECD) and the microcoulometric detector (MCD) are the primary nitrogen-selective electrochemical detectors. The major photoemission detectors for nitrogen analysis include the microwave plasma detector (MPD) and the chemiluminesence detector (CLD). Other detectors, such as the electron capture, mass spectrometer, or the fluorescence detector, also can be used for the selective detection of certain nitrogen-containing compounds. However, the response of these detectors is not directly dependent upon the presence of a nitrogen atom and therefore will not be discussed in this review.

Specific analytical requirements must be considered before the proper detector choice can be made. As shown in Table 1, response characteristics of the nitrogen detectors vary widely. Although sensitivity, linearity, and specificity are the primary factors which characterize the detector's performance, other factors, such as uniformity of response to various nitrogen compounds, ease of use, and stability of response characteristics, should also be considered.

From the response parameters listed in Table 1, it can be concluded that in certain trace analyses in which the sample size is limited the N-P detector is clearly the best choice. However, this detector would not be the best choice for samples which might contain phosphorus compounds. Similarly, selection of either the thermal energy analyzer or the ECD would be advantageous for the analysis of nitrosamines in the presence of other nitrogen compounds. Choosing a general purpose nitrogen detector is not a simple matter, however. In this case, response characteristics of the various detectors must be compared and matched to individual laboratory requirements and maintenance capabilities. The primary goal of this review is to present information that can be used to aid the analyst in choosing a nitrogen detector for a given analysis. To this aim, the theory of operation and response characteristics of the various nitrogen detectors are discussed in detail.

TABLE 1

Response Parameters of Nitrogen-Selective Detectors

Detector class	Detector	Sensitivity	Specificity	Linearity	Interference
Thermionic	Alkali flame	High picogram	10^3	10^3	P, S
	Flameless alkali sensitized	Picogram	10^4 to 10^5	10^4	P
Electrochemical	Electrolytic conductivity	High picogram	10^5 to 10^6	10^3	Large quantities of S
	Microcoulometric	Nanogram	10^5 to 10^6	10^3	Large quantities of CO_2, S, and halogen
Photoemission	Microwave discharge	Nanogram	Footnotes a and b	10^3 to 10^4	Footnote b
	Chemiluminescence	Nanogram	High[a]	—	
	Thermal energy analyzer	High picogram	High[a]	10^5	Nitrites
Infrared	Infrared	High nanogram	Footnotes a and b	10^3	Footnote b

Has not been studied in detail.
Depends upon operating conditions.

II. THERMIONIC DETECTORS

A. Alkali Flame Ionization Detector

1. Background and Theory of Operation

The use of an alkali metal to sensitize the response of the flame ionization detector (FID) to phosphorus and halogen compounds was reported by Karmen and Guiffrida in 1964.[1] A number of variations of their original device have been described, which are extensively reviewed by Brazhnikov et al.[2] The most distinctive difference between the detectors described is in the use of either a single flame, as in the original device, or the use of two flames, as reported by Karmen[3] and later improved by Abel et al.[4] Of these devices, only the single flame detectors have been successfully applied to the determination of nitrogen compounds.

Although the AFID has been extensively studied for almost 15 years, and at one time commercial versions were offered by almost every major chromatograph manufacturer throughout the world, the mechanism of response of the AFID is still not understood. Proposed operating mechanisms of various thermionic detectors have been reviewed by Brazhnikov et al.[2] Only a limited number of proposed mechanisms can be applied to detector designs that are capable of detecting nitrogen compounds. The mechanism that comes the closest to explaining the response of the AFID involves gas-phase reactions of the alkali atom and the compounds containing the heteroatom. Another mechanism, suggested by Brazhnikov et al.[2] and based on the work of Somorjai[5], that can be applied in some cases involves photoevaporation of the alkali salt by photons generated in the combustion of organophosphorus compounds. However, work conducted by Scolnick[6] with a flameless chemical ionization detector and later studies by Brazhnikov and Shmidel[7] using a specially designed AFID indicate that the gas-phase reaction mechanism is indeed the most probable.

Brazhnikov and Shmidel suggest that the useful AFID signal is created by enhanced ionization of the alkali atoms due to increased flame temperatures when phosphorus- and nitrogen-containing compounds are present in the flame. They concluded this by assuming that the main contribution to the background current of the detector was due to thermo-emission of aerosol particles of the alkali atom and alkali oxide formed in the cool region near the collector electrode. Thermo-emission of the aerosols is believed to occur because they absorb radiant energy from the flame. The following facts were considered by Brazhnikov and Shmidel in proposing this mechanism:

1. The alkali metal salts are active inhibitors of combustion.[8]
2. Among the products of the combustion of phosphorus- or nitrogen-containing organic compounds in the flame, heavy ions are formed whose mobility is 1000 times less than that of light ions.[9] These ions combine with alkali ions to form even heavier ions.
3. When the hydrogen flow rate is sufficient, a reducing pyrolysis of phosphorus- and nitrogen-containing compounds in the flame occurs, resulting in the formation of radicals.[10]

The authors reasoned that the concentration of alkali metal salt in the flame is reduced due to the formation of less mobile alkali species. Since the alkali content of the flame is reduced, the inhibiting effect of the salt is also reduced, and the flame temperature increases. The increase in flame temperature then results in an increase of the ionization efficiency of the alkali atoms. Thus, there is an increase in the thermo-emission of aerosol particles, thereby creating the detector signal.

The conclusion that ionization takes place in the gas-phase is substantiated by the work of Scolnick[6], who constructed a detector that consisted of three stacked tubes comprising an alkali saturation zone, a reaction zone, and a detection zone (Figure 1). The temperatures of these zones were independently variable by electrical heating. Pure carrier (N_2) passed through the saturation zone and was mixed with the chromatograph carrier stream in the reaction zone. Ions formed by the interaction of phosphorus-containing compounds and the alkali salt were monitored in the detection zone. Scolnick found the following;

1. The type of metal used for the collector electrode was not critical; steel performed as well as platimum.
2. The temperature of the collector electrode during detector operation was only about 300°C.
3. The presence of salt or carbon deposits on the collector electrode made little difference.
4. Detector response was observed with a reaction zone temperature of 800 to 850°C.
5. The detector was more specific than the AFID, but less sensitive.
6. Detector operation does not require oxygen or hydrogen.
7. Detector response is reduced by the presence of hydrocarbons.

From these observations, Scolnick concluded that the mechanism responsible for the detector signal occurs in the gas-phase and is due to the direct interaction of alkali and phosphorus species. However, it was not concluded what particular species were involved. It is difficult to determine whether these observations can be directly applied to the processes occurring in alkali flame detectors.

2. Response Characteristics

The AFID was originally developed for the analysis of phosphorus- and halogen-containing compounds.[1,3,4,11,12] It was later extended to the analysis of nitrogen compounds by Wells[13] and Aue et al.[14] Aue et al. used a single flame detector in which the flame burned up on the surface of the salt source. The source (Figure 2) was a modification of that originally suggested by Coahran.[15,16] The collector electrode consisted of a single loop of platinum wire so constructed that the vertical distance of the loop from the alkali source could be varied in a reproducible manner.

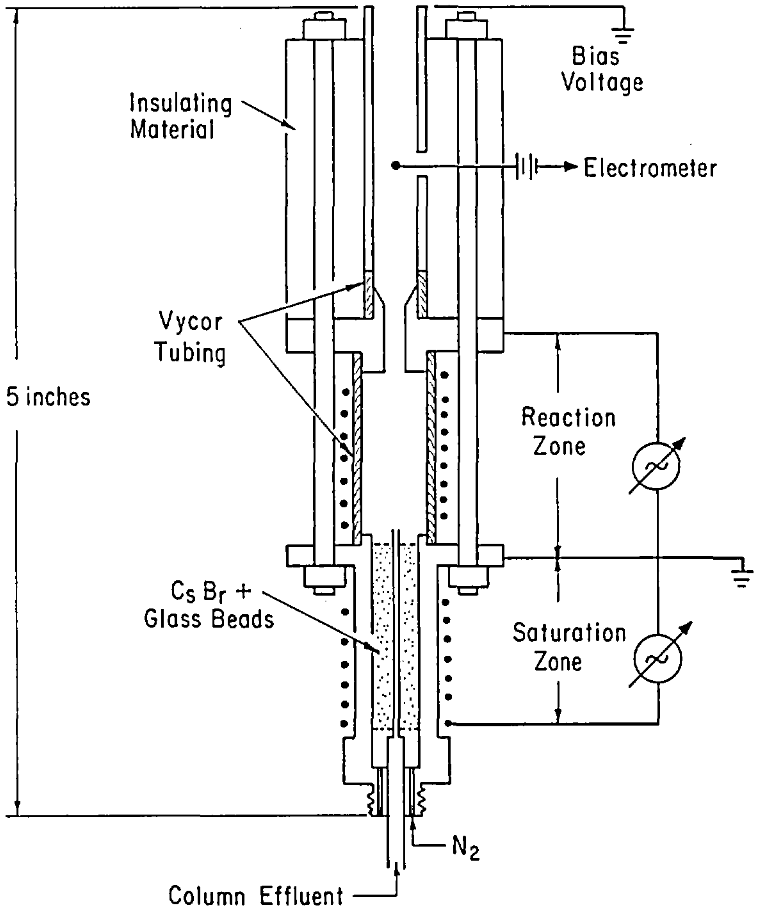

FIGURE 1. The Chemi-ionization detector. (From Scolnick, M., *J. Chromatogr. Sci.*, 8, 462 (1970). With permission.)

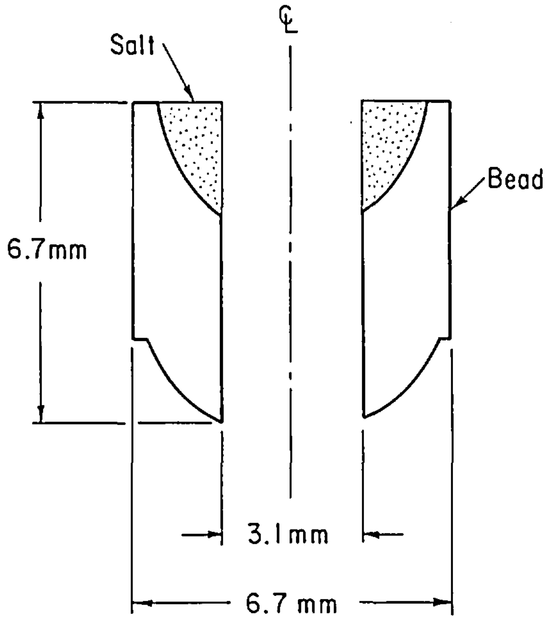

FIGURE 2. Detector bead design. (From Aue, W. A., Gehrke, C. W., Tindle, R. C., Stallings, D. L., and Ruyle, C. D., *J. Gas Chromatogr.*, 5, 381 (1967). With permission.)

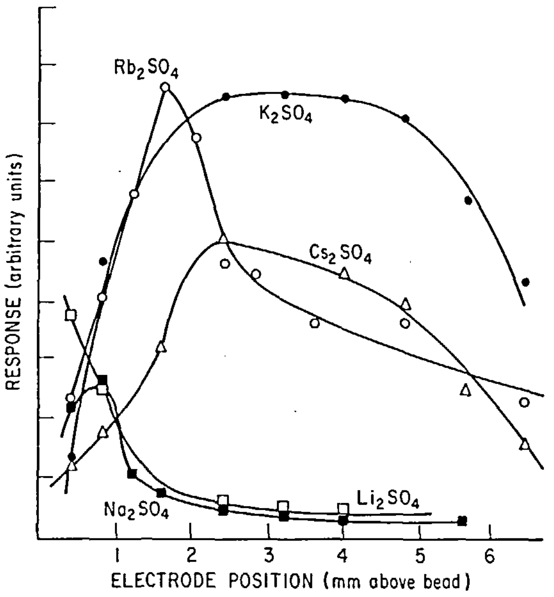

FIGURE 3. Nitrobenzene response profiles: H_2 flow in cm^3/min; Li, 25; Na, 28; K, 25; Rb, 25; Cs, 15. (From Aue, W. A., Gehrke, C. W., Tindle, R. C., Stallings, D. L., and Ruyle, C. D., *J. Gas Chromatogr.*, 5, 381 (1967). With permission.)

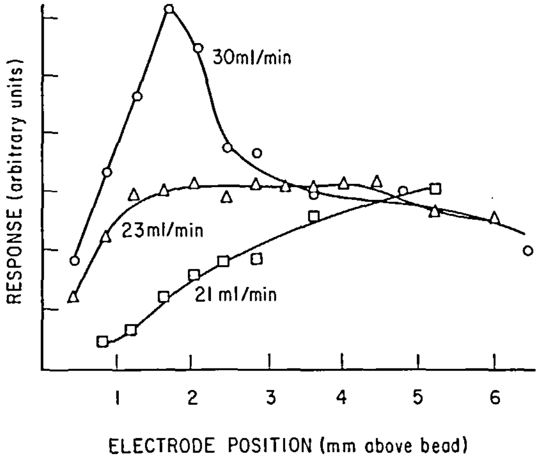

FIGURE 4. Effect of H_2 flow rate in response to nitrobenzene with a Rb_2SO_4 bead. (From Aue, W. A., Gehrke, C. W., Tindle, R. C., Stallings, D. L., and Ruyle, C. D., *J. Gas Chromatogr.*, 5, 381, (1967). With permission.)

Detector response to nitrobenzene was used by Aue et al. to evaluate the sulfate salts of all the alkali metals except francium. The particular salt used, electrode distance from the salt, and hydrogen flow rate were found to be interrelated parameters. They found that it was necessary to adjust the hydrogen flow rate for each salt to obtain maximum response at acceptable noise levels. The influence of collector electrode position for the alkali sulfates under these conditions is shown in Figure 3. The response profiles are very dependent upon hydrogen flow rate (Figure 4), and thus, the comparison of alkali metals is only qualitative.

Rubidium sulfate was found to give the best performance in terms of baseline stability and response. However, Aue et al. found that the purity of the alkali salts was a critical factor that influenced the noise level. Although all salts were recrystallized, the degree to which their results were influenced by impurities was not established. Thus, it is possible that the superiority of rubidium could have been due to indirect circumstances. Rubidium salts have also been used by other workers,[17,18] though their reason for choosing rubidium was not stated. It should be noted that potassium sulfate has also been successfully used for the detection of nitrogen compounds.[19]

Comparison of the response of the normal FID and AFID to a variety of nitrogen compounds revealed that chemical structure is not a significant factor in the magnitude of the response of the AFID.[14] Response profiles vs. collector electrode height are also little influenced by chemical structure (Figure 5). As shown in Table 2, the response of the AFID (when corrected for nitrogen content) is approximately 1500 to 2000 times greater than that given by the FID. Under the same conditions, a variety of carbon compounds (phenol, cyclohexanol, decane, and naphthalene) gave enhancements close to unity.

Although the response of the AFID is not sufficiently uniform to allow the nitrogen content of the chromatographed substances to be accurately determined, it is useful for qualitative purposes. Other compounds to which the AFID is sensitive usually give

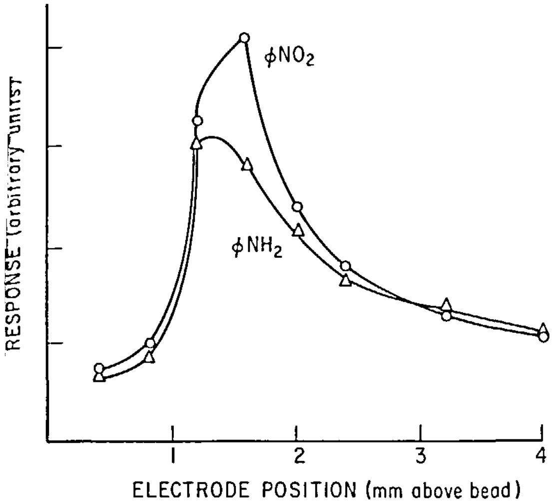

FIGURE 5. Effect of electrode position in response to nitrogen compounds. H_2 flow rate: 25 cm^3/min. (From Aue, W. A., Gehrke, C. W., Tindle, R. C., Stallings, D. L., and Ruyle, C. D., *J. Gas Chromatogr.*, 5, 381 (1967). With permission.)

TABLE 2

Response Enhancement of the AFID for Nitrogen Compounds

Compound	Enhancement*
Aniline	2045
(N)-Methylaniline	1764
Nitrobenzene	2213
1,3-Dimethyluracil	1612
Lysine	1423
Proline	1606

* Enhancement = response with Rb_2SO_4 bead/response with normal FID × %N.

Response data obtained from Aue., W. A., Gehrke, C. W., Tindle, R. C., Stallings, D. L., and Ruyle, C. D., *J. Gas Chromatogr.*, 5, 381 (1967).

substantially different responses. The response ratio of chlorine, nitrogen, and phosphorus compounds is approximately 1:100:1000, respectively.[19,21] The direction of response can also provide useful qualitative information. Operating conditions have been reported that result in negative responses for chlorinated hydrocarbons[22] and sulfur compounds,[23] as displayed in Figure 6.

The response of detectors with an adjustable collector electrode can be optimized for the determination of a given element. Detector response vs. collector height above the salt source exhibits distinct curves for nitrogen, phosphorus, bromine, chlorine, and iodine (Figure 7). The response profile is critically dependent upon the hydrogen flow rate (see Figure 4); however, due caution must be exercised in using such relationships. The interrelationship of electrode position, hydrogen flow, flame geometry, and condition of the alkali salt surface requires that the electrode height and/or hydrogen flow be checked from time to time for optimum performance.[14]

Although detectors have been constructed with special design features, such as adjustable collector electrodes,[14] stacked flames,[3] and variable selectivity,[24] the design requirements for a nitrogen sensitive AFID (Figure 8) are essentially the same as those of the FID. In fact, most FIDs can be easily converted to AFID operation. An alkali bead was described by Craven[25] that could be placed onto the flame tip of an ordinary flame ionization detector. The bead was constructed by fusing a 1:1 mixture of Rb_2SO_4–KBr at 20,000 psi for about 2 hr using a KBr dye. The resulting disc was then shaped with emery cloth and bored to the dimensions shown in Figure 9. The only adjustment required was to optimize the hydrogen flow. Other similar alkali sources[16] and improved fabrication techniques[17] have been reported. The selectivity of converted FIDs to nitrogen compounds is very similar to that achieved with the commercial AFID. A N:C selectivity of 1:3780 was calculated by Johnson et al.[26] using response data for pentamethylmelamine and phenanthrene.

The flame in the AFID serves a dual purpose: it volatilizes the alkali salt and produces the ions that are collected. Since the amount of hydrogen determines the flame

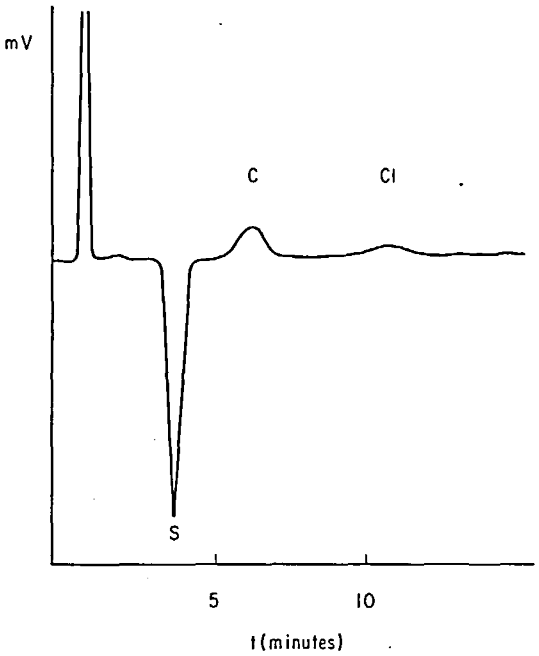

FIGURE 6. Chromatogram of a model mixture. (S) Thiophene (1.6 × 10^{-6}g); (C) Toluene (2.8 × 10^{-6}g); (Cl) Chlorobenzene (3.5 × 10^{-6}g). (From Dressler, M. and Janak, J., *J. Chromatogr. Sci.*, 1, 451 (1969). With permission.)

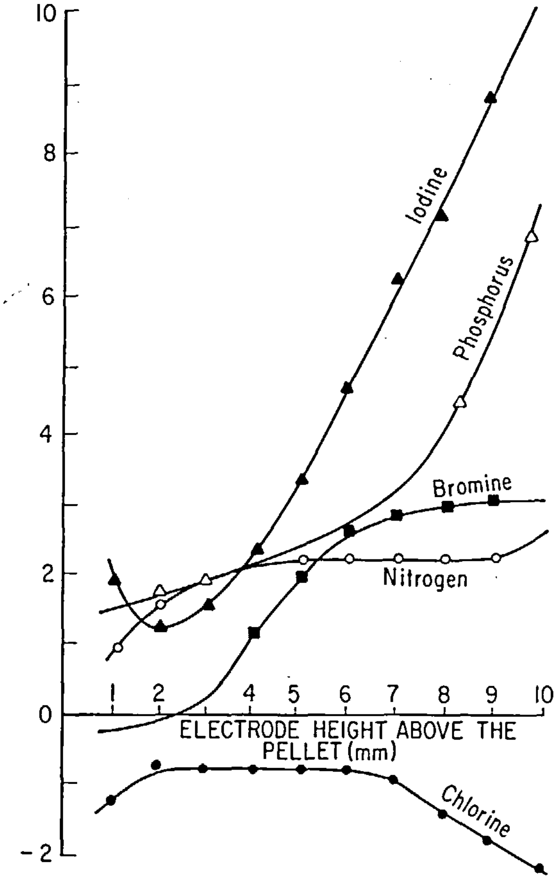

FIGURE 7. Effect of electrode height. Electrode, 7 mm I.D.; pellet, pressed Rb_2SO_4, 1 mm bore; potential, + 240 V; flow rate, H_2, 33; N_2, 50; air, 215 ml/min; injections 1 μl of hexane solution containing 1 μg/ml each of chlorobenzene, bromobenzene, iodobenzene, and benzylamine and 10 μg/ml of tri-*n*-butylphosphate. (From Lakota, S. and Aue, W. A., *J. Chromatogr.*, 44, 472 (1969). Witl mission.)

temperature and, thus, the degree of the above processes, small changes in the hydrogen flow rate effect detector response considerably. For some detector designs, the hydrogen flow must be regulated with exceptional accuracy.[2] The flame temperature is also influenced by the flow rates of the carrier gas and air. In actual practice, it is difficult to maintain gas flows within the required tolerances for stable operation at high detector sensitivities.

The difficulty of maintaining very accurate hydrogen flow rates and the problems associated with the ever-changing salt surface have resulted in reduced interest in the AFID in favor of "flameless" alkali detectors which have been recently developed. Nevertheless, the low cost and ease with which the FID can be converted to AFID operation makes this device extremely attractive for analyses that do not require the higher stability of the "flameless" detector.

B. Flameless Alkali Sensitized Detectors

1. Background and Theory of Operation

Electrical heating of the alkali source was suggested by Abel et al.[27] as a possible

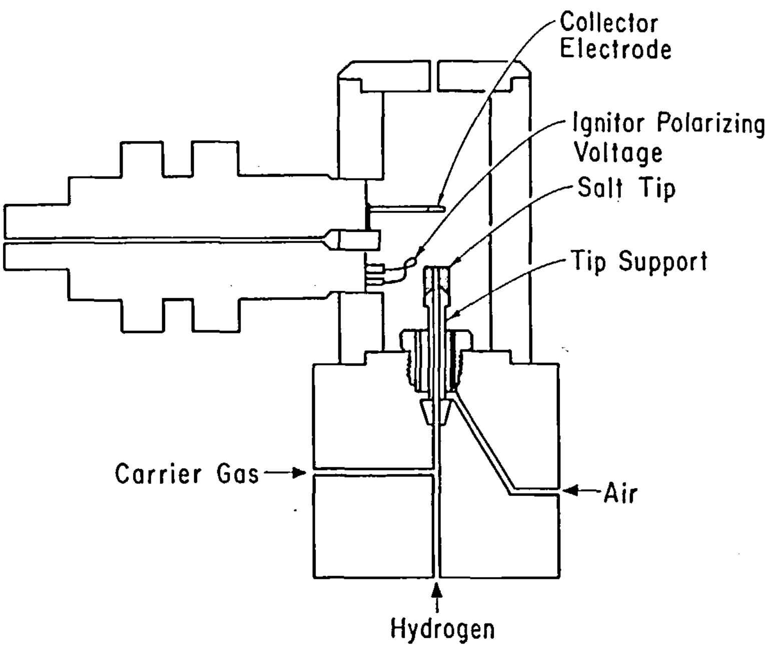

FIGURE 8. Cross sectional of alkali flame detector. (From Hartmann, C. H., *J. Chromatogr. Sci.*, 7, 163 (1969). With permission.)

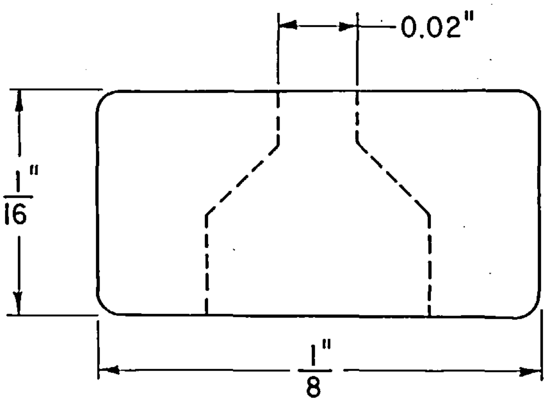

FIGURE 9. Bead design. (Reprinted with permission from Craven, D. A., *Anal. Chem.*, 42, 1679 (1970). Copyright by the American Chemical Society.)

means of stabilizing the response of the AFID. This was investigated by Prager and Deblinger[28] and later incorporated into a commercial detector.[29] Prager and Deblinger used a nonvolatile rubidium silicate source. Although not employed for chromatographic detection, alkali metal silicate sources were described by Blewett and Jones[30] as early as 1936. A patent was granted to Rice[31] in 1951 for an ion source consisting of a ceramic cylinder coated with alkali salts and glasses. A detector with an alkali source similar to that described by Rice has been developed.[32]

The flameless alkali sensitized detectors (FASD) described so far have exhibited se-

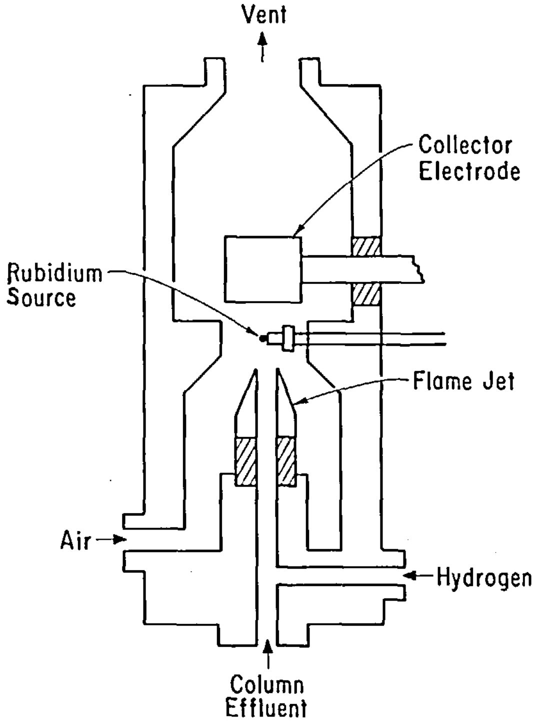

FIGURE 10. Schematic diagram of the Perkin-Elmer nitrogen-phosphorus detector. (From Kolb, B., Auer, M., and Pospisil, P., *J. Chromatogr. Sci.*, 15, 53 (1977). With permission.)

lective responses to only nitrogen- and phosphorus-containing compounds. For this reason, they are usually referred to as N-P detectors. Due to their recent development, a limited number of detectors have been described and geometry requirements are not fully known. The only detectors described to date are those available from Hewlett-Packard Co., Perkin-Elmer & Co., and Tracor, Inc. Compared to the AFID, these detectors offer an order of magnitude improvement in sensitivity and selectivity.

The general features of the available FASD are shown in Figures 10, 11, and 12. These figures illustrate some similarities in these detectors. The alkali source is approximately 0.050 to 0.150 in. above the detector jet. The collector electrodes are all cylindrical and not rings as in most AFIDs. A negative potential is applied to the source in all instances. Although hydrogen and air are required, the quantity of hydrogen used (1 to 5 cm^3/min) is not sufficient to sustain a common flame. Instead, a low temperature plasma surrounds the source.

The detectors are distinct in geometry, alkali source, and electrical technique used for heating the source. The Perkin-Elmer detector employs a metal jet at the same potential as the source (N-P mode), a rubidium silicate bead, and a negatively polarized environment from the jet to the collector electrode. The Hewlett-Packard detector features a jet and detector body at ground potential and a source-collector assembly at a negative potential of 240 V. The Tracor detector has a quartz jet, a negatively polarized environment surrounding the jet, and a collector electrode considerably removed from the alkali source. The Hewlett-Packard detector uses a "novel alkali source"[32] consisting of an unspecified alkali salt contained in a ceramic reservoir similar to that de-

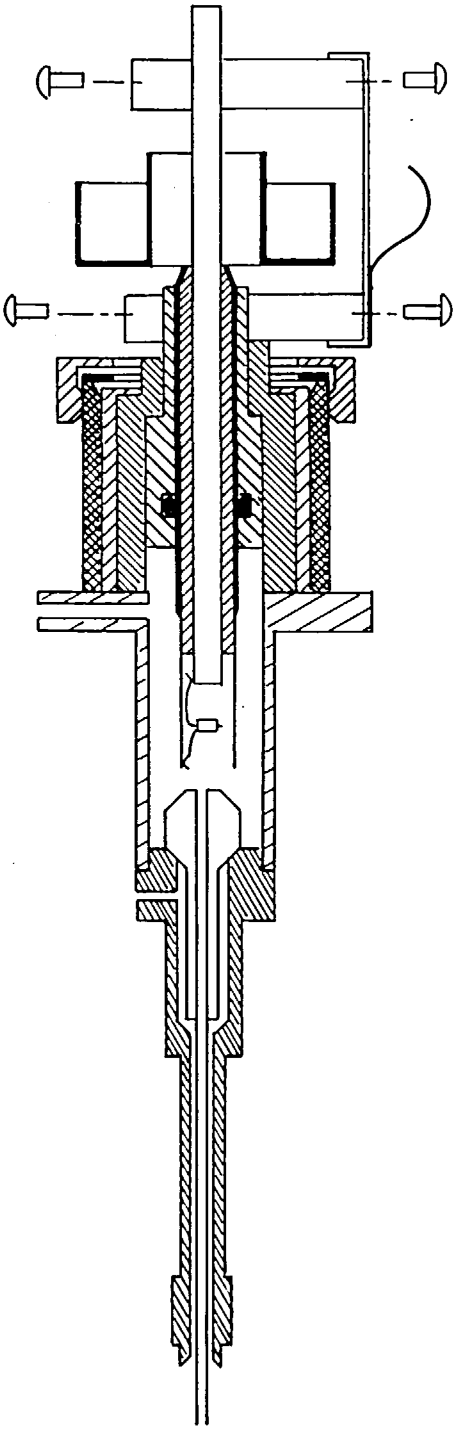

FIGURE 11. Crosssection of the Hewlett-Packard nitrogen-phosphorus detector. (From Burgett, C. A., Smith, D. H., and Bente, H. B., *J. Chromatogr.*, 134, 57 (1977). With permission.)

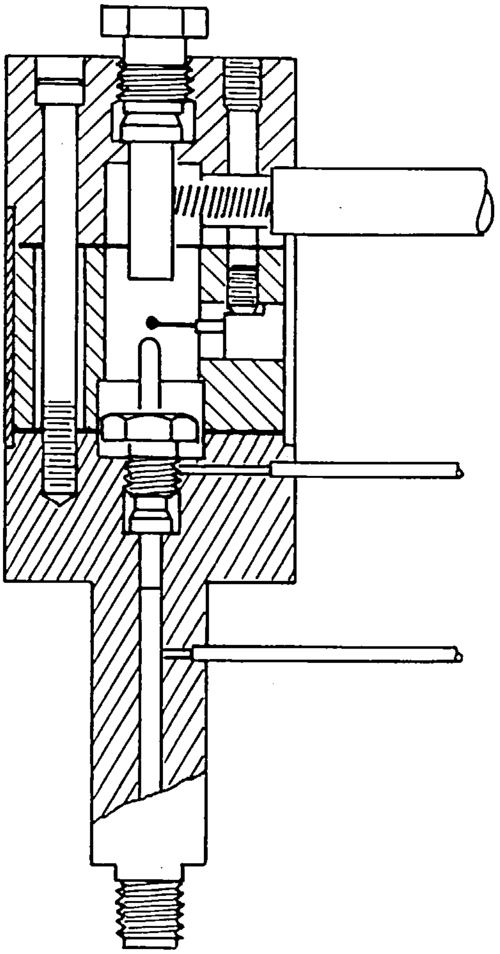

FIGURE 12. Crosssection of the Tracor nitrogen-phosphorus detector.

scribed by Rice.[31] The Tracor detector has a source described as a mixture of alkali salts in a silica gel matrix.[32]

The Tracor detector is unique in that it utilizes the resistance of the platinum heating wire (resistance of platinum increases linearly with temperature) as a feedback element to temperature lock the alkali source,[34] whereas the other detectors use a regulated voltage supply to heat the source to a steady-state temperature. The advantage of the Tracor circuit (Figure 13) is that the temperature of the heating element is independent of gas flows, which allows all flows to be shut off without source destruction. The Perkin-Elmer detector utilizes a circuit breaker to protect the alkali source. A timed source desensitizer circuit is featured in the Tracor detector. When energized, the desensitizer reduces the temperature of the source to a level that is said[34] to prevent destruction by reactive solvents or derivatizing reagents.

As is the case for the AFID, the mechanism of response of the FASD is not clearly understood. The FASD is similar in design to the AFID and can be considered as a modified AFID with an electrically heated source that is operated with reduced hydrogen and air flow rates. The FASD (with the exception of the Hewlett-Packard detector) also exhibits similar rations of response to phosphorus and nitrogen compounds as that of the AFID.

A reaction mechanism for the FASD with a nonvolatile rubidium silicate alkali source has been proposed by Kolb et al.[35] In the formation of this theory, the authors considered retention of an odd number of electrons by elements in the odd-number main groups during radical chain reactions in the flame and the acquisition of a stable electron shell with an even number of electrons by a radical losing or gaining an electron or combination of the radical with another radical. They suggest that the alkali atom could supply the required electron since it has the lowest electron affinity of any odd-number elements or related species. In this manner, an ion pair would be formed and the ion current of the flame increased. The charge carriers would then undergo other reactions in which they lose their charge and leave the flame as stable uncharged compounds.

Kolb et al.[35] suggest that the alkali atom enters the flame as a neutral atom by thermal evaporation. Simple vaporization of the rubidium silicate was considered unlikely at the source temperatures used (600 to 800°C). The alkali ion would be converted to a neutral species by accepting an electron from the negatively polarized bead as expressed in Equation 1:

$$A^{+} + e^{-} \longrightarrow A.\uparrow \qquad (1)$$

The neutral atom was then pictured as entering the reaction zone by vaporization where it interacts with phosphorus- and nitrogen-containing radicals (Figure 14).

Thermal vaporization of neutral alkali atoms is consistent with the background currents normally observed (10 to 20 pA). When the electrical gradient is reversed (the source at a positive potential with respect to the collector), the background increases by a factor 1000,[35] which is in the range of background currents observed for the AFID.[2] However, operation of the detector in this mode is precluded, since the quantity of alkali is very small and consequently rapidly depleted.

Thermal vaporization of a neutral alkali atom appears to be a satisfactory explanation for the presence of the alkali atom in the reaction zone. The alkali sources of the Hewlett-Packard and Tracor detectors are not specified, and it is possible that other mechanisms may be involved in these detectors. Nevertheless, the Kolb theory sufficiently explains the long-term stability of the FASD and the formation of the analytical response.

The long-term stability of the detector is readily explained by the alkali recycling mechanism shown in Figure 14. The vaporized alkali atoms are oxidized to positive

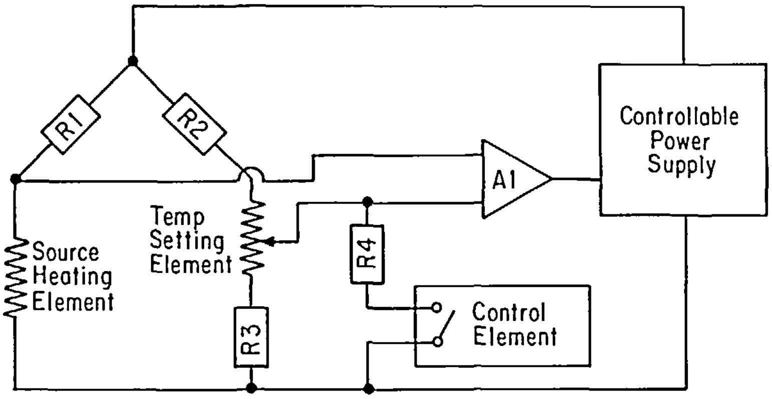

FIGURE 13. Simplified schematic of the Tracor source heating circuit.

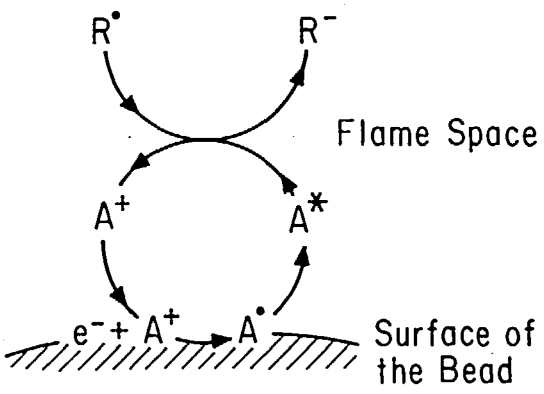

FIGURE 14. Alkali recycling mechanism in the N-P detector. e^- electron; R·, radical; A, alkali (rubidium); A·, alkali atom; A^*, excited alkali atom; A+, excited alkali ion; R·, CN or PO_2. (From Kolb, B., Auer, M., and Pospisil, P., *J. Chromatogr. Sci.*, 15, 53 (1977). With permission.)

ions in the flame plasma and are immediately returned to the bead for recycling. Hartigan et al.[36] studied the long-term stability of response to 50- and 500-ng quantities of methamphetamine. The relative standard deviation was found to be 1.5% over a period of 1 month. In a similar study, Burgett et al.[37] calculated a standard deviation of less than 5% for 199 determinations of amphetamine and methamphetamine injected by an autosampler at a level of 1.4 ng. Internal standards were used in both studies.

Ionization of the alkali atom can occur by two possible means: thermal ionization or the three-body reaction proposed by Page and Woolley.[38] Thermal ionization was rejected by Kolb et al.[35] because the degree of ionization in a cool hydrogen/air flame as it exists in the detector was believed to be extremely small. The authors, however, caution that thermal ionization should not be entirely discarded. In the mechanism of Page and Woolley, the energy resulting from the combination of two hydrogen atoms (H·) is used for ionization of an alkali atom (A·):

$$2H\cdot + A\cdot \rightleftarrows H_2 + A^+ + e^- \quad (2)$$

TABLE 3

Electron Affinities of Ions

	>2.57 eV		<2.57 eV
Cl^-	3.61	H^-	0.80
Br^-	3.36	O^-	1.47
I^-	3.06	O_2^-	0.45
F^-	3.45	S^-	2.07
NO_2^-	3.91	CH_3^-	1.08
CN^-	3.17	OH^-	1.83
PO_2^-	?	SH^-	2.19

From Kolb, B., Auer, M., and Pospisil, P., *J. Chromatogr. Sci.*, 15, 53 (1977). With permission.

Equation 2 was expanded by Kolb et al. to include the recombination of any radicals present in the reaction zone. In this manner, the background current of the detector is established. Since the concentration of alkali atoms in the reaction zone is determined by a vapor phase equilibrium, an increase in bead temperature will increase the background current due to enhanced vaporization of the alkali.[35]

As a result of Equation 2, the background current is an electron current and not an ion current. According to Kolb et al., the occurrence of additional ionization reactions will disturb the alkali concentration. The loss, however, will be immediately compensated by vaporization of additional alkali atoms since the concentration is maintained by the vapor phase equilibrium of the alkali. Thus, the electron current remains constant; the additional ionization produces an ion current that is observed as the detector signal, according to Equation 3:

$$A\cdot \;+\; R\cdot \rightleftarrows A^+ \;+\; R^- \qquad (3)$$

The reaction displayed by Equation 3 can occur when the energy resulting from the electron affinity of the radical equals the ionization energy of the alkali atom. Kolb et al. screened a variety of nitrogen- and phosphorus-containing radicals that could possibly exist in the reaction zone, but could find none that would liberate sufficient energy equal to the ionization potential of rubidium. For this reason, ionization of an excited rubidium atom was considered. An excitation energy of 1.59 eV was calculated using 780 nm line of the rubidium flame spectrum. This results in a required ionization energy of 2.57 eV. Of the radicals screened (Table 3), the halides, nitrogen dioxide, cyan, and phosphorus dioxide radicals have sufficient energy to ionize rubidium.

Although the halides have sufficient energy to ionize excited rubidium atoms, the FASD is not sensitive to halogen-containing compounds. The lack of response to halogens was explained[35] by the postulated formation of neutral alkali halogenide molecules that are exhausted from the detector. It has been shown[39] that the dehalogenation of organic halides in a quartz reaction tube is greatly reduced at temperatures below 800°C. Thus, the low source temperature used (600 to 800°C) and the extremely short residence time for molecules on the source would create an unlikely environment for efficient dehalogenation, which should further desensitize the detector to halogen compounds. Kolb et al. have observed detector responses for large quantities of halogen compounds that indicate the formation of alkali halogenides. In this case, a negative peak was observed with such a long tail that it took up to 10 min. to reestablish a baseline. The peak was negative since the surface of the bead was temporarily exhausted of alkali, causing a reduction in the electron current. The neutral alkali halogenide thus formed is not further ionized since it does not come into contact with a red-glowing surface, which is required for the halide-specific response based on the lowering of the work function of such surfaces.[31]

Nitrogen dioxide and cyan radicals (Table 2) are both potentially capable of producing the nitrogen-specific response. Preference is given to the cyan radical[29,35] because nitrogen dioxide was believed to be disassociated into nitric oxide and oxygen at the temperature involved. The proposed mechanism, based on a cyan radical, is supported by the fact that only organic nitrogen compounds that contain a carbon atom covalently bonded to the nitrogen atom are detected. Thus, inorganic nitrogen oxides and nitrogen give no response.[35] Compounds, such as barbiturates and similar compounds that contain nitrogen atoms flanked by two carbonyl groups, are not readily converted to cyan radicals and give a response approximately ten times less than alkylated nitrogen compounds. Sensitivity to these compounds is still approximately 15 times greater than that achieved with the FID.[41] The response mechanism presented by Kolb et al.[35] satisfactorily explains the response characteristics of the FASD manufactured by Perkin-Elmer. Though detailed information concerning the Hewlett-Packard and Tracor detectors is not yet available, the mechanism also seems to fit the response characteristics of these detectors.

Throughout the work of Kolb et al.,[35] a flame was considered to be present and the detector was thought of as an AFID. Development of their mechanism was partially dependent upon processes known to occur or not to occur in flames. They did, however, classify their flame as a "cool" flame. Nevertheless, a flame is not present in the Hewlett-Packard detector,[32] as in the Tracor detector.[42] Instead, a low temperature plasma is believed to be present. In the Tracor detector, a distinct "pop" occurs at a hydrogen flow of around 15 cm^3/min.[42] Water vapor was observed to condense on a cold mirror at this time. It is therefore unlikely that a flame, as classically conceived, is present in the Perkin-Elmer detector at low hydrogen flow rates.

If a flame is not present, the nature of the reaction zone is uncertain. A low temperature plasma is probably present. Experiments conducted using the Tracor detector,[42] which has a temperature-locked alkali source, support the plasma theory of Burgett et al.[32] The temperature of the Tracor source is regulated by using the resistance of the platinum heating element as one leg of a resistance bridge. Since the resistance of platinum is directly proportional to its temperature, the voltage drop across the source can be related to the power required to heat the source in order to maintain a fixed resistance (temperature). The following observations were made at a fixed source temperature:

1. The power required to maintain a fixed source temperature was directly proportional to the carrier flow rate and inversely proportional to the hydrogen and air flow rates.
2. A distinct corona surrounded the heating element, and its intensity was related to the hydrogen and air flow rates.
3. The corona surrounding the heating element appeared to be several millimeters in diameter when hydrogen and air were present. There was no distinct corona surrounding the heating element when only helium carrier gas was present.

These observations suggest that a plasma is actually present, and it is sufficiently hot to significantly reduce the power required to heat the source.

Based on the above discussion, the presence of a plasma is easily acceptable. The role of the plasma is not so easy to determine when one considers that high background currents are readily achieved at low temperatures when the source is new.[42,43] The greatest magnitude of response is also usually observed for new beads operated at relatively low temperatures.[42] Thus, the temperature of the source and associated reaction zone does not appear to be as important as the condition of the source (the source exhibits a gradual deterioration, and higher source temperatures must be used to maintain response).[43] Although low source temperatures are sufficient to vaporize neutral alkali atoms (as evidenced by high background currents for new beads), they should not promote the efficient production of cyanide radicals.

Reactions resulting in the specific detector response are considered to take place in the immediate area of the source.[43] Experiments conducted with the Tracor detector[42] support this hypothesis. The distance between the source and collector electrode was altered by using cylindrical electrodes of different lengths. Approximately the same sensitivities towards nitrogen- and phosphorus-containing compounds (atrazine and methyl parathion) were observed for sources to collector distances of 0.330 to 0.035 in. If distinct reaction zones existed outside of the immediate area of the source, a change in response should have been found.

There appears to be some confusion regarding the role of the cyan radical and its pyrolytic formation from a variety of organic nitrogen-containing compounds. Kolb et al.[35] reported the sentivity of their rubidium silicate detector was approximately ten times less for barbiturates and similar compounds whose structures prevent the efficient formation of the cyan radical. Compounds that do not contain an N-C covalent bond, such as butyl nitrate, gave no response. On the other hand, Burgett et al.[32] claimed that the Hewlett-Packard detector does not require HCN bonding (interpreted as a nitrogen organic carbon atom) for a sensitive response. Nevertheless, a reduced response ($\sim$ 5 times) was found for barbital. Response values for compounds that do not contain a C-N covalent bond, such as butyl nitrate, were not reported. Nitrogen carrier gas, however, can be used[37] with the Hewlett-Packard detector. Since the same compounds were not investigated and it was not stated by either group of researchers whether response data were corrected for chromatographic efficiencies, it can not be determined for certain if the two detectors actually display different response characteristics.

There is also some confusion regarding the general applicability of the Kolb mechanism. It has been suggested[32] that this mechanism does not hold for the Hewlett-Packard detector because the collector is at a negative potential and good sensitivity is achieved for barbiturates. This does not appear to be adequate evidence for rejection of the mechanism proposed by Kolb and co-workers. The source in the Hewlett-Packard detector is at a negative potential, which allows the alkali regeneration scheme to operate. The presence of a negative potential on the collector merely means that the detector current would be due to an alkali ion current and not to the electron current and radical-ion current as portrayed by the Kolb mechanism.

2. *Response Characteristics*

The influence of operating parameters on response of the FASD to nitrogen compounds has been described only for the rubidium silicate detector manufactured by Perkin-Elmer. A detailed characterization of this detector has been presented by Lubkowitz et al.[43] The detector has also been studied by Hartigan et al.[36] and Kolb et al.[35] Sensitivity of the detector is dependent upon detector background. The background is affected by bead heating current, gas flow rates, and condition of the bead. The background at constant gas flows increased exponentially as the heating current is increased linearly.[35,43] Background vs. heating current relationships are time-dependent functions. Studies[43] over a 20-day period revealed that a new bead can age rapidly and shift the background heating current curve (Figure 15) to higher currents. At a fixed heating current, the background of a new bead was found[43] to decrease from 51 to 0.8 pA over a 16-day period. Since the current handling capacity of the bead and power supply are limited (the power supply of the detector studied was designed to shut off at 4.0

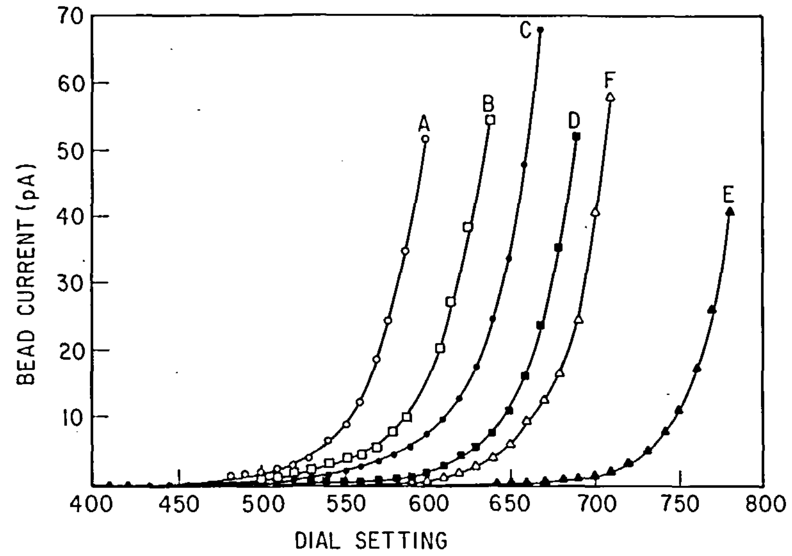

FIGURE 15. Bead current as a function of dial setting and time elapsed from bead installation. A, Day 1; B, Day 4; C, Day 8; D, Day 11; E, Day 16; F, Day 20. (From Lubkowitz, J. A., Glajch, J. L., Semonian, B. P., and Roders, L. B., *J. Chromatogr.*, 133, 37 (1977). With permission.)

to 4.5 A), the background required for good sensitivity will eventually be unobtainable and the source must be replaced.

Bead heating currents required to obtain a background of 50 to 70 pA, which are the limiting values consistent with noise and drift, rapidly aged the source. This rapid deterioration of the bead is not consistent with the self-regeneration theory of Kolb et al.[35] The presence of salt deposits, as is the case with the thermionic detector, were not found on the inner surfaces of the detector.[43] This indicates that an alteration of the bead surface took place, rather than depletion of the alkali content of the bead.

It has been found[42] that the rate of deterioration of the alkali source can be reduced by using well-conditioned columns and polyimide-coated septa. The performance of deteriorated sources can be partially restored by heating the bead with a micro-torch. Turning the source so that its upper surface is presented to the carrier stream partially restores performance. Although not extensively investigated, operation of the detector with silicone columns appears to age the source faster than if columns such as Carbowax® 20M were used. These observations indicate that coating of the source with silicone decomposition products may be a primary cause of aging. The rate of silicone decomposition on the source surface should be proportional to the source temperature, which is consistent with the aging studies conducted by Lubkowitz et al.[43] Thus, it would be advantageous to heat the bead only when the detector is used.

Magnitude of detector response was found to increase linearly as a function of background current up to a value of 200 pA[43] (Figure 16). This relationship was consistent for a variety of hydrogen flow rates.[35] The noise level also increased with bead current (Figure 17), and a limiting value of response vs. minimum detectable quantity is reached as shown in Figure 18. As shown in this figure, a minimum sensitivity of 0.2 to 0.1 pg N per second is obtainable over a relatively wide range of response from 0.4 to 1.4 C/gN. These values correspond to a background current of 5 to 20 pA.[35]

Although maximum detector sensitivity can be achieved with a fairly wide range of detector background current, the magnitude of response is very sensitive to background current. Reproducibility studies conducted by Lubkowitz et al.[43] (Table 4) revealed that response varied greatly during a 48-hr period when the detector was oper-

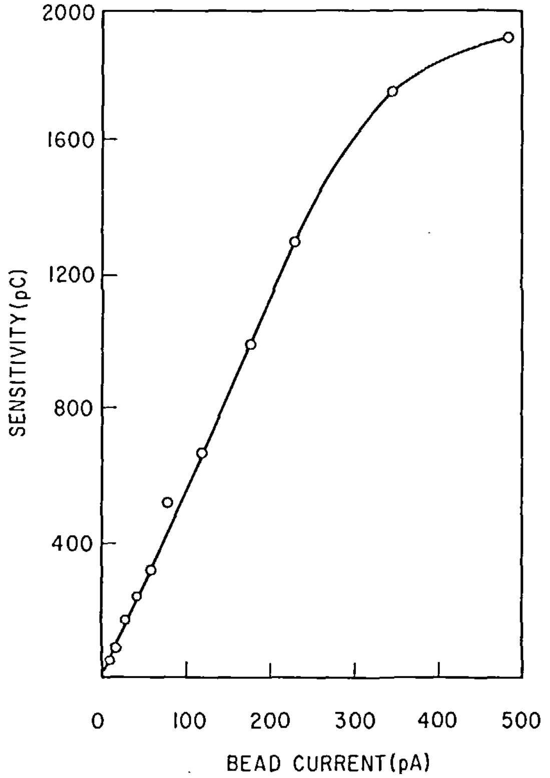

FIGURE 16. Sensitivity as a function of bead current. Azobenzene, 7.88 ng; hydrogen flow rate, 2.50 ml/min; air flow rate, 83.5 ml/min; carrier gas flow rate, 38.0 ml/min. (From Lubkowitz, J. A., Glajch, J. L., Semonian, B. P., and Rogers, L. B., *J. Chromatogr.*, 133, 37 (1977). With permission.)

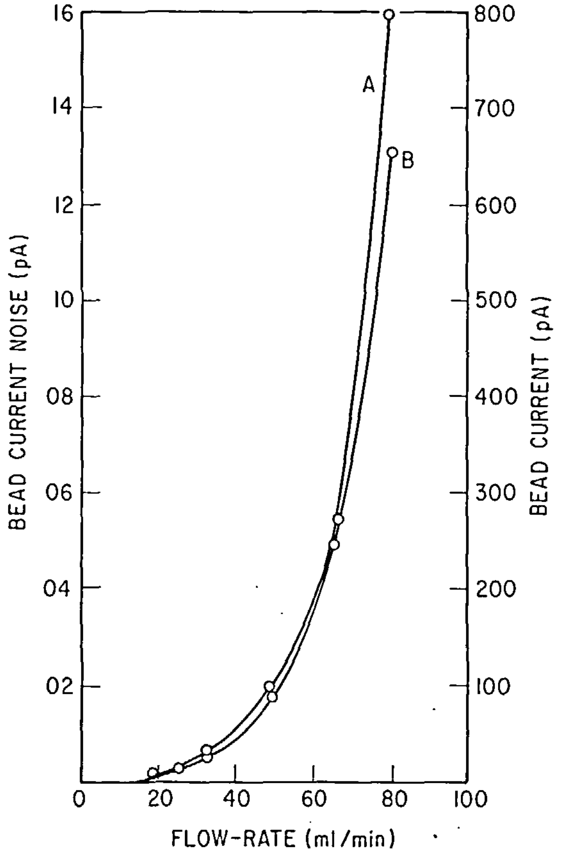

FIGURE 17. Bead current noise (A) and bead current (B) as a function of hydrogen flow rate. Air flow rate, 83.5 ml/min; carrier gas flow rate, 38.0 ml/min. (From Lubkowitz, J. A., Glajch, J. L., Semonian, B. P., and Rogers, L. B., *J. Chromatogr.*, 133, 37 (1977). With permission.)

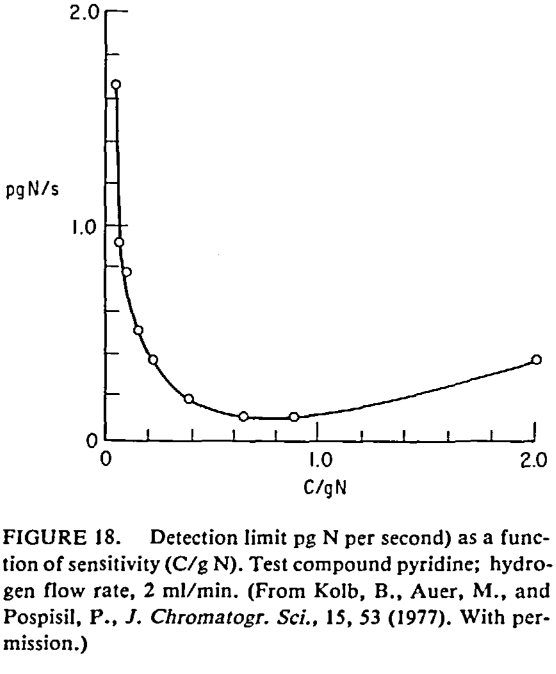

FIGURE 18. Detection limit pg N per second) as a function of sensitivity (C/g N). Test compound pyridine; hydrogen flow rate, 2 ml/min. (From Kolb, B., Auer, M., and Pospisil, P., *J. Chromatogr. Sci.*, 15, 53 (1977). With permission.)

TABLE 4

Reproducibility Studies of Peak Areas

Time elapsed (h)	Heating current (dial setting)	Bead current (pA)	Area response[a] (arbitrary units)
Constant bead current			
0	7.236	14.3	4622
1	7.242	14.3	4606
2	7.264	14.3	4718
3	7.278	14.3	4659
4	7.298	14.3	4690
5	7.320	14.3	4704
6	7.345	14.3	4705
			Average 4672
			RSD[b] 0.94%
Constant heating current			
0[c]	6.600	14.3	7320
6	6.600	11.3	5823
24	6.600	7.20	3462
48	6.600	4.17	1685

[a] Constant azobenzene injection of 11.8 ng.

[b] RSD, relative standard deviation.

[c] Initial setting not changed over a period of 48 hr.

From Lubkowitz, J. A., Glajch, J. L., Semonian, B. P., and Rogers, L. B., *J. Chromatogr.*, 133, 37 (1977). With permission.

ated at a fixed bead heating current. Operation of the detector at a fixed background current resulted in a very uniform response with time, however. These authors found hourly adjustments in bead heating current were required to maintain sensitivity.

The influence of hydrogen flow rate on detector response has been studied with conflicting results. Kolb et al.[35] report that an increase in hydrogen flow decreases sensitivity, but Lubkowitz et al.[43] found the opposite. Both studies were conducted at constant background currents. The former study used pyridine as the test compound and the latter used azobenzene, which could possibly account for these differences. The hydrogen flow rate also affects the noise level[43] and should be optimized for maximum signal/noise (Figure 19).

The air and carrier gas flow rates have been found to influence detector background and response. The sensitivity of detector background to air flow rate depends on whether helium or nitrogen is used as the carrier gas.[36] Maximum detector background was reached with very low air flow rates with nitrogen carrier gas. Considerably higher flow rates were required for maximum background with helium (Figure 20). Detector response changes with detector background and a maximum in signal/noise is exhibited.[43] Detector background (Figure 21) and response (Figure 22) reach a maximum at low flow rates (∿ 5 cm^3/min) of helium carrier gas.[43] The effects of carrier and air flow rates are attributed to cooling the bead and dilution of the hydrogen plasma gas.[36]

C. Applications

The list of applications of the thermionic detector is extensive, and a comprehensive treatment of the literature will not be attempted. Instead, representative applications that demonstrate the capabilities of available detectors will be presented. The chromatograms presented were obtained with various operating conditions and therefore

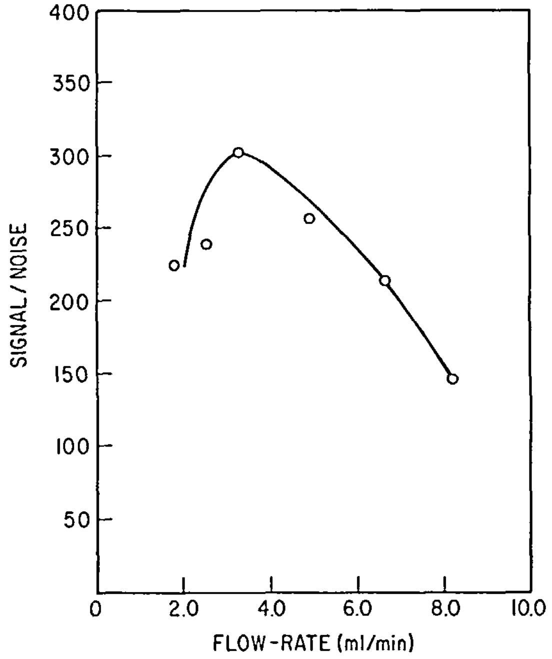

FIGURE 19. Signal-to-noise ratio as a function of hydrogen flow rate. Azobenzene, 7.88 ng; air flow rate, 83.5 ml/min; carrier gas flow rate, 38.0 ml/min. (From Lubkowitz, J. A., Glajch, J. L., Semonian, B. P., and Rogers, L. B., *J. Chromatogr.*, 133, 37 (1977). With permission.)

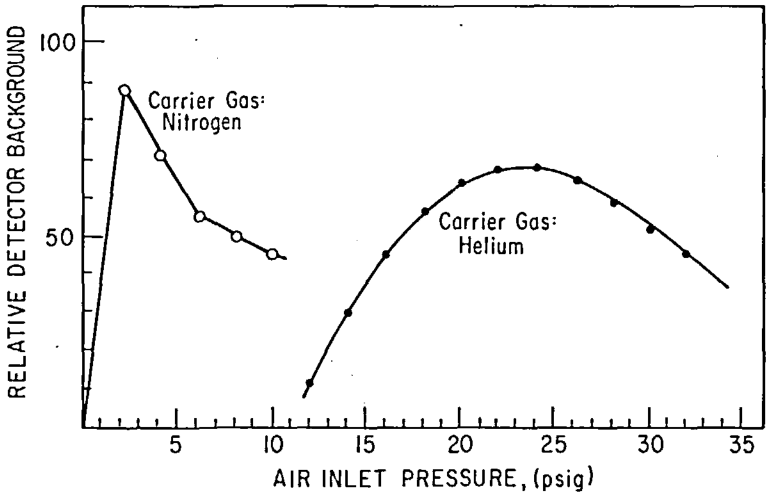

FIGURE 20. Dependence of the relative detector background on air inlet pressure (flow) for two different carrier gases. Constant settings: carrier gas flow rate, 16 ml/min; hydrogen flow rate, 5 ml/min. (From Hartigan, M. J., Purcell, J. E., Novotny, M., McConnell, M. L., and Lee, M. L., *J. Chromatogr.*, 99, 339 (1974). With permission.)

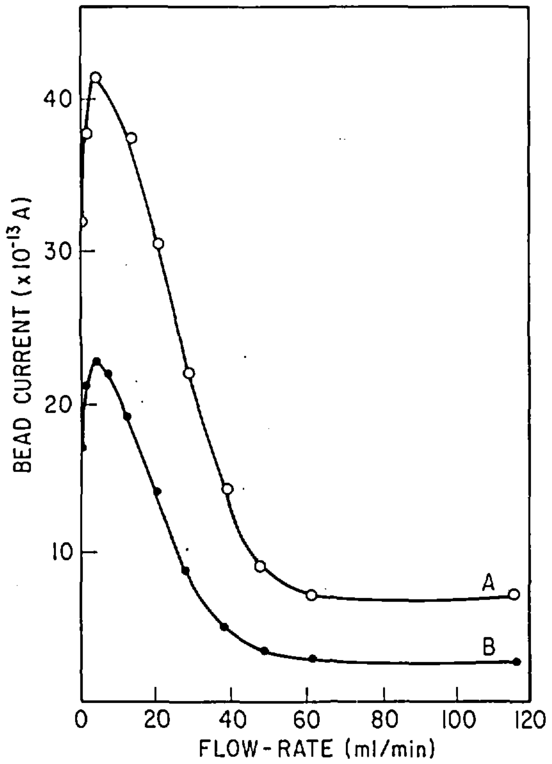

FIGURE 21. Bead current as a function of carrier gas flow rate. Hydrogen flow rate, 2.50 ml/min; air flow rate, 83.5 ml/min. A, 3.20 A heating current; B, 3.14 A heating current. (From Lubkowitz, J. A., Glajch, J. L., Semonian, B. P., and Rogers, L. B., *J. Chromatogr.*, 133, 37 (1977). With permission.)

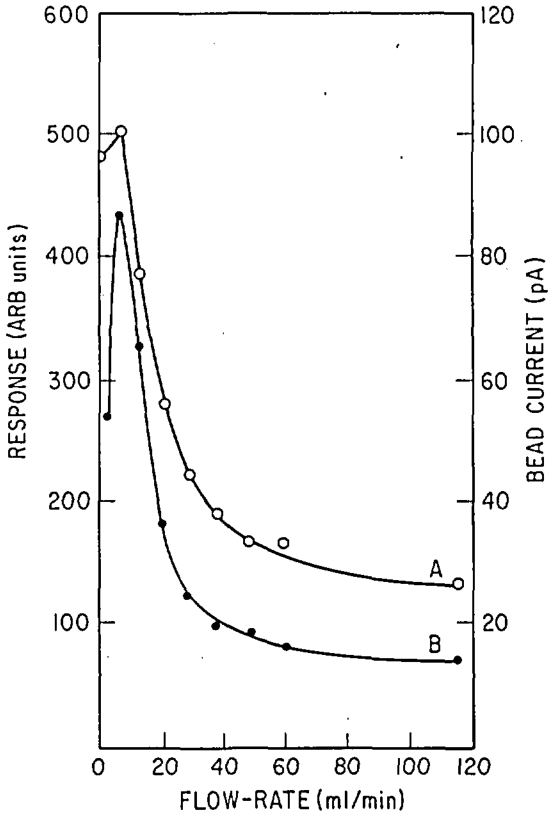

FIGURE 22. *Sensitivity (A) and bead current (B) as a function of carrier gas flow rate.* Azobenzene, 7.88 ng; hydrogen flow rate, 2.50 ml/min; air flow rate, 83.5 ml/min. (From Lubkowitz, J. A., Glajch, J. L., Semonian, B. P., and Rogers, L. B., *J. Chromatogr.*, 133, 37 (1977). With permission.)

should not be used for direct comparison of different detector designs. The advantages of using element-selective detectors to increase method sensitivity and reduce interference are well known and will not be discussed.

The improved salt tip described by Johnson et al.[18] and the AFID attachment of Karmen and Haut[44] are easy and inexpensive to make and can be used to convert most flame ionization detectors to AFID operation with surprisingly good results. As shown by these authors, good sensitivity and selectivity for nitrogen compounds can be achieved with a converted FID.

The advent of commercial "flameless" alkali sensitized detectors has greatly facilitated the determination of nitrogen-containing compounds. The stability of these detectors as compared to the AFID allows the analyst to concentrate his effort on application of the detector to analytical problems rather than optimizing parameters to maintain detector performance. Nanogram to picogram quantities of most nitrogen compounds can be routinely determined with only an occasional adjustment to the detector background.

Response of the commercial FASD to a variety of nitrogen-containing drugs and pesticides is shown in Figures 23 through 28. As can be determined from these figures, picogram sensitivity can be achieved for a wide variety of compounds. Detector response to nitrogen and hydrocarbon is compared in Figure 29. The chromatogram in this figure demonstrates a N:C selectivity of 3×10^5.

Novel operating features are available in several of the commercial detectors. The FASD manufactured by Perkin-Elmer can be operated in several different modes.[45] A simplified schematic of the detector is displayed in Figure 30. Modes of operation can be selected by merely changing positions of a toggle valve and polarity switch and include N-P, P, and FI modes. The N-P mode uses a negatively polarized jet and low hydrogen flow rates. Responses are obtained for nitrogen and phosphorus. The jet is grounded in the P mode and the hydrogen flow rate is increased to approximately ten times that used in the N-P mode. Nitrogen-containing compounds give a reduced response in this mode. The alkali source is removed from the flame zone and is not heated electrically in the FI mode. The jet is polarized negatively and normal flame ionization gas flows are used. The detector behaves as a flame ionization detector in this mode and no enhancement of response to nitrogen or phosphorus compounds is produced. Chromatograms obtained with the various operating modes are reproduced in Figure 31.

A time-selectable source desensitizer is incorporated in the detector manufactured by Tracor. Activation of the source desensitizer reduces the temperature of the source for the period of time selected. This allows reactive solvents and derivatizing reagents (BSA) to be used without harm to the source.[34] Use of the source desensitizer is demonstrated by the chromatograms in Figure 32.

Advantages of the N-P detector for the analysis of drugs,[46-56] natural products,[57,58] pesticides,[59-61] and general analysis[62] have been presented. Besides the usual benefits of increased method sensitivity and less extensive sample cleanup, the N-P detector can be used to obtain qualitative information. Ratios of response of the N-P detector and the FID have been suggested for the qualitative analysis of drugs.[63] The response index thus obtained for drugs showed a change from 1 to 17% over a 2-month period. The change in the response index is presumably due to aging of the alkali source.

III. ELECTROCHEMICAL DETECTORS

A. Electrolytic Conductivity Detectors

1. Background and Theory of Operation

The electrolytic conductivity detector was originally developed by Piringer and Pascalau[64] for the detection of carbon-containing compounds. In this detection system,

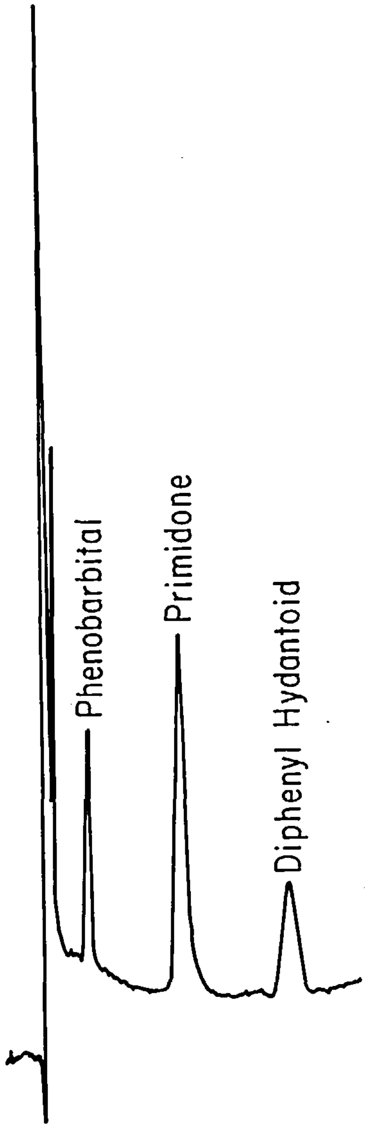

FIGURE 23. Analysis of anticonvulsants and sedatives using the N-P FID. Concentration approximately 1 ng each. Column is 0.25% NPGS + 0.025% H_3PO_4. (From Burgett, C. A., Smith, D. H., Bente, H. B., Wirfel, J. C., and Goodhart, S. E., Application note ANGC2-76, Hewlett-Packard, Avondale, Pa., (1976). With permission.)

organic compounds are combusted to CO_2 in a furnace containing CuO. The CO_2 is dissolved in deionized water in a long class capillary tube, and the conductivity of the resulting solution is continuously displayed on a strip chart recorder. This detection system was modified by Coulson[65] for the selective detection of halogen- , sulfur- , and nitrogen-containing compounds. Simplified[66] and improved[67] ECDs for the selective determination of these elements have since been described. A review of ECDs prior to 1972 has been prepared by Selucky.[68]

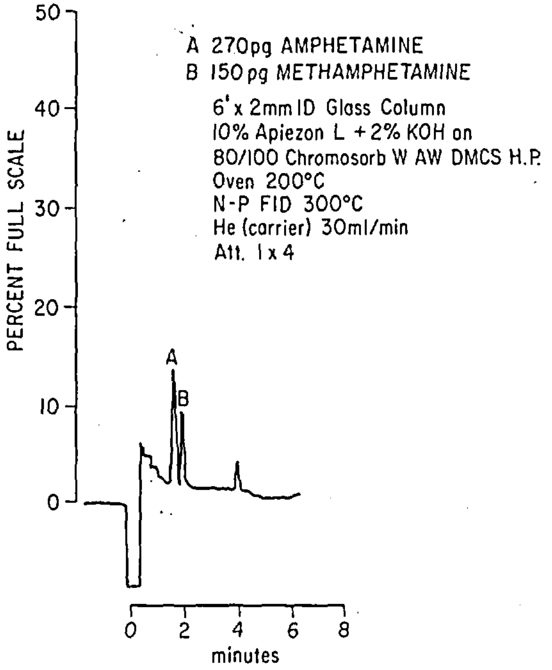

FIGURE 24. Analysis of amphetamines. (From Burgett C. A., Smith, D. H., Bente, H. B., Wirfel, J. C., an Goodhart, S. E., Application note ANGC2-76, Hewlett Packard, Avondale, Pa., (1976). With permission.)

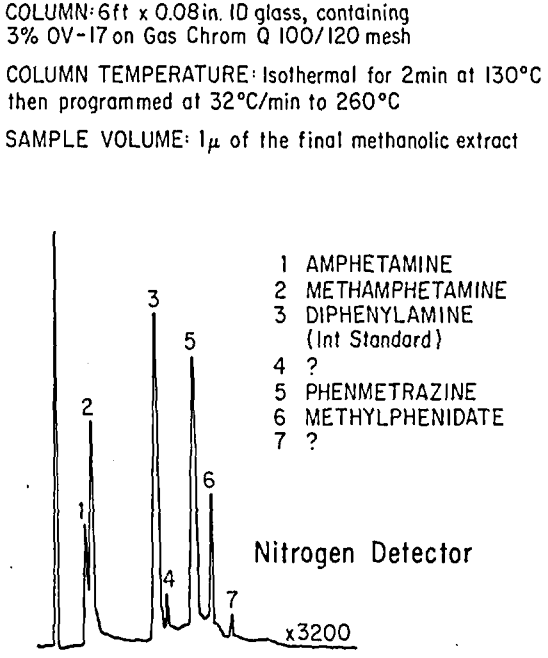

FIGURE 25. Analysis of drug extracted from serum. (From Kolb, B. and Bichoff, J., *J. Chromatogr. Sci.*, 12, 625 (1974). With permission.)

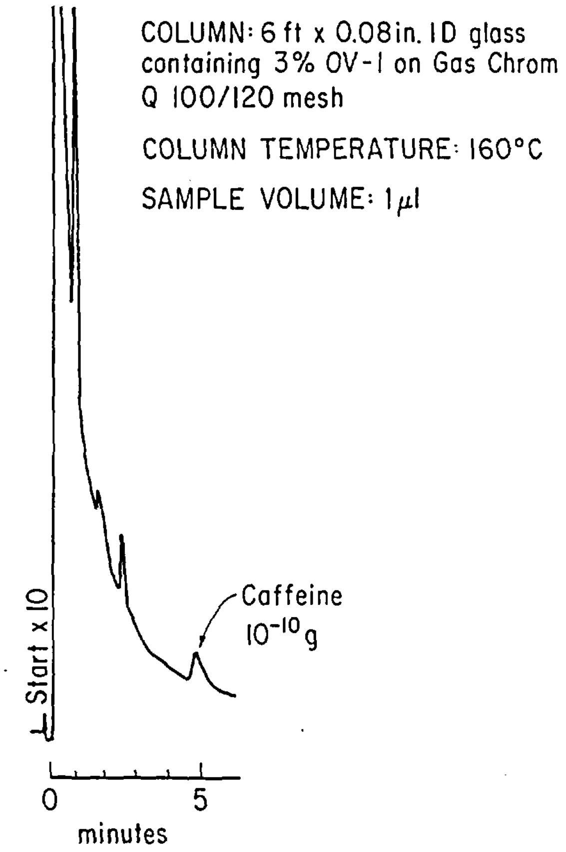

FIGURE 26. Analysis of caffeine in hexane solution. (From Kolb, B. and Bischoff, J., *J. Chromatogr. Sci.*, 12, 625 (1974). With permission.)

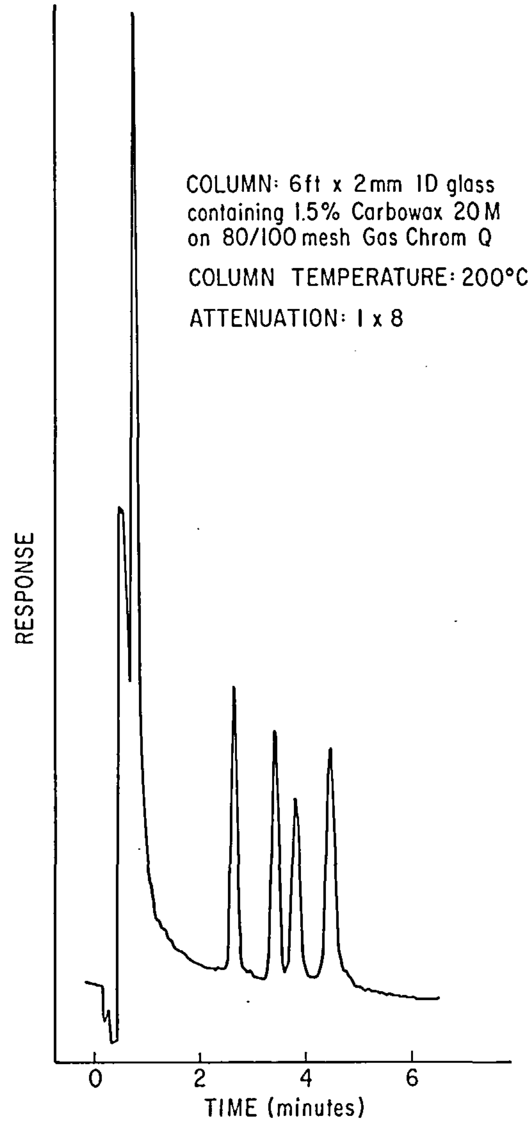

FIGURE 27. Analysis of triazine herbicides. Sample: 200 pg each of Atrazine, Simazine, Propazine and Prometryne. (From Retention Times, Tracor, Inc., August 1977. With permission.)

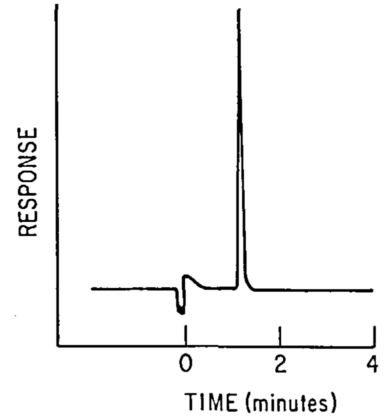

FIGURE 28. Analysis of azobenzene in hexane. Sample size: 4 ng in 2 μl of hexane. Attenuation, 10 × 8.

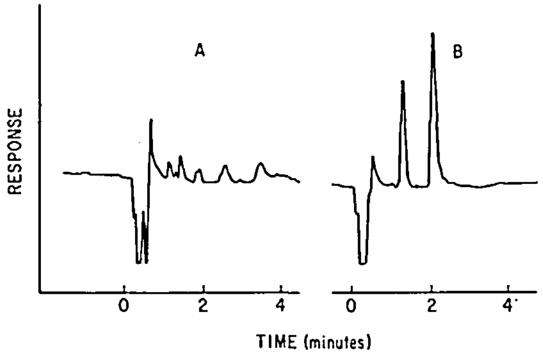

FIGURE 29. Selectivity of the N-P detector. A: 5 ng each of C_{17}, C_{18}, C_{19}, and C_{20} normal hydrocarbons; B: 200 pg of atrazine and 100 pg of methyl parathion. Attenuation, 10 × 4.

The basic components of the ECD are displayed in Figure 33. The chromatographed sample is converted to the monitored species by oxidative or reductive pyrolysis in the high-temperature furnace. The reaction products are swept into a gas-liquid contactor where they are mixed with an appropriate conductivity solvent. The liquid phase is separated from insoluble gases in a gas-liquid seperator and then passed through a conductivity cell. The detectors described for the determination of nitrogen compounds have differed widely in detector geometry, electronics for monitoring conductivity, and the chemistry involved.

Organic nitrogen-containing compounds are converted to NH_3 at 800 to 900°C with a nickel catalyst and hydrogen reaction gas, according to Equation 4.

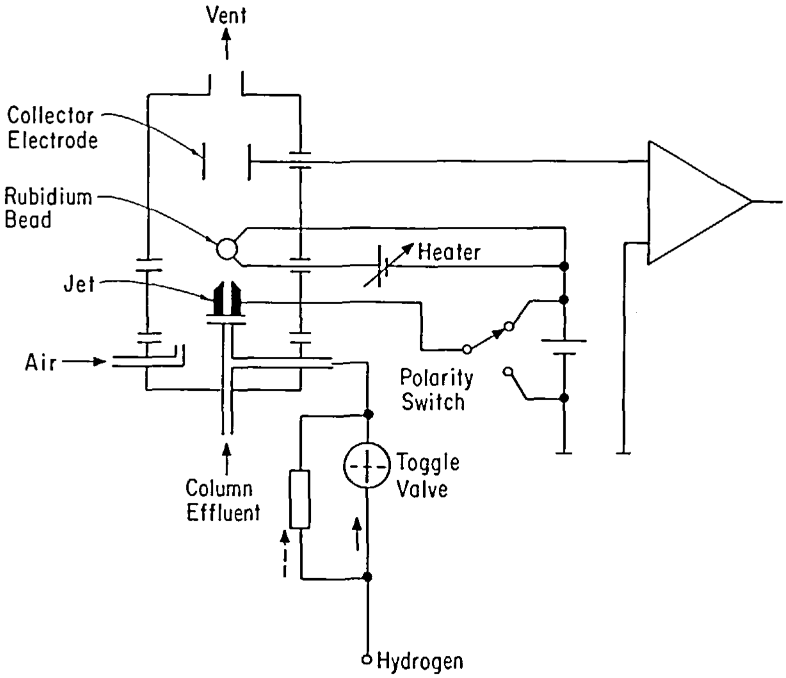

FIGURE 30. Schematic of the nitrogen-phosphorus detector (NPD). (From Kolb, B., Auer, M., and Pospisil, P., *J. Chromatogr.*, 134, 65 (1977). With permission.)

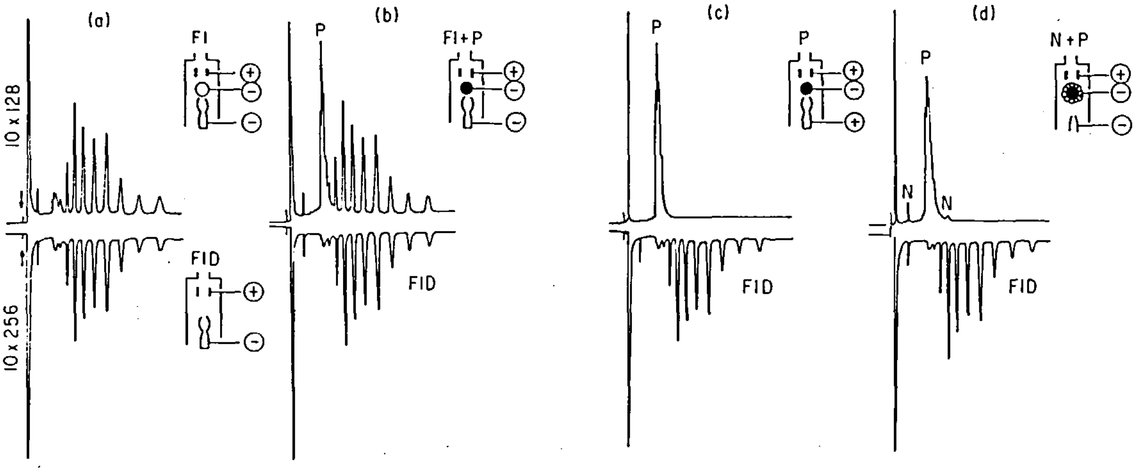

FIGURE 31. Operational modes of the NPD, exemplified by the analysis of an ester oil with nitrogen- and phosphorus-containing additives. Perkin-Elmer F22 chromatograph with a 1-m glass column packed with 3% OV-1 on Chromosorb® W-HP; carrier gas (nitrogen) flow rate, 20 ml/min; outlet splitter, 1:1; temperature programmed, 270 to 300°C at 8°C/min; attenuation, FID 10 × 256 and NPD 10 × 128. Compounds: P, P-containing additives (tricresyl phosphates); N, N-containing additives (first N peak: diphenylamine). In (a) to (d) with FID:H_2, 35 ml/min; air, 400 ml/min. (a) NPD, FI mode: H_2, 35 ml/min; air, 400 ml/min; heating position "off". (b) NPD, P + FI mode: H_2, 35 ml/min; air, 400 ml/min; heating position 250. (c) NPD, P mode; H_2, 35 ml/min; air, 400 ml/min; heating position 280. (d) NPD, NP mode: H_2, 2 ml/min; air, 100 ml/min; heating position 710. (From Kolb, B., Auer, M., and Pospisil, P., *J. Chromatogr.*, 134, 65 (1977). With permission.)

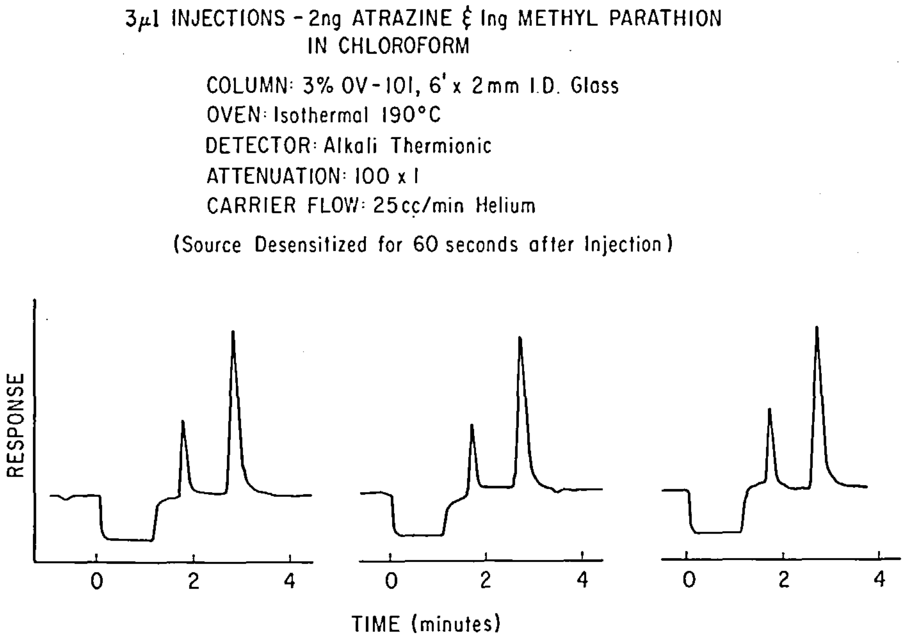

FIGURE 32. Analysis of Atrazine and Methyl Parathion in chloroform using the Tracor source desensitizer. Chromatogram shows three repetitive injections of 3 μl sample. (From Anonymous, Retention Times, Tracor, Inc., August (1977). With permission.)

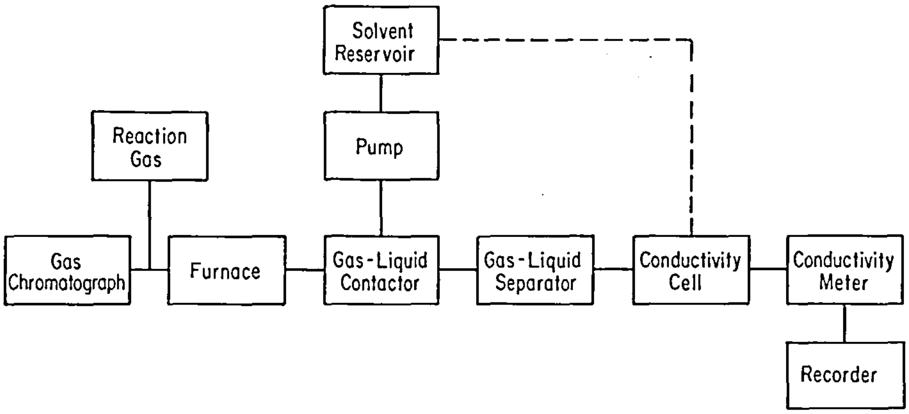

FIGURE 33. Block diagram of the electrolytic conductivity detector.

$$\text{R-CN} \xrightarrow{\text{Ni, H}_2} \text{NH}_3 + \text{lower alkanes} \qquad (4)$$

This has been accomplished with a quartz reaction tube containing a catalyst bed of nickel wire strands,[65,67] a quartz capillary tube with a single piece of nickel wire,[66] or a nickel reaction tube.[67] The increase in conductivity due to the formation of ammonium hydroxide was used as the basis of response in the detectors described by Coulson[65] and Hall,[67] as in Equation 5.

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \qquad (5)$$

In contrast, the decrease in conductivity of a dilute hydrochloric acid solution was the basis of response in the detector described by Jones and Nickless,[66] according to Equation 6.

$$NH_3 + H_3O^+ + Cl^- \rightleftharpoons NH_4^+ + Cl^- + H_2O \quad (6)$$

A reduction in conductivity occurs because the greater ionic conductance of the H_3O^+ ion is replaced by that of the NH_4^+ ion, which has an equivalent conductance of 73 vs. 350 for the H_3O^+.

The mechanisms of selectivity of the ECD to nitrogen compounds is based on the conversion of potentially interfering substances to reaction products that either produce little electrolytic conductivity or can be easily removed with an abstractor prior to the cell. Organic compounds containing halogens, sulfur, and oxygen are converted to HX, H_2S, H_2O, and lower alkanes.

$$RX \xrightarrow{Ni,\ H_2} HX + \text{lower alkanes} \quad (7)$$

$$RSH \xrightarrow{Ni,\ H_2} H_2S + \text{lower alkanes} \quad (8)$$

$$ROH \xrightarrow{Ni,\ H_2} H_2O + \text{lower alkanes} \quad (9)$$

Water gives little or no response since it is already present in the conductivity solvent. Lower alkanes (primarily CH_4) have low solubilities in the conductivity solvent and are not ionized when dissolved. HX and H_2S can be removed with a scrubber, such as strontium hydroxide on quartz wool or Fiberfrax®. Thus, NH_3 is the only product from common organic compounds that gives a response. Consequently, the detector exhibits exceptionally high specificity to nitrogen compounds.

The conductivity cell developed by Coulson is presented in Figure 34. The cell is made of glass and consists of separate gas-liquid contactor, gas-liquid separator, and electrode sections. A siphon leg is used to draw deionized water across the electrodes at a constant velocity. The flow rate of water entering the gas-liquid contactor is controlled by a fixed pressure head. Cell operation must be started by partially closing the vent port to force water through the conductivity cell and start siphon action.

The conductivity cell has two platinum wire electrodes separated by a distance of approximately 1 cm. A DC voltage conductivity bridge, adjustable from 1 to 30V, is employed. A DC conductivity bridge would be expected to have poor response characteristics due to electrode polarization; however, cell geometry was optimized to have minimum polarization.

Modified cells for the Coulson detector (commercially available until 1973) have been reported by Lawrence and Moore[69] and Lawrence and Sen.[70] The Coulson cell was modified to include a restrictor for reducing the quantity of water entering the gas-liquid contactor.[70] This was accomplished by inserting stainless steel wire in the capillary arm through which water is introduced into the gas-liquid contactor. Wire diameters of 0.003, 0.004, and 0.005 in. were studied. A wire diameter of 0.003 in. was found to provide the best overall improvement in sensitivity and peak shape. The presence of this size wire did not appreciably affect the detector background or noise level and resulted in a > two fold increase in response. The 0.005-in. diameter wire resulted in erratic response and increased detector noise and peak tailing.

A cell similar to that described by Coulson was constructed by Lawrence and Moore.[69] The cell (Figure 35) featured a water jacket and modified electrode spacing. The cell was evaluated using the Coulson detector system. Sensitivity of this cell was reported to be approximately five times greater than the standard Coulson cell. Re-

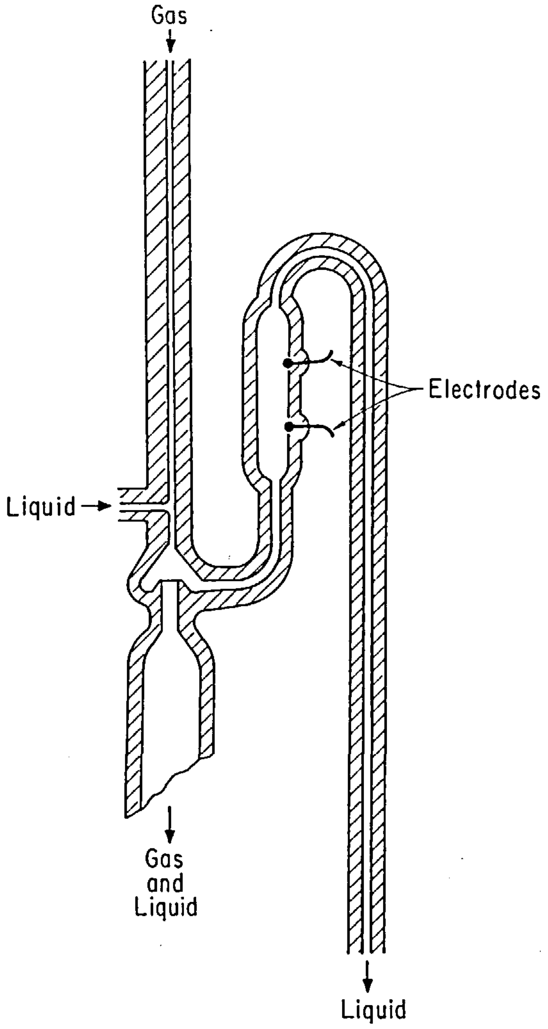

FIGURE 34. Coulson electrolytic conductivity detector cell. (From Coulson, D. M., *J. Gas Chromatogr.*, 3, 134 (1965). With permission.)

sponse was not significantly influenced by water temperature, although the background and noise level were. A water temperature of below 20°C was found to provide optimum response. The cell was more compact that the Coulson cell and less fragile. Part of the increase in response was due to the closer electrode spacing.

The improved electrolytic conductivity detector described by Hall[67,71-73] had the same components depicted in Figure 33, but featured significant improvements. The greatest improvements were in the cell, conductivity bridge, furnace temperature controller, and solvent system. The conductivity cell consisted of a unitized, concentric electrode cell made of Teflon® and stainless steel. Electrolytic conductivity was monitored with an AC conductivity bridge with synchronous detection. Solvent systems were optimized for each mode of operation.

The conductivity cell of this detector, now commercially available, is shown in Figure 36. The conductivity solvent and gaseous reaction products are combined in a small Teflon tee (the gas-liquid contactor). Since the solvent has little affinity for the Teflon surface and the I.D. of the tee is small, the gas and liquid phases are well mixed. The

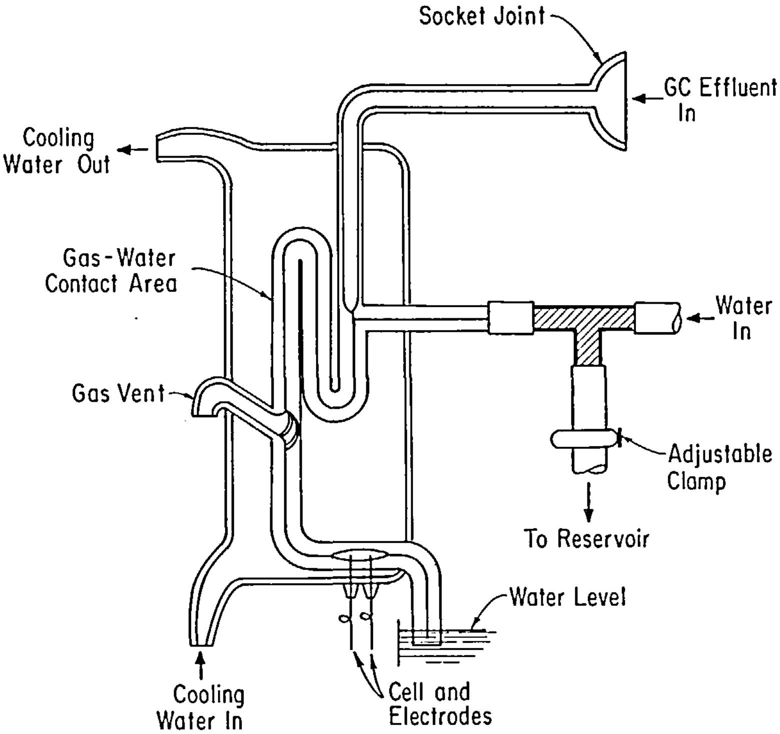

FIGURE 35. Scale diagram of the modified conductivity detector and water jacket. (Reprinted with permission from Lawrence, J. F. and Moore, A. H., *Anal. Chem.*, 46, 755 (1974). Copyright by the American Chemical Society.)

heterogeneous gas-liquid mixture thus formed separates into two smooth flowing phases upon contact with the inner surface of the outer electrode. The liquid phase flows down the wall as a sheath with the gas phase as the core. In so doing, the liquid phase passes between the inside wall of the outer electrode and the outside wall of the inner gas exit tube (inner electrode). The solvent is vented via the solvent exit hole in the inner gas exit tube. The solvent and gas phases are recombined at this point and exhausted from the bottom of the gas exit tube.[71]

It is reported[67] that the driving forces that make the cell function are the downward force of the moving liquid phase, the bonding attraction between the liquid phase and the detector surfaces, and the positive pressure on the liquid phase in the detector. Construction materials and detector geometry are therefore critical factors. Metal surfaces (stainless steel) are claimed[71] to be superior to glass, which is in turn superior to most plastics for the separation of gas and organic liquids. Clean glass surfaces, however, were found slightly superior for the separation of gas and water mixtures. The original cell described[67] did not vent the solvent into the inner gas exit tube. Instead, the solvent was vented via a capillary tube in the side of the outer electrode. This required that the backpressure on the solvent be adjusted by balancing the inside diameter and/or length of the solvent exit tube to the cell geometry and flow conditions. This requirement is totally eliminated in the cell design described later.[71,72] The cell is self-starting and is not susceptible to the capture of bubbles that stop solvent flow (i.e., Coulson cell). A commercial version based on this design is available from Tracor, Inc., the only company that produces an ECD for gas chromatography.

Theoretical and practical considerations of this cell have been discussed by Hall.[67]

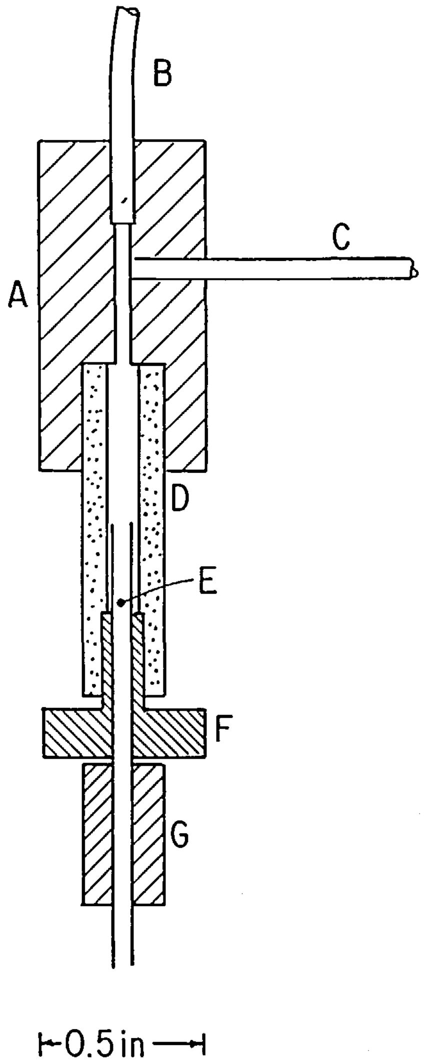

FIGURE 36. Microelectrolytic conductivity detector cell assembly. A, gas-liquid contactor; B, Teflon® solvent delivery tube; C, Teflon reaction products delivery tube; D, stainless steel detector block; E, solvent vent; F, Teflon insulator sleeve; G, gas-liquid exit tube and center electrode.

An equation that describes the relationship of cell response to geometry was developed by considering:

1. The electrolytic conductivity (C) of the solution is directly proportional to the specific conductance (C_{sp}) of the solution and inversely proportional to the cell constant (A).
2. The specific conductance depends upon the ions in solution, temperature, and their concentration.
3. The cell constant depends upon electrode area (A) and the interelectrode distance (d).

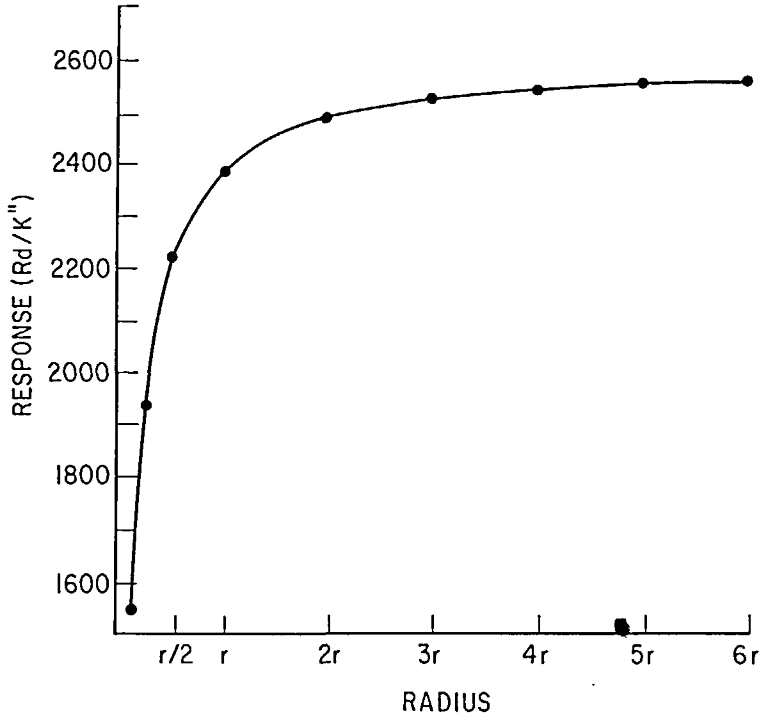

FIGURE 37. Calculated detector response vs. radius of inner electrode. Interelectrode distance fixed at 0.0139 cm (r, 0.0826 cm). (From Hall, R. C., *J. Chromatogr. Sci.*, 12, 152 (1974). With permission.)

4. Detector response (R_d) depends upon the amount of compound (M) entering the furnace per unit of time, the weight percent of the monitored element (W), the conversion efficiency (E) to the monitored species, solvent flow rate (f), cell temperature (T_c), cell voltage (v), and the cell constant.

From these considerations, it was shown that detector response is described by:

$$R_d = K\,(MWEA/fd).\ aT_cv \qquad (10)$$

for a fixed cell purge time (2 sec was determined to be sufficient for packed columns) and constant conditions including sample size.

$$R_d = 2K'\,Av/V_cd \qquad (11)$$

which results in:

$$R_d = K''\,\frac{r_1}{(r_2{}^2 - r_1{}^2)\,d} \qquad (12)$$

since $f = V_c/2$, where V_c = cell volume; and $A = 2\pi rl$, where r_1 = radius of inner electrode, r_2 = radius of outer electrode, and $V = l\pi\,(r_2{}^2 - r_1{}^2)$.

Difficulties in construction and perturbations in solvent flow rate were found to limit the interelectrode distance to $\geqslant$ 0.0139 cm. Thus, substitution of this value into Equation 12 allowed the relationship of detector response to the radius of the center electrode (Figure 37) and interelectrode distance (Figure 38) to be calculated. As exhib-

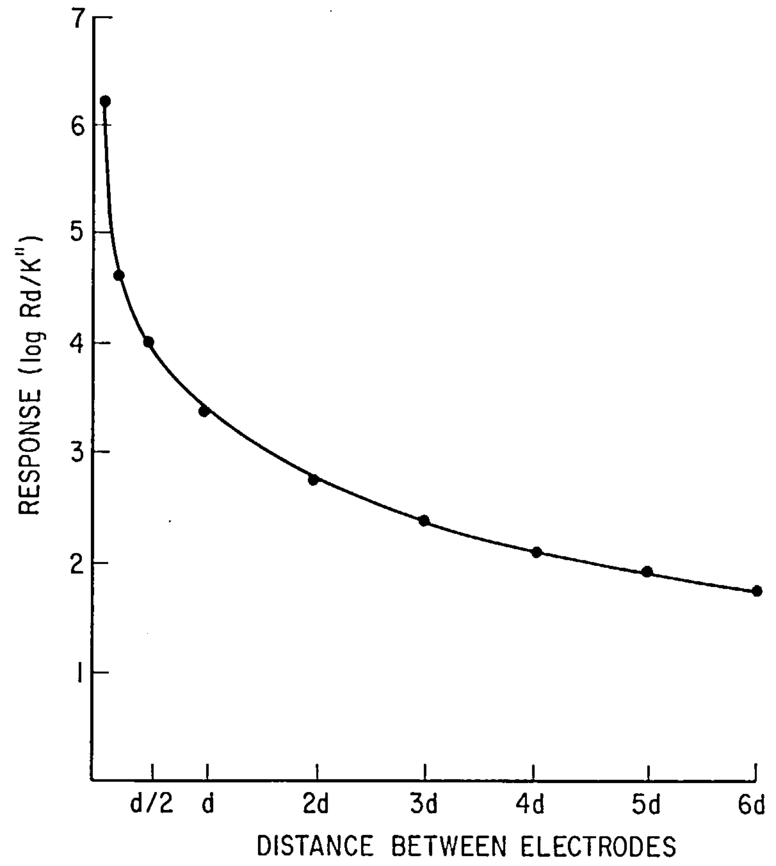

FIGURE 38. Calculated detector response vs. inter-electrode distance (d). Radius of inner electrode fixed at 0.0826 cm. (From Hall, R. C., *J. Chromatogr. Sci.*, 12, 152 (1974). With permission.)

ited in Figures 37 and 38, response decreases rapidly for values less than approximately 0.0826 cm for the center electrode, but increases rapidly as the interelectrode distance is decreased.

It should be noted that the above treatment concerns only the effects of cell geometry on response and does not consider the solution chemistry. The theoretical relationship between the equivalent conductance of several electrolytes in pure water and their concentration has been presented by Coulson.[74] A lower limit was found to exist due to the autoprotolysis of water (Figure 39), according to Equation 13:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (13)$$

The formation of OH^- ions from Equation 5 would thus drive Equation 13 to the left, producing a buffering effect. This problem has been essentially eliminated by Patchett,[75] who employed an ion exchange tube that contained an excess of anion resin to maintain the pH of the water as slightly basic, thus greatly reducing the effects of autoprotolysis. This problem has also been eliminated by using nonaqueous conductivity solvents[67] (for halogen analysis) and dilute acid solutions.[66]

2. Response Characteristics

For a given detector design, response to nitrogen compounds depends upon the conversion efficiency of the nitrogen-containing compound to the detected species (usually

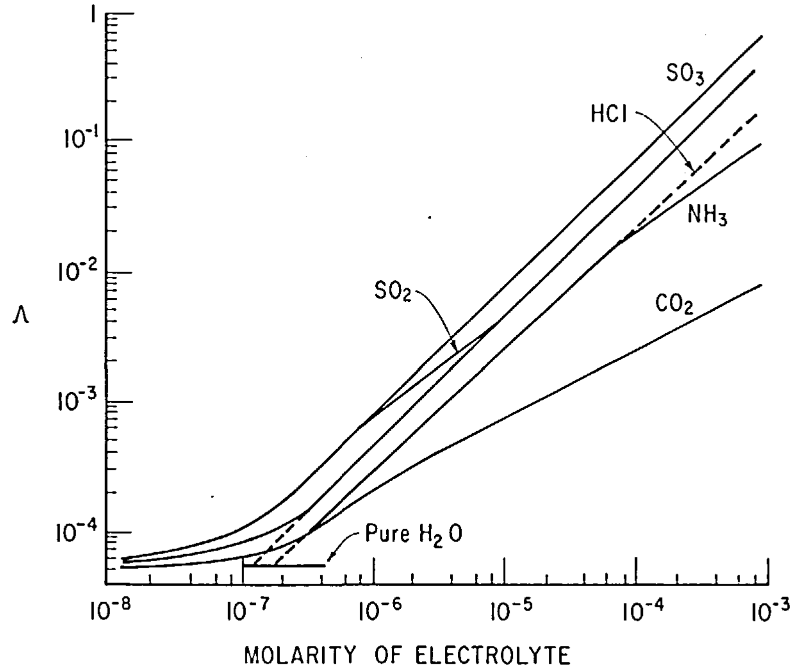

FIGURE 39. Equivalent conductance of several electrolytes in water (From Coulson, D. M., *Am. Lab.*, May 1969. With permission.)

NH_3), the influence of abstractors and related gas-phase reactions, the conductivity solvent used, and the flow rate of solvent. The detector can be operated with reaction parameters (furnace chemistry) that convert all organic nitrogen compounds to NH_3 or conditions that will only convert certain types of compounds to a detectable species. The various modes of operation include the catalytic reductive, pyrolytic reductive, pyrolytic, pyrolytic oxidative, and catalytic oxidative. The catalytic reductive, pyrolytic reductive, and pyrolytic modes are the most useful for the detection of nitrogen compounds. Response in a given mode can be altered by furnace temperature and reaction gas flow rate.

Response vs. furnace temperature for the detector (Model 310 Hall Electrolytic Conductivity Detector) operated in the catalytic reductive mode using a 2-mm I.D. quartz reaction tube containing a nickel wire catalyst bundle and a strontium hydroxide scrubber was investigated by Wilson and Cochrane,[76] Hall,[73] and Pape et al.[77] Atrazine was used as a test compound by Wilson and Cochrane, and a mixture of atrazine, simazine, and chloroisopropyl carbonate (CIPC) was used by Hall. A wide variety of nitrogen-containing drugs was studied by Pape et al. Response was found to increase rapidly from about 700°C to a maximum at 850 to 900°C for all compounds. Response to atrazine decreased slightly from 900 to 1000°C (Figure 40). Detector response above 850°C was not investigated by Hall due to the presence of nitrogen added to the reaction gas to prevent problems associated with the autoprotolysis of water (a small amount of N_2 is converted to NH_3). The relationship of response to furnace temperature was also studied by Lawrence,[78] but with different results. Only a twofold increase in response was observed over a temperature range from 450 to 840°C. This work, however, was done with the Coulson detector that had a reaction zone approximately four times longer than that of the 310 Hall detector. Also, the reaction tube had an I.D. of 4 mm instead of 2 mm. Detector response to most of the drugs studied increased rapidly from 700 to approximately 800°C and then remained constant to 1000°C (Figures 41 and 42).

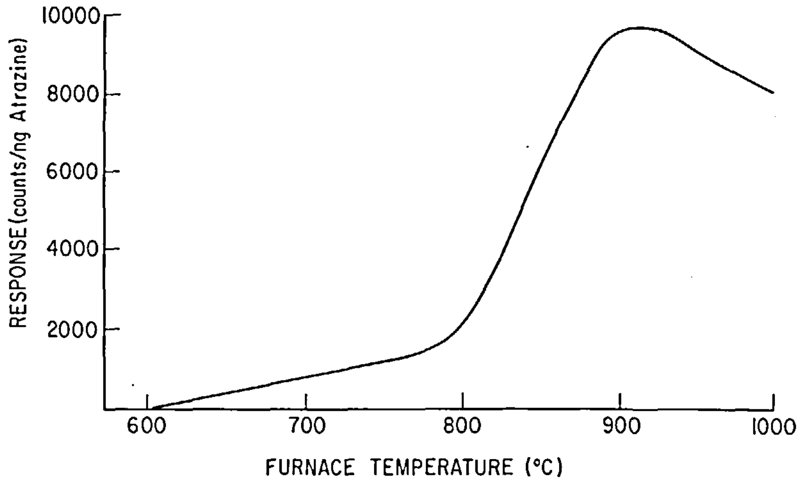

FIGURE 40. Variation in response with increase in temperature. (From Wilson, B. P. and Cochrane, W. P., *J. Chromatogr.*, 106, 174 (1975). With permission.)

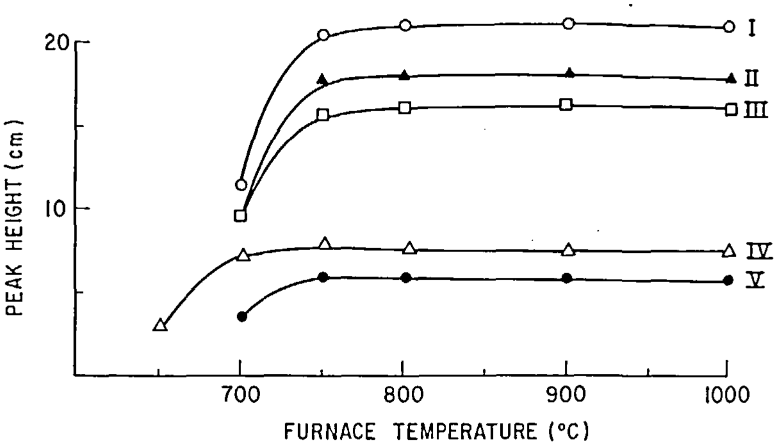

FIGURE 41. Furnace temperature profiles for phenathiazines. Compounds: I, Trimeprazine; II, Methdilazine; III, Thioridazine; IV, Phenothiazine; V, 2-Chlorophenothiazine. (From Pape, B. E., Rodgers, D. H., and Flynn, T. C., *J. Chromatogr.*, 134, 1 (1977). With permission.)

The profile of the temperature-response curves was found by Pape et al. to depend upon the temperature sequence used. Temperature-response profiles for imipramine obtained by different temperature sequences are shown in Figure 43. As exhibited in this figure, the initial temperature used and whether the sequence started from a high temperature or a low temperature significantly influenced the profiles obtained. Pape believed dependence of the profile on temperature sequence was due to catalyst deactivation at low temperatures. Silicone bleed was also found to influence the profile. Risk and Hall[79] examined the temperature-response relationships of a variety of barbiturates in the reductive pyrolytic mode (H_2 reaction gas and no catalyst) and found response increased by a factor of two to three over the temperature range of 750 to 950°C.

The relationships of response of the Hall detector to solvent flow rate (Figure 44) found by Wilson and Cochrane[76] and Hall[73] do not agree with simple theory. Since

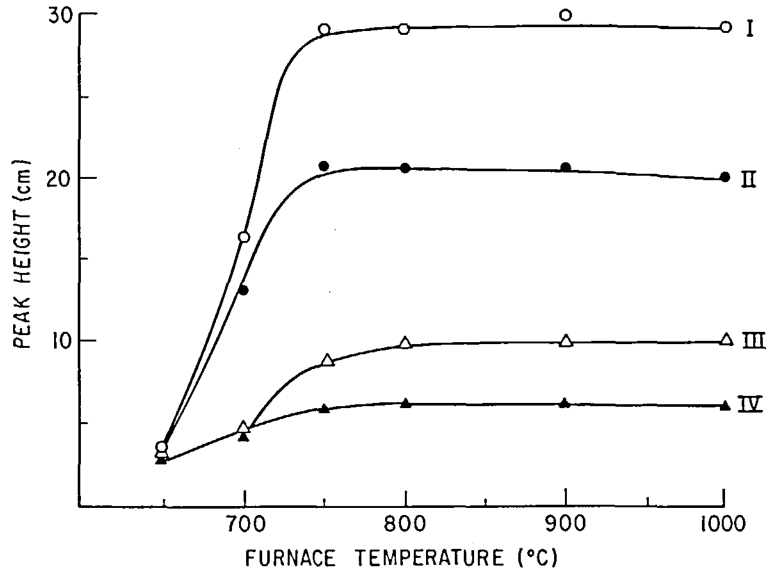

FIGURE 42. Furnace temperature profiles for phenothiazines. I, Trifluoperazine; II, Chlorpromazine; III, Fluphenazine; IV, 2-Chlorophenothiazine. (From Pape, B. E., Rodgers, D. H., and Flynn, T. C., *J. Chromatogr.*, 134, 1 (1977). With permission.)

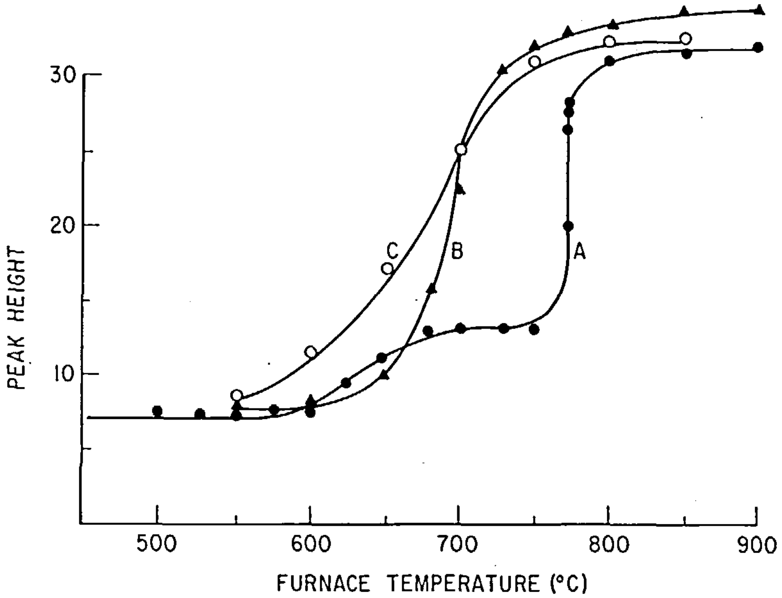

FIGURE 43. ELCD temperature profiles of imipramine in the N-selective catalyst-reductive mode illustrating differences in catalytic activity. Profile A, 500 to 900°C sequence; B, 550 to 900°C sequence; C, 900 to 550°C sequence. (From Pape, B. E., Rodgers, D. H., and Flynn, T. C., *J. Chromatogr.*, 134, 1 (1977). With permission.)

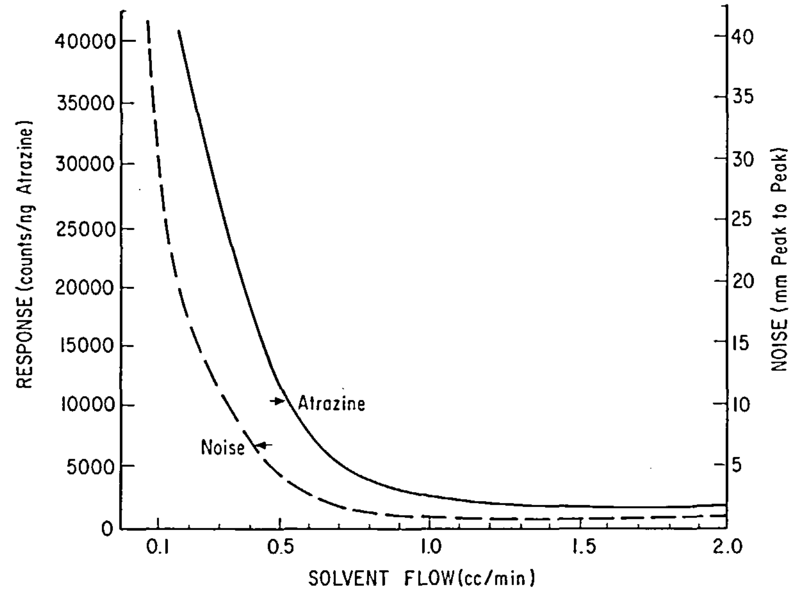

FIGURE 44. Variation in response with increase in solvent flow-rate. Solid line, Atrazine; dotted line, noise. (From Wilson, B. P. and Cochrane, W. P., *J. Chromatogr.*, 106, 174 (1975). With permission.)

the solvent flow rate determines the ion concentration, a linear inverse relationship should exist as found by Lawrence.[78] However, there are distinct differences in these studies. The experiments conducted by Lawrence were based on the Coulson cell (which has different flow characteristics than the Hall cell) and pure water as the conductivity solvent, whereas Wilson and Cochrane used the Hall cell with a 50% isopropyl alcohol conductivity solvent, and Hall used the Hall cell with a 15% isopropyl alcohol conductivity solvent.

The nonlinearity of response to solvent flow rate observed with the Hall cell can be explained by considering solvent evaporation in the cell and a limited capacity of the gas-liquid contractor for exposing all of the solvent entering the cell to the reaction product stream. Gas flowing through the cell causes the solvent to evaporate (the degree of which depends upon the solvent used), which changes the composition of alcohol-water mixtures and reduces the amount of solvent actually flowing through the cell. Thus, as the flow rate of solvent is reduced, the polarity of the solvent increases (the alcohol evaporates), and the actual quantity of solvent becomes considerably less as the capacity of the cell for evaporating the solvent is reached. Therefore, the response becomes greater than expected as the flow is reduced. The independence of response with solvent flow rates greater than 1 to 2 cm^3/min is explained if one assumes that at these flow rates large drops of solvent are formed instead of a fine mist, and these drops are expelled through the hole in the gas exit tube without touching the electrode working surfaces. The number of large drops should increase with solvent flow rate, and the effective ion concentration does not change. These effects are not observed with the Coulson cell since its design minimizes gas-liquid contact and pure water is used as the solvent.

The effect of hydrogen reaction gas flow rate on detector response in the catalytic reductive mode with helium carrier gas was investigated by Wilson and Cochrane[76] and Hall.[73] Response was founded by Wilson and Cochrane to increase rapidly up to approximately 25 cm^3/min and then remain essentially constant to 100 cm^3/min. Hall, however, found little change in response with hydrogen flow rate (Table 5) when hy-

TABLE 5

Influence of Hydrogen Reaction Gas Flow-Rate in Response to Nitrogen-Containing Compounds[a]

	Response		
Flow rate (cm^3/min^b)	CIPC	Atrazine	Simazine
10	27	89	78
20	32	109	95
40	37	121	109
60	32	108	95
80	38	131	116
100	31	108	96

[a] Furnace temperature 800°C

[b] Total flow also contained 40 cm^3/min of H_2 carrier.

[c] Response is peak heights (mm)

drogen was also used as the carrier gas. The influence of hydrogen reaction gas flow rate on detector response to a number of barbiturates and caffeine detected in the reductive pyrolytic mode was also studied by Hall.[73] Although these compounds could be detected with no reaction gas flow (nitrogen carrier gas), the best results were obtained with low flow rates of hydrogen. Sensitivity was decreased slightly with no hydrogen or flow rates higher than approximately 5 cm^3/min. This relationship was temperature dependent, however.

Detector response in the catalytic reductive mode at high furnace temperatures is proportional to the quantity of nitrogen entering the detector. Response has not been found to depend upon the molecular structure of organic compounds as long as the strontium hydroxide scrubber is operating properly and the pH of the conductivity solvent is slightly alkaline.[77] Utilization of detector response to determine the nitrogen content of a chromatographed substance must take into account chromatographic efficiency. Corrected and uncorrected response values for a variety of drugs and model compounds are given in Table 6.

In contrast to the catalytic reductive mode, the reductive pyrolytic or pyrolytic modes can be highly specific for certain types of nitrogen compounds such as nitrosamines. The pyrolytic mode was used by Rhoades and Johnson[80] to selectively detect nitrosamines in the presence of other nitrogen compounds. A furnace temperature of 400 to 600°C and a strontium hydroxide scrubber were used.

Problems which can be encountered in the use of the electrolytic conductivity detector have been discussed in detail by Hall,[73] Patchett,[75] and Pape et al.,[77] and Webster.[81] As emphasized by Pape, detector operating problems can usually be recognized prior to significant deterioration in performance if the analyst is familiar with the chemistry of the detector. Solutions to these problems are usually simple and immediate.

The problems most commonly encountered are poor linearity and peak shape. Poor linearity is usually caused by neutralization of the NH_4OH (See Equation 6). This is due to insufficient basicity of the conductivity solvent and/or exhausted scrubber. Neutralization problems are readily recognized by a sharp dip in the baseline just prior to the peak, followed by a negative dip after the peak that gradually increases to the baseline (Figure 45). The peak may be totally negative if the solvent is acidic or the quantity of nitrogen compound is very small. Peak tailing is usually due to a contaminated scrubber, contaminated transfer line from the furnace to the cell, deactivated catalyst, or the presence of acidic reaction products that are not removed by the scrubber. The presence of acidic reaction products is also normally indicated by negative peaks.

TABLE 6

Relative HECD N-Selective Catalytic-Reductive Response to Substituted Phenothiazines, Diphenymethanes, and MODEL Compounds vs. 2-Chlorophenothiazine at 850°C Furnace Temperature.

Compound	N-equivalent response	
	Uncorrected	Corrected
Phenothiazine (I)	1.45	1.04
2-Chlorophenothiazine (II)	1.00	1.00
Promazine (III)	1.44	1.10
Chlorpromazine (IV)	1.32	1.07
Trimeprazine (VI)	1.42	1.05
Methotrimeprazine (VII)	1.38	1.07
Thioridazine (VIII)	1.26	1.05
Mesoridazine (IX)	0.57	0.94
Methdilazine (X)	1.32	1.07
Prochlorperazine (XI)	1.07	0.98
Trifluoperazine (XII)	1.17	0.98
Thiethylperazine (XIII)	1.06	0.99
Fluphenazine (XIV)	0.40	0.90
Chlorprothixene (B)	0.60	0.89
Chlorcyclizine (A)	1.01	1.06
Hydroxyzine (C)	0.04	0.84
Buclizine (D)	0.85	0.97
Thioxanthine-9-one (IX)	$<10^{-3}$	
Anthracene (X)	$<10^{-3}$	

From Pape, B. E., Rodgers, D. L., and Flynn, T. C., *J. Chromatogr.*, 134, 1 (1977). With permission.

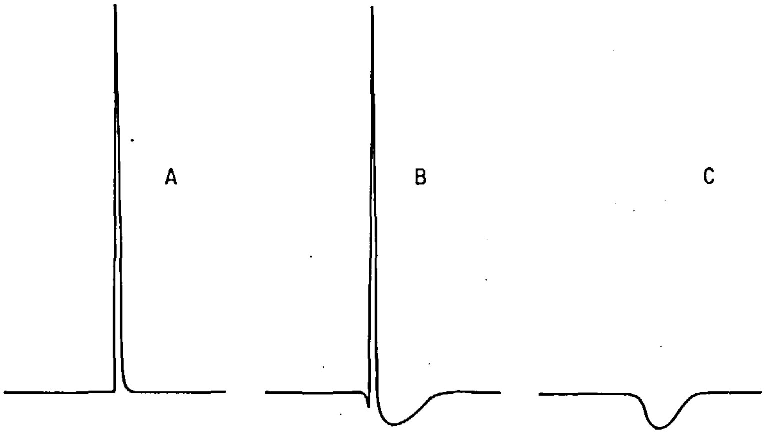

FIGURE 45. Peak shapes obtained for nitrogen-containing compounds: A, normal peak; B, peak obtained with an insufficiently basic conductivity solvent; C, peak obtained with an acidic conductivity solvent.

Negative peaks are prevented[73] by using an ion exchange tube packed according to Patchett,[75] high purity gases, and an efficient scrubber. Other solutions are obvious and include replacing the catalyst, ion exchange resin, scrubber, and transfer line as required.

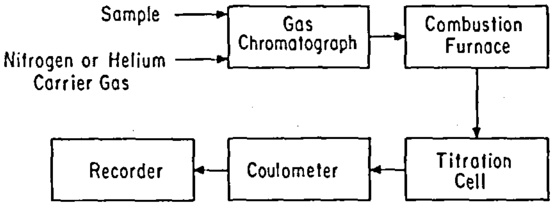

FIGURE 46. Block diagram of microcoulometer. (From David, D. J. *Gas Chromatographic Detectors,* John Wiley & Sons, New York, 1974, 199. With permission.)

3. New Developments

A bipolar pulse differential ECD has been investigated[82] and found to provide significant improvements in response characteristics over a nondifferential detector with an AC conductivity bridge. Although it was not evaluated for nitrogen analysis, this detector provided approximately a three- to five-fold increase in sensitivity for halogen and sulfur compounds. The detector employed a series conductivity cell in which the conductivity of the solvent was monitored in the first part of the cell and the conductivity of the solvent plus that due to the reaction products in the second part of the cell. The outputs of the two conductivity cells are summed differentially. In this manner, effects common to both cells (such as fluctuations in temperature and solvent purity) are reduced to negligible levels.

B. Microcoulometric Detector

1. Background and Theory of Operation

The microcoulometric detector was described by Coulson and Cavanagh[83] and Coulson et al.[84] in 1960. The detector was originally developed for the determination of halogen-containing pesticides. It was later modified for the detection of organic nitrogen by Martin.[85] The detector can also be used for the determination of sulfur- and phosphorus-containing compounds.[86-89]

Simplified diagrams of the MCD are shown in Figures 46 and 47. The detector shares several features with the ECD. They both employ a furnace for the high temperature reductive conversion of organic nitrogen to NH_3, which is the species detected. Other similarities include the use of nickel as the reduction catalyst, the optional use of a solvent vent valve to extend the lifetime of the catalyst, and the use of scrubbers to remove undesirable constituents from the reaction product stream. The major difference between these detectors is the method used for detecting the NH_3 produced.

Ammonia is detected in the MCD (available from Dohrmann-Envirotech, Santa Clara, Calif.) with a four-electrode titration cell (Figure 48). The NH_3 is automatically titrated to a constant pH in a slightly acidic Na_2SO_4 solution. Typical cell reactions (Equation 5) are as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (5)$$

$$NH_4^+ + OH \overset{H^+}{\rightleftharpoons} NH_4^+ + H_2O \qquad (14)$$

The decrease in hydrogen ion concentration is detected by the reference/sensor electrodes and replaced according to the reactions below:

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad (15)$$

$$2H_2O + 2e^- \rightleftharpoons 2OH^- + H_2 \qquad (16)$$

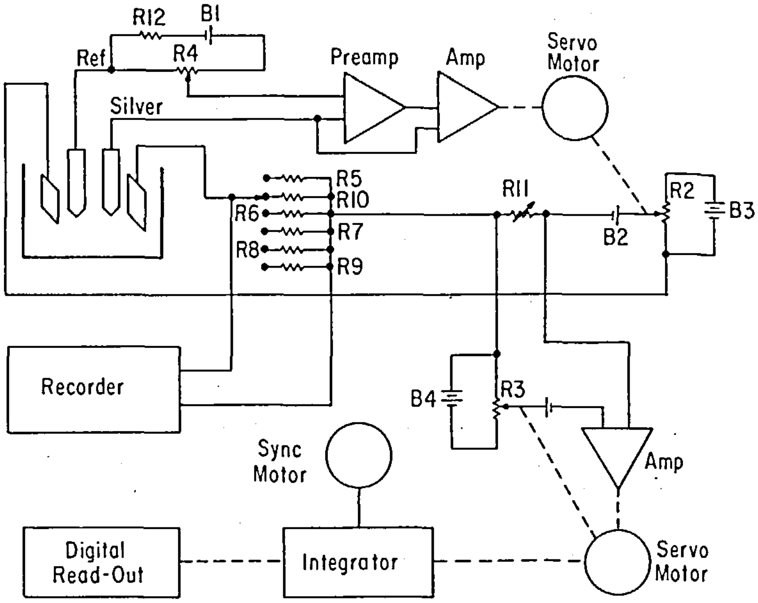

FIGURE 47. Coulometer system. (From David, D. J. *Gas Chromatographic Detectors*, John Wiley & Sons, New York, 1974, 197. With permission.)

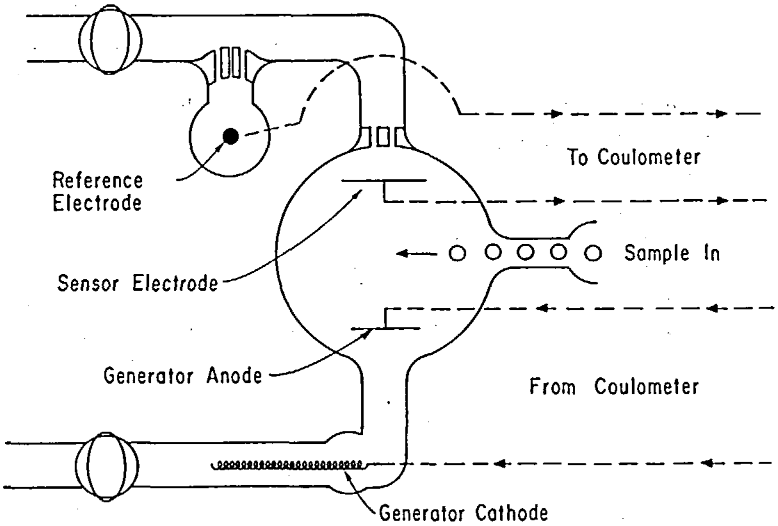

FIGURE 48. Schematic of Coulometric cell. (From Anonymous, Microcoulometric Titrating System, MCTS Data Sheet AI-II, Dohrmann-Envirotech, Mountain View, California. With permission.)

The commercial cell uses 0.04% sodium sulfate as the electrolyte, platinum black as the sensor electrode, lead in saturated lead sulfate as the reference electrode, and platinum as the generator electrode. The action of the microcoulometer is described by Dohrmann-Envirotech[90] as follows. The titrant ion concentration within the reaction zone of the titration cell produces an electrical signal at the surface of the sensor electrode. This signal, coupled with stable signals from the reference electrode and bias supply, is input to the amplifier of the coulometer. A change in titrant ion concentration caused by the sample (NH_3) produces a change in the sensor electrode signals, thereby causing the amplifier to apply power to the generating electrodes. The titrant ion is thus replaced to the original titrant ion concentration. The energy consumed in regenerating the titrant ion is monitored with a precision resistor. This energy consumption is displayed as a voltage-time interval. Integration of this interval reveals the total number of coulombs used in the reaction.

The total number of coulombs used in the reaction can be used to determine the microequivalents of sample entering the titration cell from the Faraday and the equivalent weight of the element of compound analyzed. This is calculated from the error signal, ΔE, according to the equation.

$$\Delta E = (R\tau/nF) \ln (H_1^+) / (H_0^+) \qquad (17)$$

The error signal is caused by the decrease in the hydrogen ion concentration due to NH_3. The potential difference between the reference electrode and the sensor electrode is equal to an external bias which is chosen for maximum performance. Thus, if one assumes quantitative conversion of the nitrogen compound to ammonia, Equation 17 can be used to calculate the quantity of NH_3 produced. Equation 17 simplifies to:

$$\Delta E = 0.06 \log (H_1^+) \qquad (18)$$

2. *Response Characteristics*

The MCD is normally operated with furnace reaction conditions that produce a quantitative conversion of organic nitrogen to ammonia. Detector response is therefore dependent only upon the nitrogen content and quantity of the chromatographed substance. Sensitivity is approximately 3 to 5 ng of nitrogen, injected directly into the furnace. Linearity is three orders of magnitude. Selectivity is generally very high, but depends upon the condition of the scrubber and catalyst. Selectivity for nitrogen over hydrocarbons is normally 10^6. Selectivity for nitrogen over other elements such as halogen and sulfur is at least 10^4.

Since the detector output signal is dependent upon the change in hydrogen ion concentration, any substance that can change this concentration will produce a detector response. Thus, sulfur- and halogen-containing compounds are potential interferences, because they are converted to the acids H_2S and HX. Surprisingly, water can also produce a response. This is caused by the formation of carbon dioxide from the water-gas reaction, according to Equation 19.

$$2H_2O + C \rightleftharpoons CO_2 + 2\,H_2 \qquad (19)$$

Absorption methods must therefore be used for specific detection.[86,91] Potassium carbonate is recommended by Dohrmann[90] when a nickel catalyst is used. Magnesium oxide can also be used for the conversion of nitrogen compounds to NH_3, and has the benefit of irreversibly absorbing H_2S and HCl below 480°C. Other materials, such as aluminum oxide and silica gel, which are commonly used as scrubbers for the detection of other elements, are of little use in the nitrogen mode of operation.

The analysis of nitrogen compounds by microcoulometry is generally quite complicated due to the necessity of converting the compound(s) of interest into NH_3 with a reactive catalyst such as Ni or MgO. The catalytic properties of the catalyst change with time, being poisoned by condensed aromatics and sulfur compounds. The presence of acidic substances on the catalyst and reaction product stream cause peak tailing that degrades chromatographic performance. Little research has been done on improving the nitrogen performance of the MCD in recent years, and the peak tailing problem has thus received little attention. Techniques used to reduce peak tailing in the detection of nitrogen compounds with the ECD, such as specially prepared catalysts,[66] the addition of N_2 to the reaction gas,[73] and the use of ultra-pure gases,[73] should help this problem. The microcoulometric detector cell, however, does have a relatively long response time constant[88] (2 to 5 sec),[92] and some peak broadening will be present.

C. Applications

Of the available nitrogen-selective detectors, the electrochemical detectors exhibit the highest total selectivity and uniformity of response to nitrogen-containing compounds. These detectors, particularly the ECD, have greatly facilitated residue analysis of nitrogen pesticides for many years.[93] Recent applications[77,79,94] of the ECD have also facilitated the qualitative and quantitative analysis of nitrogen-containing drugs.

Sensitivity of the Coulson ECD to a large number of organonitrogen pesticides has been reported by Laski and Watts.[95] Cochrane and Wilson[96] compared the Coulson and electron capture detectors for the analysis of a wide variety of nitrogen-containing herbicides using several stationary phases. The Coulson detector has also been compared to the AFID[97] for the analysis of a variety of nitrogen compounds. The selectivity of the ECD to nitrogen over carbon, chlorine, and sulfur was investigated by Coulson[98] and O'Donnell.[99] In general, these authors have demonstrated that the ECD has sufficient sensitivity for pesticide residue analysis and greater selectivity for nitrogen than other detectors such as the alkali flame, but has less sensitivity than that of the electron capture detector.

Although the high selectivity of electrochemical detectors is an important attribute, versatility of operation may prove to be their most important quality. For example, the Hall ECD can be used for the selective determination of either halogen- , sulfur- , nitrogen- , or ester-containing compounds. It can also be used for the determination of certain compounds in the presence of other compounds that contain the same element. Dolan and Hall[39] described the selective detection of aliphatic halogen compounds in the presence of aromatic halogen compounds. The selective detection of nitrosamines in the presence of other nitrogen-containing compounds was reported by Rhoades and Johnson.[80] The selective detection of sulfates in the presence of other sulfur-containing compounds should also be possible, though it has not been reported.

The ECD has been shown to be a very powerful and unique analytical tool for the analysis of nitrosamines.[80,100] It is the only detector, with the exception of the thermal energy analyzer, that can be used for the specific detection of these compounds in the presence of other nitrogen-containing compounds. It has, however, not received the attention that one would expect in view of the increasing concern for these compounds as widespread potential environmental carcinogens[101] and the unique capability of this relatively inexpensive detector. The popularity and greater sensitivity of the flameless alkali sensitized detector and certain operational problems associated with early versions of the ECD have probably slowed the application of this detector for nitrosamine analysis.

The analysis of a number of nitrosamines in a variety of foods by ECD was studied in detail by Essigmann and Issenbery.[100] The Coulson detector proved adequate for the analysis of these compounds to approximately 2ng/g without interference. Fine et al.[102] have compared the Coulson ECD and thermal energy analyzer for the analysis of several nitrosamines in bacon and fish meal and report greater sensitivity and specificity for the thermal energy analyzer under the experimental conditions employed.

Application of the improved Hall ECD would be expected to provide a seven- to tenfold increase in sensitivity over that of the Coulson detector.[67,76] Also, optimization of pyrolysis conditions should improve sensitivity and selectivity for nitrosamine analysis (influence of pyrolysis conditions on this analysis has not been reported). Detector

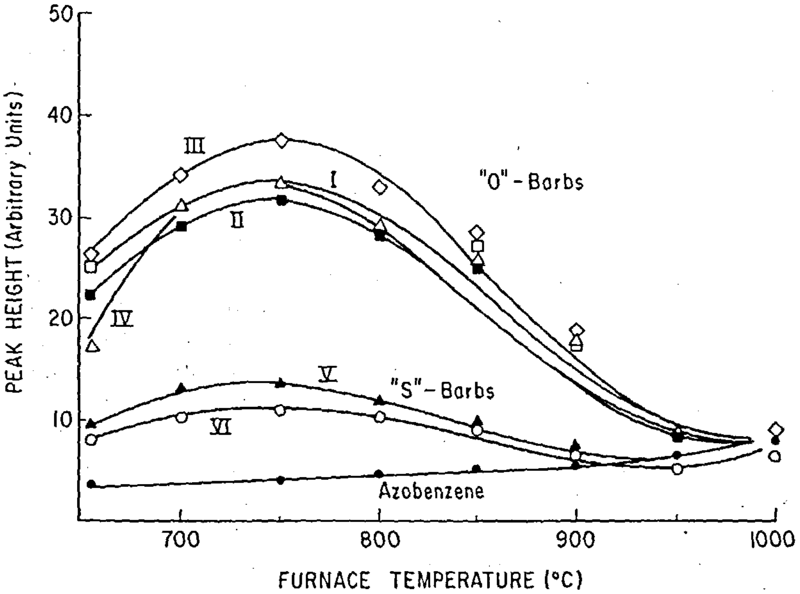

FIGURE 49. Furnace temperature profiles for barbiturates and azobenzene. Compounds: I, Butabarbital; II. amobarbital; III, pentobarbital; IV, secobarbital; V, thiopental; VI, thiamylal. (From Pape, B. E., Rodgers, D. H., and Flynn, T.C., *J. Chromatogr.*, 134, 1 (1977). With permission.)

response of the Hall ECD vs. furnace temperature was presented by Pape et al.[77] for the qualitative differentiation of certain drug classes. As shown in Figure 49, considerably greater sensitivity is displayed for oxygen analogs of barbiturates than the corresponding sulfur analogs. These compounds, however, display similar response-temperature profiles. Azobenzene exhibits little response in the pyrolytic mode and does not exhibit a significant response-temperature relationship. This pyrolytic selectivity has been used by Pape[103] to distinguish barbiturates from other drugs commonly encountered in biological extracts. Chromatograms of a variety of pesticides and drugs obtained with the Hall ECD are shown in Figures 50 through 53. Peak tailing, which can be a problem, was minimized as previously discussed. As shown in these figures, there is little peak spreading that can be attributed to the detector, particularly when one recognizes the difficulty of chromatographing compounds such as free barbiturates and carbamates.

IV. PHOTOEMISSION DETECTORS

A. Microwave Plasma Discharge Detectors

1. Background and Theory of Operation

The application of a microwave sustained plasma-emission spectrometer as a gas chromatograph detector was first reported by McCormack et al.[104] These authors used a 2450-Mc electrodeless discharge, which produces greater emission intensities than alternating and direct current glow discharges. This detector was further developed by Bache and Lisk[105] and McLean et al.[106] Bache and Lisk found that a helium plasma at reduced pressure was effective for producing strong emissions from the free elements produced by the plasma. McLean et al. reported that all the elements normally found in organic compounds could be analyzed with equipment similar to that used by Bache and Lisk. Characteristic atomic emission lines were found for C, H, D, O, N, F, Cl, Br, I, S, and P.

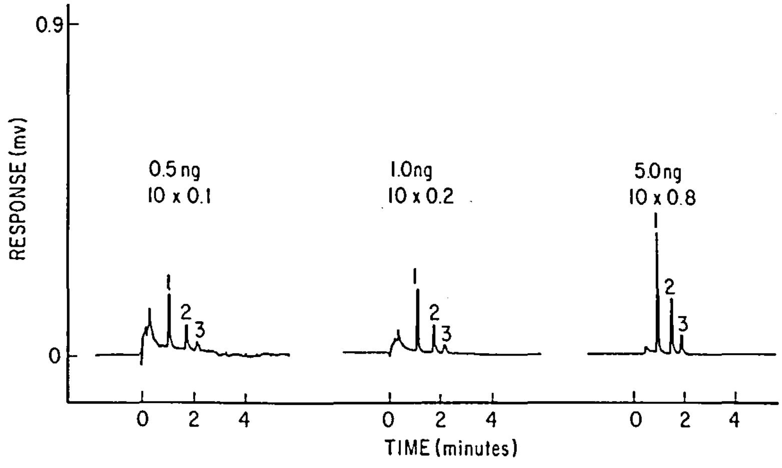

FIGURE 50. Chromatograms of low levels of trifluralin (1), IPC (2), and PCNB (3).

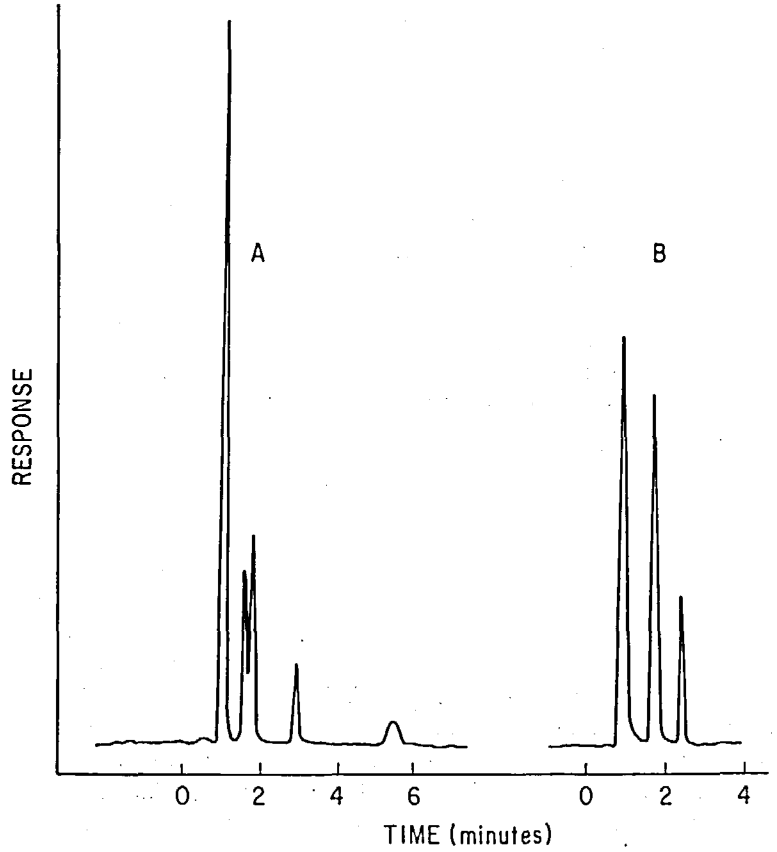

FIGURE 51. Chromatograms showing separation and peak symmetry obtained with 5% OV-101 on Chromosorb® 750 (100/120). A. A 20-ng alkaloid mixture chromatographed at 235°C. Peaks in order of elution are methapyrilene, methadone, cocaine, codeine, and heroin. Sensitivity: 20 μmho/mv. B. A 20-ng phenothiazine mixture chromatographed at 265°C. Peaks in order of elution are phenothiazine, promazine, and chlorpromazine. Sensitivity: 10 μmho/mv. (From Risk, C. A. and Hall, R. C., *J. Chromatogr. Sci.*, 15, 156 (1977). With permission.)

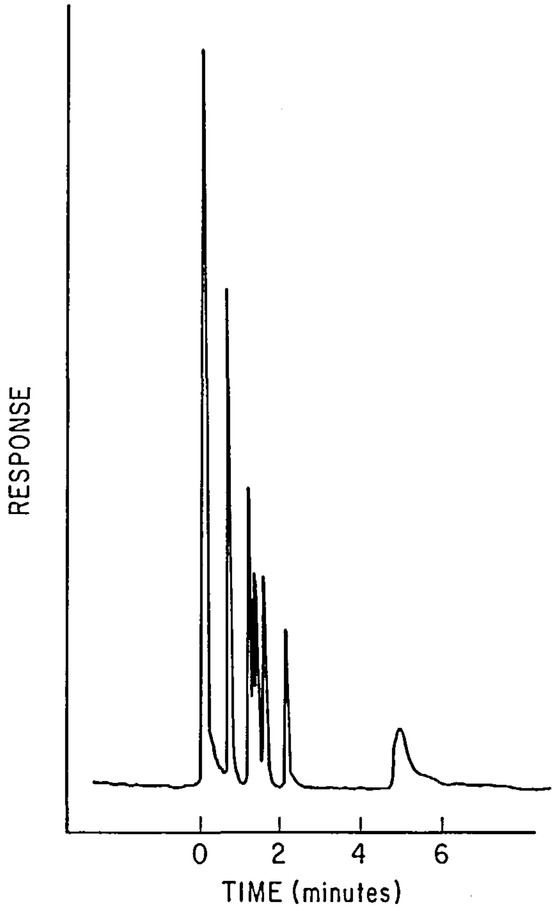

FIGURE 52. Chromatograms showing separation of barbiturates and glutethimide with 3 % SP-2250 on deactiivated Chromosorb® 750. Peaks in order of elutin: solvent, barbital, amobarbital, pentobarbital, secobarbital, glutethimide, and phenobarbital. Sample: A, 10 ng of each component in 4 μl of 1:25 ethanol-hexane. (From Hall, R. C. and Risk, C. A., *J. Chromatogr. Sci.*, 13, 519 (1975). With permission.)

A commercial instrument similar to that described by McCormack et al. is available from Applied Research Laboratories, Ltd, Luton, England. A block diagram of this system is shown in Figure 54. Atomic emissions created by the helium plasma are monitored using a direct reading optical-emission spectrometer with a line grating. These emissions are isolated by secondary slits located on the Rowland circle of the grating. Slit positions are chosen so as to isolate the most intense lines in the first order spectra of the elements. Photomultiplier tubes with appropriate filters are used to measure the light intensity through each slit. In this manner, up to 12 elements can be simultaneously determined.

High-purity helium is used as the carrier gas, and the column effluent is passed directly to the quartz plasma tube or divided between a conventional detector such as an FID. A quarter wave, microwave cavity surrounds the plasma tube. The plasma is initiated by means of a Tesla coil and afterwards is self-sustaining. The microwave cavity power is usually maintained at 150 W.

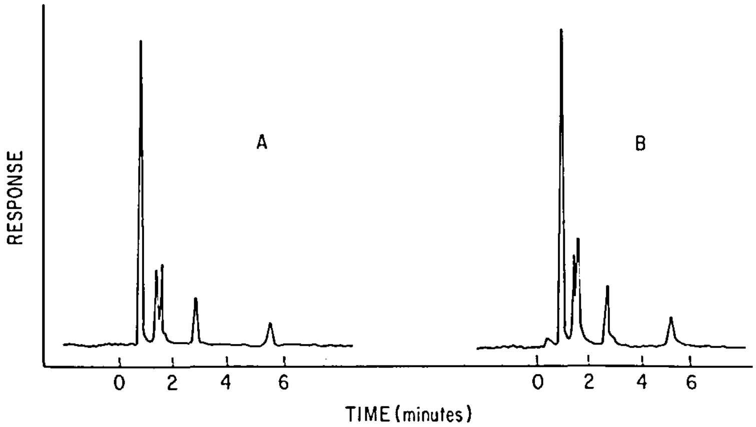

FIGURE 53. Chromatograms of alkaloid mixture. A: Chromatogram obtained using a nickel catalyst in a quartz reaction tube. B: Chromatogram obtained using a nickel reaction tube. (From Risk, C. A. and Hall, R. C., *J. Chromatogr. Sci.*, 15, 156 (1977). With permission.)

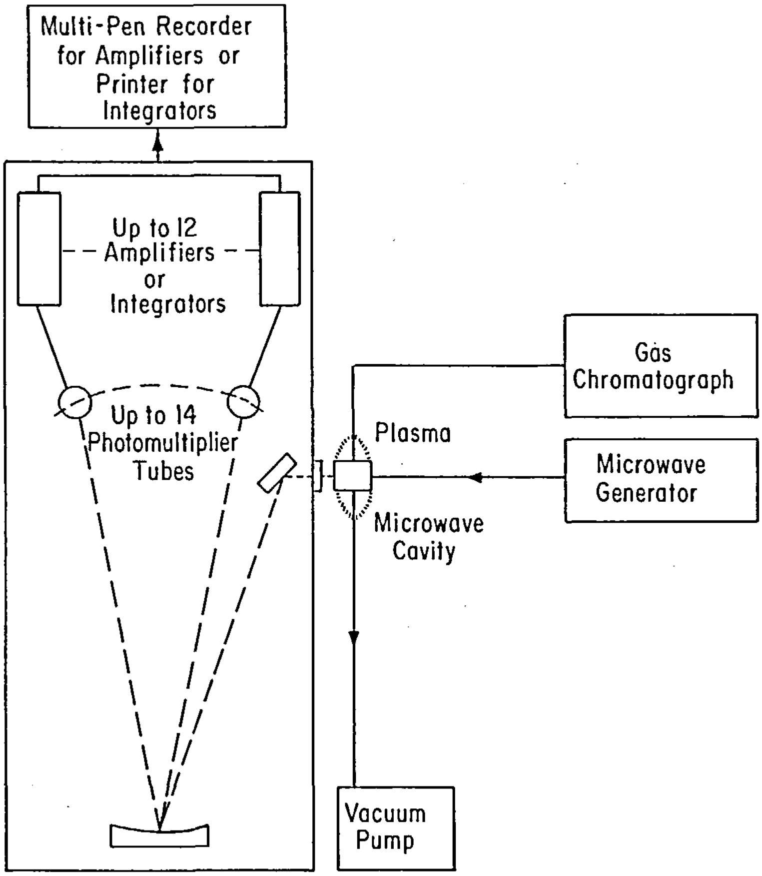

FIGURE 54. Schematic of microwave plasma detector. (Courtesy of J. S. Hobbs, Applied Chromatography Systems Ltd., Luton, England.)

According to Hobbs,[107] the signal output of the MPD is described by Equation 20:

$$I_{total} = I_o + I_e + I_{c'} \qquad (20)$$

where I_{total} is the total observed emission intensity, I_o is the background plasma emission, I_e is the atomic emission from a particular element, and I_c^1 is the transient background due to the passage of carbon through the plasma. The plasma background, I_o, is considered to be a combination of three factors as described by Equation 21:

$$I_o = I_d + I_s + (I_e)_o \qquad (21)$$

where I_d is the dark current of the phototube, I_s is the steady plasma continuum and stray light, and $(I_e)_o$ is the atomic emission due to contaminants in the plasma gas.

The detector signal produced when an organic substance enters the plasma is primarily due to atomic emissions (I_e) since I_0 remains constant during operation. There is, however, also a weak signal at all wavelengths due to the presence of carbon (I_c).[107] This signal is linearly proportional to the carbon present and is removed in the commercial instrument by a feedback system between the carbon emission amplifier and the other amplifiers.

2. Response Characteristics

Due to the lack of information on the response characteristics of the MPD to nitrogen compounds, response characteristics to other elements (also limited) will be used as a basis for this discussion. Response characteristics, such as linear dynamic range, specificity, sensitivity, and ease of use, are dependent upon operating conditions and are therefore not necessarily fixed values.

The linear dynamic range is subject to two major factors: the lower limit of detection and plasma overload. The lower limit of detection depends upon the particular element analyzed, the presence of interfering adjacent emission lines from other elements, and operational parameters, such as slit width, type and purity of carrier gas, and pressure of the emission cavity. In general, linearity is approximately four orders of magnitude.[104,108]

The type of carrier gas and the pressure of the emission cavity have a significant influence on the intensity and type of spectra produced. McCormack et al.[104] found that band spectra rather than line spectra are produced from sulfur, bromine, and chlorine when argon is used as the carrier gas. Bache and Lisk,[105] however, used helium as the carrier gas and found line spectra of greater intensity than that exhibited by the band spectra with argon. An optimum carrier composition of 15% argon in helium was reported by Moye.[109] Detector signal-to-noise ratio, selectivity, and stability were improved by this composition, based on response to certain phosphorus compounds. The dependence of detector response on cavity pressure for phosphorus is shown in Figure 55. Sensitivity appears to be the highest at approximately 200 mmHg, and is approximately an order of magnitude greater than that at ambient pressure.

Detector response is also dependent upon the microwave power. The optimum power setting depends upon the particular compound and the discharge tube geometry.[110] Higher carrier flows require higher power settings. At a given power, response decreases as the volume of the reaction tube or the thickness of the wall is increased. The loss of response with tube wall thickness was attributed to absorption of the emitted radiation by the wall.[110]

Selectivity is influenced by the same general factors as in any emission detector (i.e., flame photometric detector). As discussed by Krejci and Dressler,[111] selectivity is influenced by overlapping of the spectra, by source background, monochromator disper-

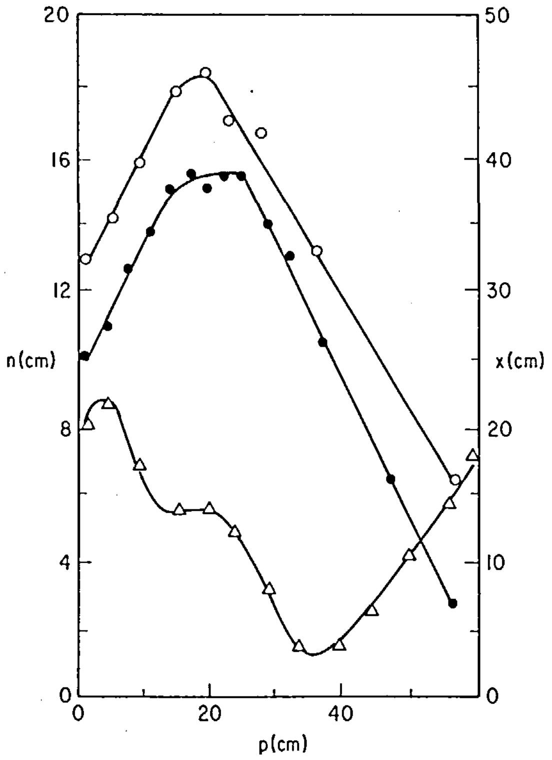

FIGURE 55. Effect of pressure on the response and baseline of emission spectrometer. h, the peak height; x, baseline shift; p, pressure; O, Dimethoate; ●, Thimet; Δ, baseline. (From Krejci, M. and Dressler, M., *Chromatogr. Rev.*, Vol. 13 (1970). With permission.)

sion, and slit width. The selectivity for iodine compounds has been found to be three orders of magnitude higher with a slit width of 50 μm when the emission is viewed at 2062 A.[104] Response is lower with the lower slit widths. Response and selectivity are also dependent upon the wave length chosen for viewing, which is not necessarily the same for all compounds that contain a given element.[112]

Those interested in other aspects of the microwave emission detector should consult papers by Talmi,[113] Talmi and Mesmer,[114] Kustom and Fuja,[115] Talmi and Andren,[116] Serravallo and Risby,[117] Dagnall et al.,[118] Kawaguchi et al.,[119] McLean et al.,[120] Dagnall et al.,[121] Grossman et al.,[122] and Freeman and Wentworth.[123] Considerable information is given in these papers on detector design, determination of atomic ratios, and determination of organometallics.

B. Chemiluminescence Detectors

1. Background and Theory of Operation

The detection of organic nitrogen by chemiluminescence was described by Parks in 1976,[124] who utilized techniques developed for the analysis of NO_x[125,126] and microcombustion techniques developed for the analysis of sulfur.[127] In this detector, nitrogen compounds are oxidized in a quartz tube in the presence of oxygen at 900 to 1000°C. The nitric oxide thus formed is reacted with ozone to produce nitrogen dioxide in the excited state, according to Equations 22,23, and 24.

$$\text{R-N} + O_2 \longrightarrow NO + CO_2 + H_2O \qquad (22)$$

$$\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2}^* + \mathrm{O_2} \qquad (23)$$

$$\mathrm{NO_2}^* \longrightarrow \mathrm{NO_2} + h\nu \qquad (24)$$

The light emitted is a broad-band emission in the far red from 650 to 900 nm. The intensity of the emission is directly proportional to the quantity of nitrogen in the sample, which is monitored with a photomultiplier tube. A block diagram of the commercial version of this detector, available from Antek Instruments, Inc. (Houston) and Dohrmann-Envirotech (Santa Clara, Calif.) is displayed in Figure 56. Water vapor can interfere and a flow-through drier is used. This detector has received little characterization and other interferences have not been reported.

2. Response Characteristics

There has been little information published on this detector. Selectivity is reported as high, but specific values have not been quoted. Sensitivity is given by the manufacturer to be 10^{-8}g nitrogen. The information that is available has been directed towards characterizing the detector as a total nitrogen analyzer and not as a gas chromatograph detector.

Possible interferences in the detection of NO by chemiluminescence has been discussed by Fontijn et al.[125] These authors found that the detection of NO at 10 ppb was not influenced by 650 ppm CO_2, 300 ppm CO, 5 ppm C_2H_4, and 25 ppm of SO_2. Since oxidative pyrolysis conditions are used in this detector, these substances can be formed from organic compounds and interference therefore may be encountered.

The influence of operating parameters for total nitrogen determination has been investigated by Drushel.[128] High flow rates of helium carrier gas and oxygen reaction gas reduced the chemiluminescent response. A tenfold increase in the oxygen flow rate from 100 to 1000 cm^3/min resulted in a linear decrease of over 50% in the response. In general, response was found to increase as the combustion temperature was increased over the temperature range 650 to 1020°C. Other parameters, such as the oxygen flow to the ozone generator, were not particularly important. It should be noted that these observations were made using direct injections of aqueous or organic solutions of nitrogen compounds, and therefore may not hold for nitrogen compounds free of large quantities of solvent.

C. Thermal Energy Analyzers

1. Background

A detection system similar to the Antek nitrogen analyzer was described by Fine et al.[129,130] for the specific detection of nitrosamines. This detector has been labeled the thermal energy analyzer (TEA) and can be used for total analyses or interfaced to a gas chromatograph for the specific detection of individual nitrosamines.[131] In this detector, nitrosamines are catalytically pyrolyzed to produce nitric oxide, which is detected by the chemiluminescent reaction with ozone. The various components of the detector are shown in the block diagram of Figure 57.

The pyrolysis products are swept through a capillary restriction into a reaction chamber evacuated with a 140-l/min rotary vacuum pump. Ozone is introduced into the evacuated chamber where it reacts with NO to produce light, according to Equations 22 through 24. The intensity of the emission is detected by means of a S-20 photomultiplier tube using a red optical filter. Photomultiplier noise is minimized by operating the tube at −20°C.

2. Response Characteristics

The response characteristics of the TEA have been studied in detail by Fine et al.[131]

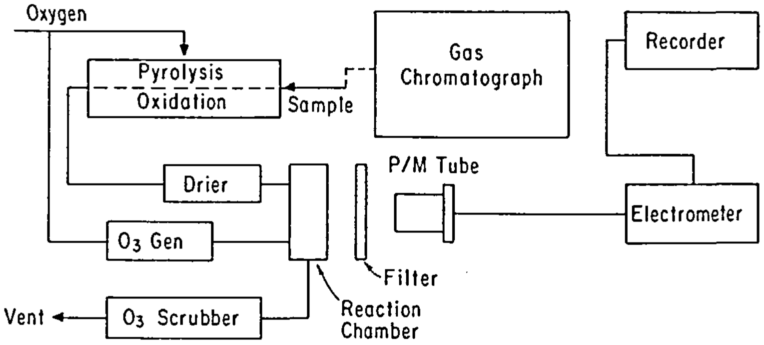

FIGURE 56. Block diagram of the nitrogen chemiluminescence detector. (Courtesy of Antek Instruments, Inc., Houston.)

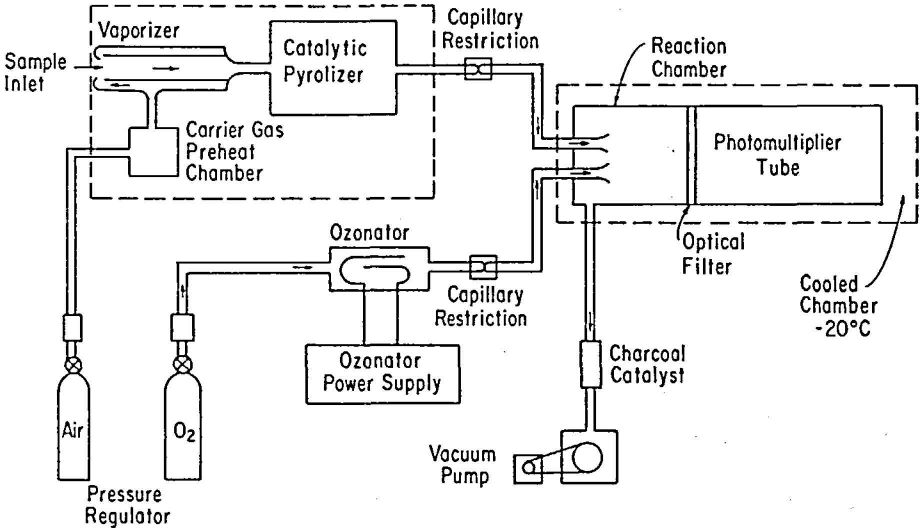

FIGURE 57. Schematic of the thermal energy analyzer (Reprinted with permission from Fine, D. H., Rufel, F., Lieb, D., and Rounbehler, D. P., *Anal. Chem.*, 47, 1188 (1975). Copyright by the American Chemical Society.)

The detector was found to be very selective for nitrosamines. Most organic compounds gave no interference; the only interference found was from organic and inorganic nitrites and a few other compounds, which are shown in Table 7. Detector response was reported to be linear over six orders of magnitude. Sensitivity, although not specifically stated, can be calculated from these authors' work to be at least 10^{-10} g of nitrosamine. The response on a mole basis of nitrosyl group was essentially the same for a wide variety of nitrosamines. The high specificity of this detector is due to the relatively low pyrolysis temperature (275 to 300°C) and the selectivity of the chemiluminescent reaction for nitric oxide. It should be possible to use this detector as a general nitrogen detector by oxidatively pyrolyzing the sample at higher temperatures, as used in the chemiluminescence nitrogen detector manufactured by Antek Instruments, Inc.

D. Applications

Photoemission detectors are relatively new and have received only limited applications interest. The MPD is particularly useful for the on-the-fly determination of ele-

TABLE 7

Mole Basis Response Ratio for Those Compounds Which Give a Detectible Response with the TEA

Compound	Response ratio (RR)
N-Nitroso compounds	1.0
2,2',4,4',6,6'-hexanitrodiphenylamine	1.4
Isopentylnitrite	1.0
d,z-Cyclohexylaminenitrite	1.0
Pentylnitrite	1.0
Sodium Nitrite (in H_2O)	1.0
Sodium nitrate (in H_2O)	≃ 1.0 (very slow response lasting from hours to days)
Nitric acid	≃1.0 (very slow response lasting from hours to days)
Dimethyl sulfoxide	0.03
Hydrazine (95%)	0.03
5-Nitrouracil	0.017
p-Nitrosodiphenylamine	0.0050
3-Nitrophtalidimide	0.0030
Nitromethane	0.0018
Ammonium hydroxide	0.0016
Dimethylglyoxime	0.0010
Dimethylamine hydrochloride	0.0009
Diphenyl carbazone	0.0007
Aniline	0.0003
2-Nitroso-1-naphthol	0.0002

Reprinted with permission from Fine, D., Rufeh, F., Lieb, D., and Rounbehler, D. P., *Anal. Chem.*, 47, 1188 (1975). Copyright by the American Chemical Society.

ment ratios and simultaneous multiple-element analysis of complex mixtures.[107] The determination of nitrogen requires oxygen to be used as a scavenge gas, whereas the determination of oxygen requires the use of nitrogen scavenge gas. Thus, these two elements cannot be easily determined at the same time. The relatively low sensitivity of this system (1 to 10 ng/sec of a given element) requires samples to be concentrated for trace analysis. The chemiluminescence nitrogen detector has been primarily applied as a total nitrogen analyzer. It can be easily interfaced to a gas chromatograph and used as a very selective nitrogen detector. The sensitivity of this detector is potentially high based on that obtained with the TEA, which is similar.

Perhaps the most important application of the photoemission detector is the specific analysis of nitrosamines using the TEA, which is the only detector available that is nitrosamine-specific. Although the ECD can be used for the selective detection of nitrosamines, it will also respond to other amines.[80] The detection of a variety of nitrosamines is illustrated in Figure 58. The use of large injections allows concentrations as low as 500 pg/ml to be detected.[132] These levels are below the no-effect level in terms of potential carcinogenic activity[132] and therefore sufficient for most analyses.

The TEA has been compared to the Coulson ECD, gas chromatography-mass spectroscopy, and thin-layer chromatography for the analysis of volatile N-nitrosamines in foodstuffs by Fine et al.[102] Although the Coulson ECD has been the detector of choice for the analysis of nitrosamines,[133] the TEA was found superior by Fine and co-workers to the Coulson detector and other techniques. As displayed in Figure 59, chromatograms obtained by GC-TEA showed no extraneous peaks. TEA analysis of dirty and cleaned-up samples produced similar results, as well as analysis of dilute and

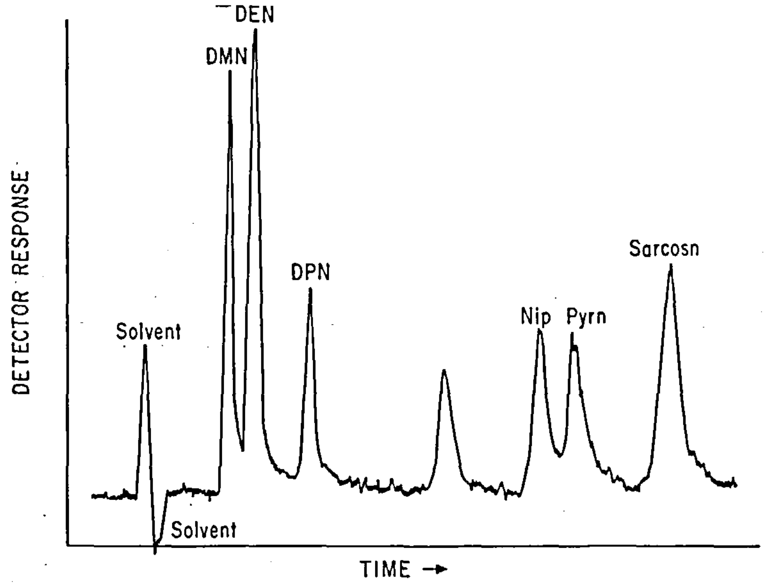

FIGURE 58. Chromatogram of 5μl of DCM solution containing 1 μg/ml of each of the following N-nitroso compounds: DMM, DEN, DPN, DBN, NIP, PYRN, and SARCOSN. (From Fine, D. H. and Rounbehler, D. P., *J. Chromatogr.*, 109, 271 (1975). With permission.)

concentrated samples. Several extraneous peaks were observed in the chromatograms of the same samples analyzed with the Coulson detector. Slightly higher nitrosamine values were usually obtained with the Coulson detector than those obtained by TEA. This was attributed to interfering co-eluting compounds or a lack of linear response at extremely low levels for the pyrolytic mode of the Coulson detector.

The TEA is truly unique in sensitivity and specificity to nitrosamines. It is a relatively new technique that has not been thoroughly characterized and therefore should be used in conjunction with other methods to prevent erroneous results. The N-P and ECD should provide adequate confirmation for this new device, particularly when analyses are performed on multiple columns.

V. INFRARED DETECTORS

Although infrared spectroscopy is one of the fundamental tools of qualitative organic analysis and the problems of interfacing to gas chromatographs have been solved for many years,[134-137] infrared techniques have made limited contributions to specific detection of chromatographic eluents. The main reason has been low detection sensitivity associated with infrared absorption techniques. Conventional spectrophotometers used at a fixed wavelength usually have a sensitivity of 0.01 μl.[138] Determination of a compound spectrum requires at least ten times that amount. Application of Fourier transform techniques greatly increases sensitivity. Commercial instruments, such as that available from Digilab, Inc. (Cambridge, Mass.) can obtain a complete spectrum on quantities of approximately 100 ng. These instruments are very expensive. They are of the same approximate complexity as a mass spectrometer and should not be considered as a gas chromatograph detector. Instead, the chromatograph is a sample introduction system for the spectrophotometer.

A major advance in the development of infrared detectors for gas chromatography was recently reported by Hausdorff.[140] He developed a nondispersive photometer that

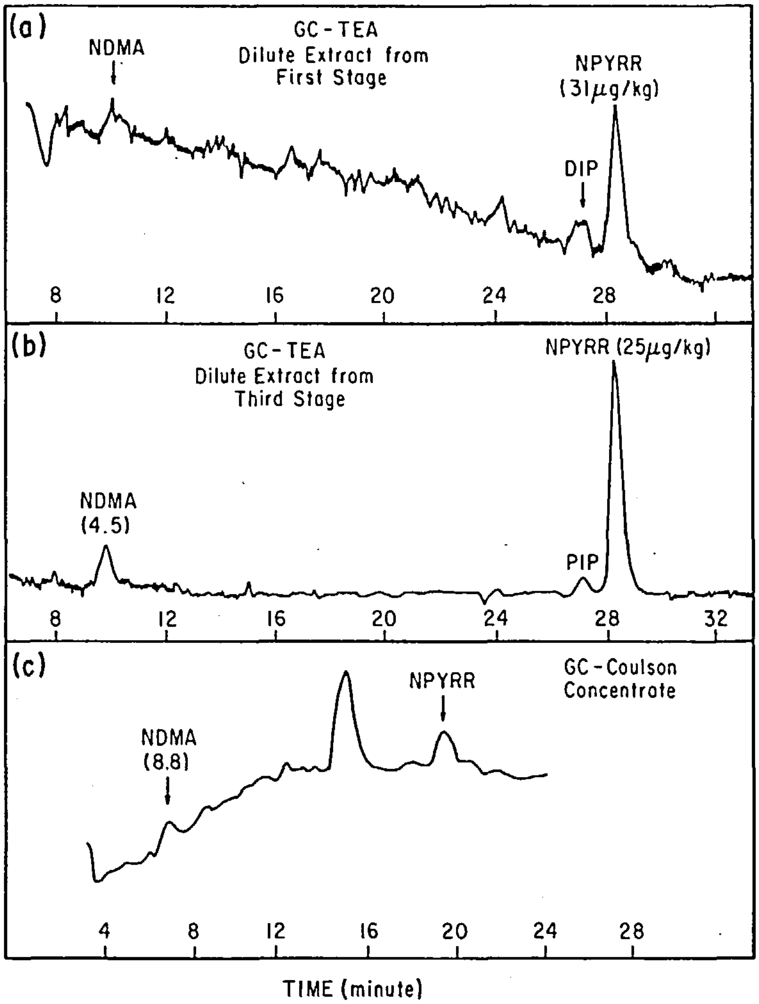

FIGURE 59. Chromatograms from clean-up of a cooked bacon fat sample. (a) The GC- TEA chromatogram of 20 µl of the aqueous distillate from the first stage, immediately after vacuum distillation. Range on TEA × 2. (b) The GC-TEA chromatogram of 20 µl of methylene chloride extract from the third stage, before concentration. Range on TEA × 4. The GC-Coulson chromatogram of 4.1 µl of the final methylene chloride concentrate. (Reprinted with permission from Fine, D. H., Rounbehler, D. P., and Sen, N. P., *J. Agric. Food Chem.*, 24, 980 (1976). Copyright by the American Chemical Society.)

had a noise of only 0.0001 absorbance units with a 0.3-sec response time. The detector employed a 1 × 10 mm heated flow cell of only 7-µl volume. Filters were used to selectively sensitize the detector to specific compound groups, such as aliphatics, alkenes, alkynes, aromatics, esters, ketones, alcohols etc. Although the detector could be operated with several different arrangements, the greatest short- and long-term stability was achieved with double-beam operation through the same cell. A reference wavelength of 4 µm was found adequate for most samples. The analytical and reference wavelengths were alternated on a thermocouple detector. The thermocouple output was preamplified and demodulated by phase-sensitive rectification with synchronization from a signal generated by the beam-switcher used to alternate the analytical and reference beams through the cell.

The detector was compatible with capillary columns and displayed excellent performance. Sensitivity for aliphatic compounds was about two orders of magnitude less than that of the FID. Sensitivity was approximately ten times better for compounds that have high infrared extinction coefficients, such as carbonyls and alcohols. Selectivity of the detector was controlled by the band width of the filter. Thus, it was possible to use relatively wide band filters to determine group functionality and then switch to narrower band filters to determine functional group type (i.e., primary, secondary, or tertiary alcohols).

VI. CONCLUSION

The flameless alkali sensitized detector and the ECD have excellent response characteristics for the general detection of nitrogen-containing compounds. Choosing between these detectors is not a simple matter since they have both advantages and disadvantages. The FASD usually exhibits an order of magnitude of greater sensitivity than the ECD. Although it is very sensitive, it is not totally selective for nitrogen. It also responds to phosphorus, and the phosphorus response is normally about ten times greater than the nitrogen response. The response depends upon the condition of the source and may require frequent adjustments of the source temperature to minimize source aging effects. Response of this detector is dependent upon the structure of the compound and is therefore difficult to predict.

In contrast, the response of the ECD is specific for nitrogen, and the response can be easily predicted since it depends upon only the nitrogen content of the compound. The response will exhibit some change with time as the catalyst and ion exchange resin become exhausted. However, this change is not as rapid as that exhibited by the FASD, and response is normally stable for a period of several weeks to several months. A serious drawback of the ECD is the peak broadening produced by the catalyst. This probably precludes the use of capillary columns with this detector in the catalytic reductive mode of operation.

The TEA is unmatched for the selective and sensitive detection of nitrosamines. Although the detector can only be used for nitrosamine analysis, the severity of nitrosamine contamination justifies the limited capability of the TEA. The TEA will respond to a few other compounds, and should therefore be used with an ancillary method of conformation.

Other photoemission detectors do not have the response characteristics to warrant their use as general purpose nitrogen detectors. The chemiluminescence nitrogen detector has been developed primarily as a total nitrogen analyzer and not as a gas chromatograph detector. However, as demonstrated by the TEA, chemiluminescence detection of nitrogen is a sensitive technique that has considerable potential for further development as a chromatograph detector.

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