# Optimizing Nitrogen–Phosphorus Detector Gas Chromatography for Pesticide Analysis

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The goal of this work was to improve the performance of the nitrogen–phosphorus detector gas chromatograph (NPD-GC) for multiresidue pesticide analysis. Severe tailing of phosphorus pesticides was found to be associated with the NPD (or thermionic ionization source) and not the column as demonstrated by matched separations using a flame photometric detector (FPD). The "source tailing" of phosphorus compounds in NPD increases as the source ages and can be reduced or eliminated by recoating the source with rubidium and alumina powder. Response to phosphorus pesticides increased 2–20-fold or more by rinsing the capillary column with organic solvents, but response factors for nitrogen-containing pesticides were unchanged by this treatment. Column tailing of polar pesticides (triadimefon, carboxin, norflurazon, bromacil, hexazinone, fenarimol, fluridone, and simazine) also was reduced by column cleaning. The fewest coelutions (for pesticides analyzed by U.S. EPA Method 507) were found with a methyl silicone capillary column.

**Keywords:** *Nitrogen–phosphorus detector; pesticide analysis; capillary gas chromatography*

## INTRODUCTION

The nitrogen–phosphorus detector (NPD) is widely used in the analysis of pesticides because of its selectivity and sensitivity. Element specificity to nitrogen and phosphorus also makes the detector useful in determination of pharmaceuticals, illicit drugs, petroleum fractions, and environmental pollutants. A thorough review of the development and features of the NPD has recently been published by Patterson (1992).

A modern NPD detector was first developed by Kolb and Bischoff in 1974 (Kolb and Bischoff, 1974). Kolb and Bischoff's detector differed from the earlier alkali flame ionization detector (AFID) in three ways: (i) the alkali metal was in a nonvolatile form, rubidium silicate ($Rb_2O{\cdot}SiO_2$) deposited in a glass bead; (ii) a platinum wire heated the bead rather than a flame; and (iii) the flow rate of hydrogen was very low (2–6 mL/min), insufficient to support combustion. The new NPD design was characterized by lower background current (picoamps vs nanoamps), high sensitivity and selectivity, and improved stability relative to AFID.

The NPD is classified as a thermionic ionization detector of which there are several types or operating modes (not just nitrogen–phosphorus). By definition, thermionic means emitting electrical current from a heated solid surface. Because the active element may no longer resemble a bead, the term thermionic ionization "source" is now preferred.

The operating principle of the NPD is not entirely established. Surrounding the functioning NPD source is a chemically reactive boundary layer (or plasma) which exists only as long as heat (600–800 °C) and hydrogen are supplied. In the boundary layer analytes are believed to decompose to electronegative products ($NO_2$, CN, and $PO_2$) which then generate negative ions ($CN^-$, $PO^-$, $PO_2^-$, and $PO_3^-$) through a process that remains obscure. Two theories have been offered to explain ionization: a gas phase process (Kolb and Bischoff, 1974; Kolb et al., 1977) and a surface ionization mechanism (Patterson, 1978; Olah et al., 1979). Negative surface ionization is consistent with the finding that the surface electronic "work function", the amount of energy required to remove an electron from the surface, is critical, whereas the source elemental composition is not (Fujii and Arimoto, 1985).

In spite of their potential, performance and reliability problems have deterred the routine use of the NPD-GC in some pesticide residue laboratories (U.S. Department of Health and Human Services, 1994). The flame photometric detector is preferable for phosphorus pesticide analysis even though the NPD response to P-compounds is 2–10 times greater than that to N compounds. Nitrogen specificity, however, is not found in any other widely available GC detector, and this feature is very important in pesticide residue analysis.

Our laboratory uses NPD-GC for monitoring pesticides in water supplies. Under the Safe Drinking Water Act (SDWA) (Friedman, 1990) public drinking water systems must routinely monitor their water for alachlor, atrazine, butachlor, metolachlor, metribuzin, and simazine. Maximum Contaminant Levels (MCLs) or Action Levels (ALs) have been established for additional pesticides by California state law (California Department of Health Services, 1990). More than one analytical method is approved for each pesticide in compliance monitoring including both GC–MS (U.S. EPA Method 525.2) and GC methods (U.S. EPA Methods 507 and 505).

The NPD-GC procedure, U.S. EPA Method 507 (M507) (U.S. Environmental Protection Agency, 1991), is very simple, involving only solvent extraction, extract concentration, and solvent exchange prior to quantitative analysis by GC. A total of ~45 target compounds, internal standards, surrogates, and pesticide decomposition products are screened with detection limits in the low micrograms per liter (parts per billion) range. After tentative identification on the primary capillary column, pesticides are confirmed usually by analysis on a second chromatographic column (GC–MS frequently does not have adequate sensitivity for confirmation).

In practical application M507 has some limitations. As with any NPD procedure, frequent recalibration is recommended because the response characteristics of

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**Table 1. Capillary Columns Used**

| stationary phase | commercial name | film thickness (μm) | dimensions (length × i.d.) | head pressure (psi) |
|---|---|---|---|---|
| methyl silicone | DB-1 | 1.0 | 30 m × 0.32 mm | 10 |
| 5% phenyl, 95% methyl silicone | SPB-5 | 0.25 | 30 m × 0.25 mm | 18 |
| | SPB-5 | 0.25 | 30 m × 0.32 mm | 10 |
| 14% cyanopropylphenyl, 86% methyl silicone | DB-1701 | 0.25 | 60 m × 0.32 mm | 20 |

[a] The recommended isothermal oven temperature limits are 325 °C for the DB-1 and SPB-5 columns and 280 °C for the DB-1701.

the thermionic ionization source change with use (U.S. Department of Health and Human Services, 1994). While not necessarily unique to NPD-GC, 40% of the M507 analytes have been characterized as "problem compounds" due to poor analysis precision (carboxin, disulfoton, ethoprophos, merphos, propyzamide, and terbufos), poor chromatography (disulfoton sulfoxide, fenamiphos, norflurazon, and tricyclazole), sensitivity to instrument contamination (hexazinone and metribuzin), or other factors affecting analysis (Thoma, 1994). Chromatographic tailing also observed in other M507 analytes (fenarimol, fluridone and tebuthiuron) confounds chromatographic resolution, which is a prerequisite for instrument calibration.

The goal of this study was to improve the performance of the NPD-GC in multiresidue pesticide analysis. As a water testing laboratory we focused on pesticides determined in M507, but the findings may be useful in other fields of residue testing as well. The specific objectives were (i) to improve the peak shape, resolution, and response of N and P pesticides from various compound classes and (ii) to identify stationary phases best suited to separation of the M507 analytes.

## EXPERIMENTAL PROCEDURES

**Chemicals.** Individual pesticide standards were obtained from the U.S. EPA (Research Triangle Park, NC) or purchased from Chem Service (West Chester, PA). Naled and simazine were purchased from Ultra Scientific (Kingston, RI), and phorate was obtained from Poly Science Corp. (Niles, IL). Disulfoton and its sulfoxide and sulfone were gifts of Mobay Corp. (Kansas City, MO), and propyzamide was provided by Rohm and Haas, Co. (Springhouse, PA). Pesticide calibration mixtures were purchased from Accustandard (New Haven, CT). Reagent grade methyl *tert*-butyl ether obtained from Spectrum Chemical (Gardena, CA) was used throughout the study.

**Instrumentation.** A Hewlett-Packard 5890 Series II gas chromatograph (Avondale, PA) equipped with an autosampler and both NPD and FPD detectors was used. Chromatography data acquisition and processing were accomplished with a Spectra Physics 4290 digitizer (San Jose, CA) linked to a computer running Spectra Physics Winner software. Detector responses were measured uniformly by peak area. The GC operating conditions were the following: splitless injector temperature, 250 °C; injector purge activation time, 1 min; NPD temperature, 310 °C; FPD temperature, 275 °C. The oven temperature program used was as follows: 40 °C for 2 min; increase from 40 to 60 °C at 40 °C/min and from 60 to 310 °C at 4 °C/min; hold at 310 °C for 10 min. When using the DB-1701 column the final oven temperature was 300 °C and the hold time 15 min.

All inlet and detector gas flow rates were set according to the manufacturer's recommendations. The FPD hydrogen flow rate was optimized for sulfur compounds at 55 mL/min (393 nm filter); in phosphorus mode with a 525 nm filter, maximum sensitivity was obtained at 95 mL of $H_2$/min. The capillary columns used in this study are listed in Table 1.

Bonded phase fused silica capillary columns were washed by rinsing with 2 mL each of hexane followed by methylene chloride followed by hexane. After the organic solvent was removed, columns were flushed with carrier gas at room temperature for ~20 min prior to reconditioning of the column according to the manufacturer's recommendations.

The thermionic ionization source was recoated several times during the course of the study by treatment with rubidium ingot (rod) and alumina powder using a protocol and materials provided by the instrument manufacturer. Briefly, the detector collector assembly was removed, sufficient current was applied to the source to give it an orange glow, and a small

**Table 2. Retention Times for U.S. EPA Method 507 Analytes on Various Columns**

| chemical common name | formula | retention time (min) SPB-5 | DB-1701 | DB-1 |
|---|---|---|---|---|
| 1,3-dimethyl-2-nitrobenzene | $C_8H_9NO_2$ | 15.68 | 23.38 | 22.98 |
| dichlorvos | $C_4H_7Cl_2O_4P$ | 18.07 | 27.05 | 24.96 |
| EPTC | $C_9H_{19}NOS$ | 21.65 | 28.34 | 29.56 |
| butylate | $C_{11}H_{23}NOS$ | 24.12 | 30.41 | 32.37 |
| mevinphos | $C_7H_{13}O_6P$ | 24.26 | 34.16 | 31.40 |
| vernolate | $C_{10}H_{21}NOS$ | 24.65 | 31.26 | 32.74 |
| pebulate | $C_{10}H_{21}NOS$ | 25.15 | 31.81 | 33.19 |
| tebuthiuron | $C_9H_{16}N_4OS$ | 26.99 | 38.80 | 34.22 |
| molinate | $C_9H_{17}NOS$ | 27.36 | 35.19 | 35.56 |
| cycloate | $C_{11}H_{21}NOS$ | 30.44[f] | 37.64 | 38.93 |
| ethoprophos[a] | $C_8H_{19}O_2PS_2$ | 30.56[f] | 39.23 | 38.55 |
| chlorpropham | $C_{10}H_{12}ClNO_2$ | 31.06 | 40.88 | 39.05 |
| atraton | $C_9H_{17}N_5O$ | 33.35 | 42.65[l] | 41.08 |
| simazine | $C_7H_{12}ClN_5$ | 33.58[g] | 44.38 | 41.22 |
| prometon | $C_{10}H_{19}N_5O$ | 33.69[g] | 42.59[l] | 41.50 |
| atrazine | $C_8H_{14}ClN_5$ | 33.92 | 44.23[m] | 41.66 |
| propazine | $C_9H_{16}ClN_5$ | 34.17 | 44.06 | 42.00 |
| terbufos | $C_9H_{21}O_2PS_3$ | 34.68[h] | 42.88 | 43.15[r] |
| propyzamide[b] | $C_{12}H_{11}Cl_2NO$ | 34.87[h] | 45.61 | 43.31[r] |
| diazinon | $C_{12}H_{21}N_2O_3PS$ | 35.48[i] | 43.03 | 43.50 |
| disulfoton | $C_8H_{19}O_2PS_3$ | 35.52[i] | 44.24[m] | 43.91 |
| terbacil | $C_9H_{13}ClN_2O_2$ | 35.92[i] | 49.33[n] | 43.12[r] |
| metribuzin | $C_8H_{14}N_4OS$ | 37.37 | 48.16[o] | 45.23 |
| parathion-methyl | $C_8H_{10}NO_5PS$ | 37.83 | 48.99 | 45.97 |
| simetryn | $C_8H_{15}N_5S$ | 37.92 | 47.80 | 46.02 |
| alachlor | $C_{14}H_{20}ClNO_2$ | 38.16[j] | 47.58[p] | 46.76[s] |
| ametryn | $C_9H_{17}N_5S$ | 38.23[j] | 47.62[p] | 46.33 |
| prometryn | $C_{10}H_{19}N_5S$ | 38.43 | 47.40 | 46.58 |
| terbutryn | $C_{10}H_{19}N_5S$ | 39.07 | 48.16[o] | 47.34 |
| bromacil | $C_9H_{13}BrN_2O_2$ | 39.46 | 53.58[q] | 46.76[q] |
| metolachlor | $C_{15}H_{22}ClNO_2$ | 40.04 | 49.43[n] | 48.86 |
| triadimefon | $C_{14}H_{16}ClN_3O_2$ | 40.45 | 50.67 | 49.10 |
| MGK 264 (1)[c] | $C_{17}H_{25}NO_2$ | 41.06 | 49.43[n] | 49.87 |
| diphenamid | $C_{16}H_{17}NO$ | 41.18 | 51.75 | 49.44 |
| MGK 264 (2)[c] | $C_{17}H_{25}NO_2$ | 41.62 | 50.47 | 50.30 |
| merphos | $C_{12}H_{27}PS_3$ | 42.05 | 48.63 | 51.10 |
| disulfoton sulfone | $C_8H_{19}O_4PS_3$ | 43.66 | 56.70 | 51.61 |
| tetrachlorvinphos[d] | $C_{10}H_9Cl_4P$ | 43.73 | 53.58[q] | 52.25 |
| butachlor | $C_{17}H_{26}ClNO_2$ | 43.95 | 52.72 | 52.81[t] |
| napropamide | $C_{17}H_{21}NO_2$ | 44.31[k] | 54.32 | 53.12 |
| fenamiphos | $C_{13}H_{22}NO_3PS$ | 44.33[k] | 54.78 | 52.58 |
| tricyclazole | $C_9H_7N_3S$ | 44.53[k] | 59.39 | 52.93[t] |
| DEF[e] | $C_{12}H_{27}OPS_3$ | 44.95 | 53.12 | 53.77[u] |
| carboxin | $C_{12}H_{13}NO_2S$ | 45.22 | 56.35 | 53.74[u] |
| norflurazon | $C_{12}H_9ClF_3N_3O$ | 48.55 | 62.00 | 56.80 |
| hexazinone | $C_{12}H_{20}N_4O_2$ | 49.18 | 62.43 | 57.47 |
| triphenyl phosphate | $C_{18}H_{15}PO_4$ | 49.73 | 59.54 | 58.33 |
| fenarimol | $C_{17}H_{12}Cl_2N_2O$ | 54.13 | 65.20 | 63.38 |
| fluridone | $C_{19}H_{14}F_3NO$ | 59.65 | 80.43 | 68.30 |

[a] Ethoprop. [b] Pronamide. [c] *N*-Octylbicycloheptenedicarboximide analytical standard gives two chromatographic peaks. [d] Stirofos. [e] *S,S,S*-tributyl phosphorotrithioate, merphos (*S,S,S*-tributylphosphorotrithioite) decomposes to DEF in the GC. [f–u] Coelutions of the U.S. EPA Method 507 target pesticides.

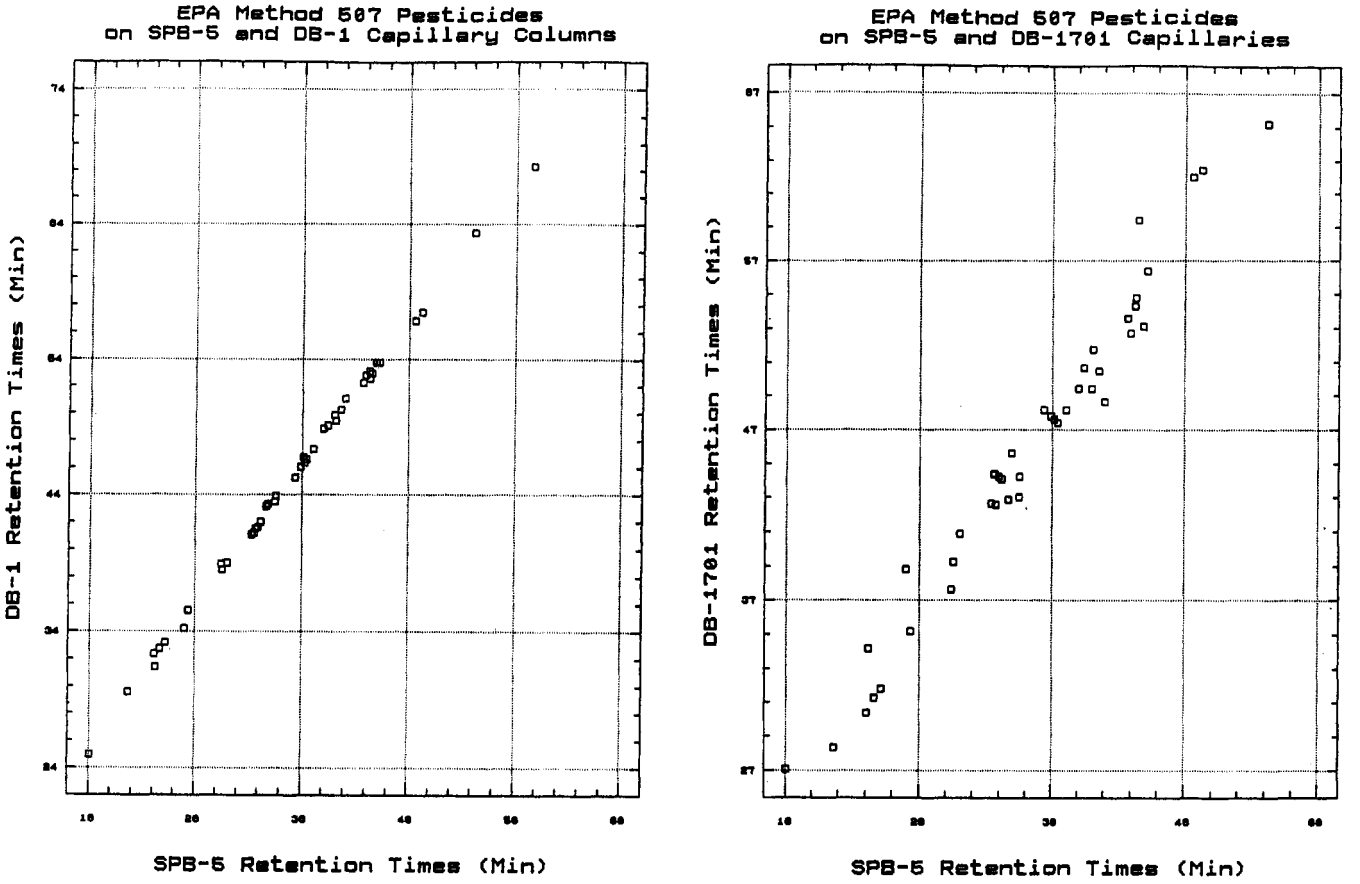


**Figure 1.** Retention times for U.S. EPA Method 507 analytes on primary and confirmation columns. Specific columns used are listed in Table 1.

amount of rubidium was melted onto the source surface. The recoated source was then dusted with aluminum oxide and the collector reinstalled in the detector.

## RESULTS AND DISCUSSION

**Chromatography of Pesticides on Recommended Columns.** Retention times for the 43 target agricultural chemicals and various internal standards, surrogates, and decomposition products are listed in Table 2. Resolution of each of these compounds was not accomplished by any one capillary column. On the primary M507 column, 5% phenyl−95% methyl silicone (SPB-5 or equivalent), 14 of the target pesticides coeluted. Similarly, using the recommended confirmation column, 14% cyanopropylphenyl−86% methyl silicone (DB-1701), 21 compounds are difficult to resolve or coelute. Using a longer DB-1701 capillary column (60 m) and an 80-min oven temperature program 13 coelutions were found: prometon/atraton, disulfoton/atrazine, ametryn/alachlor, metribuzin/terbutryn, terbacil/metolachlor/MGK 264, and tetrachlorvinphos/bromacil. A further drawback of the DB-1701 column is its low maximum isothermal operating temperature, 280 °C. Even when using an oven temperature program that reached 300 °C, seven of the target compounds had $t_R$ between 55 and 85 min (Table 2).

**Alternate Confirmation Column.** The difficulty in resolving each of the components in the calibration mixture and the need for a column with greater temperature stability led us to examine a methyl silicone (DB-1 or equivalent) column. Like the SPB-5 column, the DB-1 column tolerates isothermal operation up to 325 °C and temperature programmed operation up to 350 °C. As with the other columns, a number of the pesticides could not be resolved, but DB-1 had the fewest coelutions. Nine target compounds coeluted on a 30 m DB-1 capillary: terbacil/terbufos/propyzamide, alachlor/bromacil, tricyclazole/butachlor, and carboxin/DEF (Table 2).

**Similarity of the Phases.** Clearly, the primary and confirmation columns need to have different polarities, but there are no guidelines or theories regarding how different they should be. As the chemical compositions of the two high temperature phases (methyl silicone and 5% phenyl−95% methyl silicone) are very similar, little difference in the elution order or the relative retention times is expected. When the $t_R$ values of M507 analytes from the primary column are plotted on the $X$-axis and those from the possible confirmation columns are plotted on the $Y$-axis, a graphic representation of stationary phase similarity is obtained (Figure 1). No two capillary columns (even from the same production lot) are identical, and when $t_R$ data for two SPB-5 columns are plotted, there is some spread in the data ($m = 0.975$, $r = 0.9999$). A similar plot of SPB-5 $t_R$ vs DB-1 $t_R$ gives a line with a slope of 1.040 and more scatter in the data points with a correlation coefficient of 0.99874 (Figure 1). As expected on the basis of stationary phase chemistry, retention data for the DB-1701 confirmation column yield a line ($m = 1.103$) with the greatest dispersion ($r = 0.97558$).

The separation characteristics for a primary and confirmation column can also be compared by considering inversions in retention order. In the case of DB-1701, about 30 of the pesticide targets elute in a different order, while with the methyl silicone column only 10 inversions occur relative to the primary column.

In practical application the second column confirms the identity of detected residue in two ways. In complex samples the second column resolves the compound from

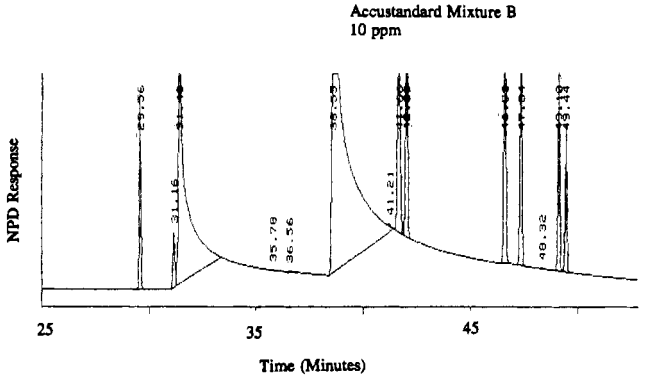


**Figure 2.** Source tailing for two OP pesticides, mevinphos and ethoprophos, in a GC-NPD chromatogram. Pesticides shown: EPTC (29.56 min), mevinphos (31.40), ethoprophos (38.55 min), atrazine (41.66 min), propazine (42.00 min), prometryn (46.58 min), terbutryn (47.34), triadimefon (49.10 min), and diphenamid (49.44 min).

coextracted interferences. In "clean" matrices such as drinking water, the second column only demonstrates that the analyte has the expected retention characteristics. The probability of any one compound behaving identically on two high-resolution capillary columns, even with only slight differences in polarity, is remote and so too is the chance of a qualitative error.

**NPD Source Tailing and Source Maintenance.** Chromatographers use the terms chromatographic tailing and column tailing interchangeably, although tailing is a function of both the analyte and the entire chromatographic system. The tailing of phosphorus compounds in NPD-GC can be very pronounced, and in this instance the term "source tailing" provides a more accurate description of the phenomenon.

In Figure 2 all of the nitrogen-containing pesticides give symmetrical and sharp peaks including EPTC, atrazine, propazine, prometryn, terbutryn, triadimefon, and diphenamid. Two phosphate pesticides, mevinphos ($t_R$ = 31.40 min) and ethoprophos ($t_R$ = 38.55 min), tail severely in the same chromatogram. Tailing of the OP pesticides was surprising as many of the N-containing pesticides are more polar.

With continued instrument use the chromatographic peak shape for phosphorus compounds deteriorates. In this case over a 2 day period tailing factors for two phosphorodithioates, terbufos and disulfoton, decreased from an average of 124 to 14. Tailing factors (McNair and Bonelli, 1968) quantify the tailing of a chromatographic peak—symmetrical or nontailing peaks have a tailing factor near 100; as tailing becomes more pronounced, the tailing factor decreases. During this time period the corresponding tailing factors for prometon and propazine, two nitrogen-containing pesticides, remained unchanged (e.g., 125 vs 127) and this was also the case for other N-containing pesticides including 1,3,5-triazines, thiocarbamates, 2-chloroacetanilides, ureas, and uracils.

The phosphorus compound peak shapes deteriorated well before the end of the source life on the basis of its background current and heater settings. Source tailing was not related to the inlet or column as sonicating the inlet liner in organic solvents and removing the first few feet of the capillary were of no benefit.

To test the hypothesis that the tailing of phosphorus compounds was related to the thermionic ionization source, chromatograms produced with an FPD were compared. The inlet and column oven operating conditions were identical, and only the means of detection was changed. As shown in Figure 3, the pronounced

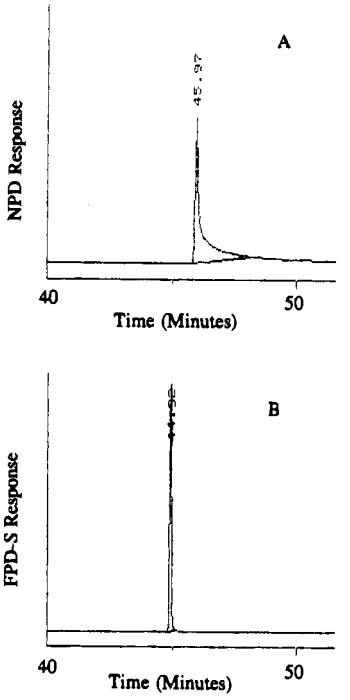


**Figure 3.** Parathion-methyl chromatographed under identical conditions on the same capillary column but detected by NPD (A) and FPD (B).

tailing of parathion-methyl (and other P-containing compounds not shown) was limited to the NPD. Source tailing can distort the apparent baseline, and even with high-efficiency capillary columns the detector baseline may not be reestablished for 2–3 min. These data demonstrate that the severe tailing of phosphorus compounds is unrelated to column performance and occurs in the NPD.

In a further example, the tailing factors for two OP pesticides, disulfoton and diazinon, are 21 and 28, respectively (Figure 4), while in the same chromatogram the tailing factors for 1,3,5-triazines (simetryn, ametryn, prometryn, and terbutryn) and a 2-chloroacetanilide herbicide (metolachlor) are in the range of 75–110. In this case the source tailing is so pronounced that the apparent baseline climbs in a stepwise manner as the phosphorus pesticides terbufos, diazinon, and disulfoton elute.

With the FPD the tailing factors for all of the pesticide classes averaged ~90, indicating symmetrical peaks. In general and across all compound classes the NPD produced broader peaks due to extracolumn band broadening, which has contributions from multiple factors. For example, the chromatographic efficiencies for the thiocarbamates butylate and molinate averaged 40 000 plates/m by NPD and 73 000 plates/m with the FPD. As before, the same column was used and injection conditions and oven temperature program were unchanged.

The symmetry of the OP peaks was restored and the source tailing eliminated by recoating the source with rubidium and alumina. After Rb treatment, the tailing factors for diazinon and disulfoton were ~125, indicating a high degree of symmetry (Figure 4). Source tailing, therefore, is an indication that the thermionic ionization source needs to be recoated (or replaced).

**Thermionic Ionization Theories and Source Tailing.** The behavior of phosphorus compounds reported here lends further support to the surface ionization theory. Because the boundary layer is efficiently swept with detector gases, any gas phase precursors to

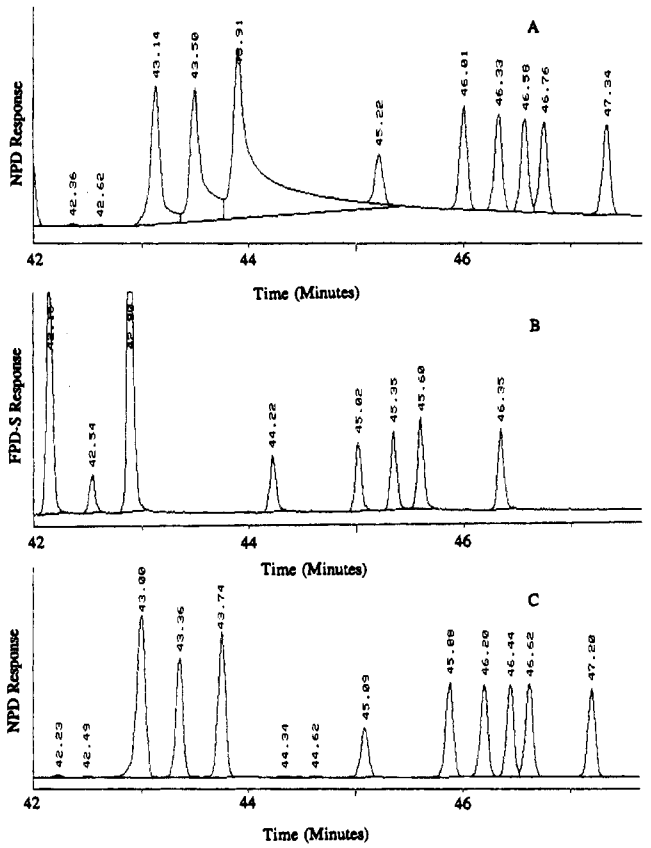


**Figure 4.** Pesticide mixtures detected by NPD (A), FPD in the sulfur mode (B), and NPD with the source recoated with rubidium (C). OP pesticides terbufos ($t_R$ 43.14 min), diazinon (43.50 min), and disulfoton (43.91 min) are sensitive to source tailing, while N-containing pesticides simetryn (46.01 min), ametryn (46.33 min), prometryn (46.58 min), alachlor (46.76 min), and terbutryn (47.34 min) are not. Alachlor is not detected by FPD.

anionic phosphorus species ($PO^-$, $PO_2^-$, and $PO_3^-$) are rapidly swept from the detector. If the gas phase ionization theory held, no unusual band broadening would be predicted. This is clearly not the case as the signal given by phosphorus compounds can persist for 2−3 min in severe cases of source tailing.

While this behavior can only be rationalized by the surface ionization theory, the mechanism of source tailing is unknown. Two steps precede ionization in the NPD: thermochemical decomposition of the analyte followed by ionization of the decomposition products. As the source ages, the surface changes, not by depletion of alkali metal but by deposition of contaminants. The deposit may act as a thermal, electrical, and chemical insulator, or the deposit may have an increased "work function". The simplest explanation for the protracted phosphorus response in the aged source is that the decomposition products must diffuse across the deposit to the reactive layer where ionization occurs, but tailing is limited to phosphorus compounds, and the decomposition products of N-containing analytes also would have to diffuse across the deposit.

It is possible that thermochemical decomposition also is a surface phenomenon, not one occurring in the boundary layer, and that surface decomposition reactions, particularly for phosphorus compounds, may be the rate-limiting step in thermionic ionization. On the contaminated source surface the thermochemical decomposition of P compounds, but not N compounds, may be too slow. Hydrogen, a necessary reactant at the active surface, may become limiting.

**Confirming Pesticides by FPD.** About half of the M507 target compounds can be detected using an FPD in the sulfur mode including S-containing OP pesticides (six compounds), thiocarbamates (six compounds), 1,3,5-triazines (four compounds), and miscellaneous pesticides from other compound classes (carboxin, metribuzin, tebuthiuron, and tricyclazole). In the phosphorus mode a further four OP pesticides are detected including dichlorvos, mevinphos, tetrachlorvinphos, and triphenylphosphate, an internal standard. The compounds not detected by FPD include certain 1,3,5-triazines (five compounds), 2-chloroacetanilides (three compounds), amides (three compounds), uracils (two compounds), a carbamate, and miscellaneous compounds including fenarimol, fluridone, hexazinone, MGK 264, norflurazon, and triadimefon.

The advantages of the FPD over the NPD include greater chromatographic efficiency for all pesticides due to reduced extracolumn band broadening, a component of which is source tailing for P compounds. In addition, resolution of the target compounds (and sample coextractives) by FPD is less difficult as fewer compounds are detected in most samples. Finally, the FPD is generally more stable.

**Response Factors, Peak Shape, and Column Cleaning.** The condition of the capillary GC column was found to be critical in the determination of many of the pesticides. In particular, the OP pesticides are sensitive to organic contaminants, which may accumulate on the column with continued use. The NPD response factors for each of the target compounds were compared on an SPB-5 column (30 m × 0.32 mm × 0.25 μm film) before and after the column was rinsed with hexane and methylene chloride. The column was ~10 years old and most recently had been used for total petroleum hydrocarbon analysis on samples containing high boiling lubricants. The column had been operated frequently at its maximum operating temperature.

The peaks given by many of the OP pesticides were broad but were most unusual because of the their low response factors relative to many of the N-containing analytes. Fenamiphos, mevinphos, tetrachlorvinphos, dichlorvos, and tebuthiuron were not detected or gave only minor peaks.

After the column was rinsed, the response factors given by most of the pesticide analytes were similar; i.e., minor changes in the NPD source temperature resulted in a slight decrease in response factors for 33 of the pesticides, which averaged 84 ± 14% of the precleaning values. The response factors for OP pesticides were substantially higher on the cleaned column with increases of 2.4-fold or greater: DEF (2.4-fold), merphos (2.7-fold), ethoprophos (2.9-fold), diazinon (3.3-fold), disulfoton and terbufos (3.7-fold), tetrachlorvinphos (10-fold), and dichlorvos (21-fold). Mevinphos and fenamiphos (20 ng each), which were not detected on the contaminated column, gave peaks with areas of $3.5 \times 10^7$ and $2.6 \times 10^7$ counts, respectively. The substantial improvement in mevinphos responses is seen in Figure 5.

Prior to cleaning of the column, severe tailing was found with some of the M507 analytes, particularly norflurazon, carboxin, fluridone, and simazine. Cleaning the column resulted in a general improvement in peak shape for many of these compounds, including triadimefon, carboxin, norflurazon, bromacil, hexazinone, fenarimol, fluridone, and simazine. The effect on simazine chromatography is demonstrated in Figure 6. In spite of cleaning, the peak shapes for the uracils (terbacil and bromacil) and particularly tebuthiuron were unacceptable on the old capillary column.

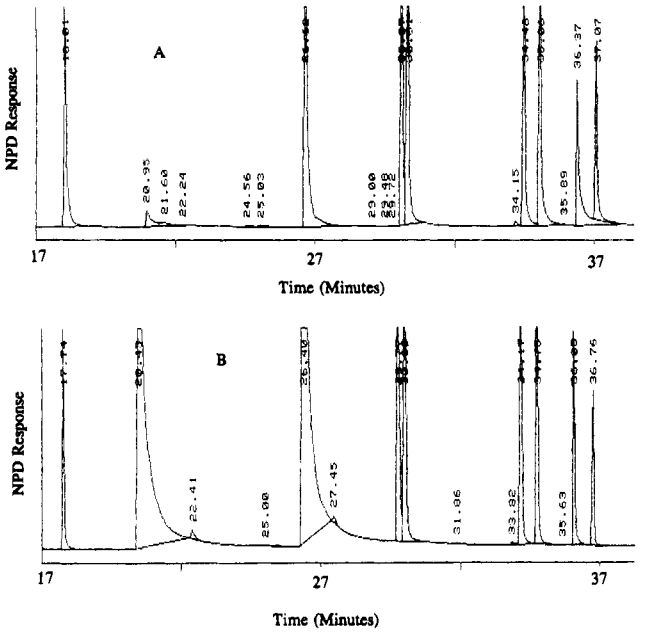


**Figure 5.** Pesticide mixtures determined on an SPB-5 column before (A) and after (B) column cleaning with organic solvents. The pesticides detected on the clean column are EPTC ($t_R$ = 17.74 min), mevinphos (20.45 min), ethoprop (26.40 min), atrazine (29.77 min), propazine (30.00 min), prometryn (34.17 min), terbutryn (34.75 min), triadimefon (36.05 min), and diphenamide (36.76 min).

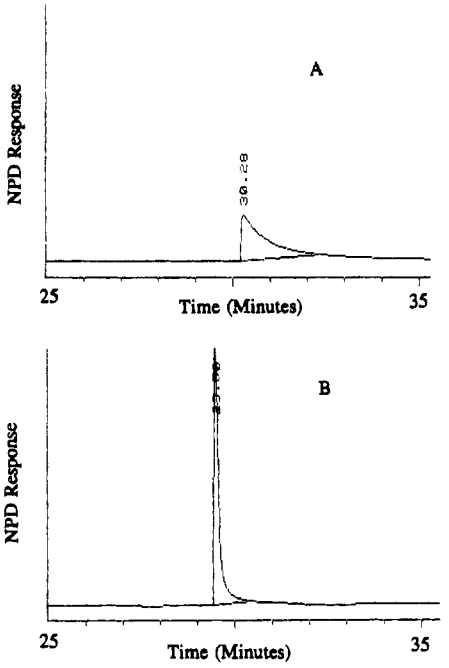


**Figure 6.** Capillary column chromatograms for simazine herbicide on an SPB-5 column before (A) and after (B) column cleaning.

**Conclusion.** The determination of pesticides by NPD-GC can be improved by attention to the condition of both the capillary column and the thermionic ionization source. Cleaning the bonded phase capillary column with organic solvent can markedly increase the response factors for phosphorus-containing pesticides, some of which (mevinphos, fenamiphos, and dichlorvos) are extremely sensitive to column contamination. Solvent cleaning also reduces the chromatographic tailing of many polar pesticides. Source tailing, the tailing of phosphorus compounds on the contaminated thermionic ionization source, increases as the source ages but can be reduced or eliminated by reimpregnating the detector source with rubidium and alumina. Chromatographic efficiencies for all pesticides were higher by FPD, which is useful in confirmation of about half of the M507 analytes when both S- and P- operating modes are considered. A methyl silicone capillary (DB-1 or equivalent) had some advantages over the recommended DB-1701 confirmation column including a higher temperature operating range (affording shorter run times and longer column life) and fewer coelutions among the pesticides analyzed.

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