



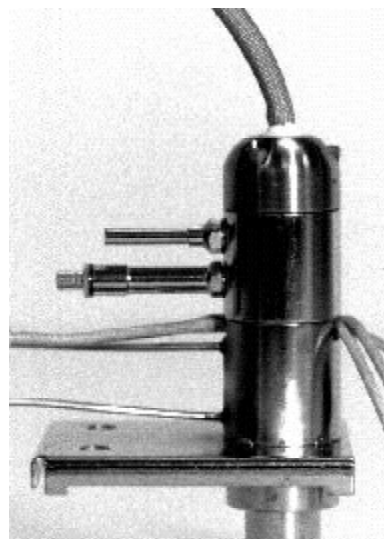
Effortless, Reliable Nitrogen-Phosphorus Detector Technology for Gas Chromatography

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The analysis of nitrogen and phosphorus pesticides and herbicides has always been a very difficult task. Two factors have complicated this analysis. The first factor has been the lack of adequate clean up procedures in the preparation of the sample extracts. In sample preparation of semi-volatile organochlorinated pesticides, a Florisil clean up removes most of the sample matrix while yielding good percent recovery of the analytes. In the more polar nitrogen containing herbicides, Florisil clean up removes the sample matrix and the analytes as well. Currently, no acceptable clean up procedures exist for these extracts. The second factor has been the unreliability of the Nitrogen Phosphorus Detector (NPD). The injection of contaminated extracts places a tremendous demand on the performance of NPDs, which traditionally have been difficult to optimize and maintain, without the added burden of contaminants. Since the NPD utilizes a catalyst, stability and sensitivity are not easily maintained when injecting these extracts. As the catalyst is consumed or poisoned, the efficiency of the reaction involved in detection drops off considerably. This paper will review the evolution of the nitrogen phosphorus detector and list the advantages of the new μ Gold Finnigan/Tremetrics NPD, offering a refreshing change in NPD technology.

Meeting the project reporting dates for NPD work has often been a risky endeavor. In the assessment of remediation sites, a late analytical report can cost a lab thousands of dollars a day in late penalty charges. The addition of an internal standard may compensate for minimal detector changes and allow the analysis to proceed in a timely manner, but one injection of a "dirty" sample could place the instrument "out of control." The source would have to be replaced and a new calibration curve generated before resuming analysis. Optimization must be quick and easy.

Some NPDs available on the market today use sources that require special alignment and conditioning periods of several hours. Batch to batch variation in source characterization may result in the operator having to find the proper optimization parameters to fit each new source. This time consuming "tweaking" of each detector source may still yield poor reproducibility in the results. The life of a source may vary as well.



The μ Gold NPD

The NPD is an element-specific detector in that it shows greatest response to organic compounds containing nitrogen and/or phosphorus atoms. The NPD evolved from an earlier type of GC detector, known as an Alkali Flame Ionization Detector (AFID). "The AFID had a hydrogen and air flame that burned near an alkali metal salt pellet so that alkali vapors were generated by the

flame. This alkali-sensitized flame exhibited a high ionization specificity for phosphorus or nitrogen compounds."¹.

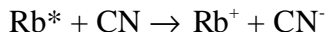
The AFID was difficult to use and was replaced by the Kolb and Bischoff design of 1974 (*Figure 1*). This NPD used " a nonvolatile rubidium silicate glass bead fused onto a platinum wire as the alkali catalyst. The wire was used to electrically heat the catalyst in place of a flame."² The hydrogen flow was reduced to 2-6 ml/min to prevent ignition of the gases; a flame was not desired in this design.

The detector was a flameless thermionic ionization detector. The term "thermionic" is used to identify the "emission of electrical charge from solid surfaces that are heated."³ The source, or glass bead, was the physical location where the ions were formed. In this generation of the NPD, the silicate alkali source was not stable at the elevated temperatures of operation and would lose rigidity and become softened. The next generation of NPDs would use a ceramic source impregnated with an alkali metal mixture and show greater stability and rigidity at elevated temperatures.

The new μ Gold Finnigan/Tremetrics NPD described in this paper has the appearance of a standard Flame Ionization Detector (FID), with a thimble-like ceramic finger, or source, oriented above the tip of the flame jet as shown in *Figure 2*. The ceramic source is designed and manufactured by Paul Patterson and is impregnated with a mixture of rubidium, cesium, and strontium. Hydrogen enters the flame jet with the column effluent and mixes with air at the surface of the source, creating a plasma. Hydrogen flows are kept below 6.0 ml/min to prevent ignition of the flame. If the flame is lit, the response is similar to a conventional FID. By applying a current of about 1.5 amps, the source or catalyst is heated to energize the plasma. A -5 volt polarization voltage is applied to the source to set up a potential driving the negative ions generated to the collector located above the source.

There are two principles of detection in the NPD. One is gas-phase ionization and the other is surface ionization. As shown in *Figure 3* for the theory of gas-phase ionization, the hydrogen and air mix and flow across the surface of the thermionic source. "When the source is raised to a temperature that is high enough to 'ignite' the H₂/air mixture the H₂ molecules will dissociate into reactive H⁺ atoms. The H⁺ atoms react further with O₂ molecules in a series of chain reactions that produce a highly reactive chemical environment containing H⁺, O⁻², (OH)⁻¹ and H₂O".⁴ This gaseous boundary exists on the surface of the source and is critical to response for the NPD.

In the theory of gas-phase ionization, Kolb and Bischoff speculated that "the rubidium in the glass bead vaporized as a neutral radical to react with CN formed in the excited gaseous boundary to be converted to a positive ion, Rb⁺ and be pulled back into the negatively polarized source. The Rb* was a rubidium radical excited to its first energy level. The electron affinity of the CN radical exceeds the ionization potential of Rb* to pull the electron from the Rb* to the CN radical, thus creating a positive ion of Rb to be attracted back into the negatively charged source.



The reaction for phosphorus involved PO or PO₂ as the intermediate electronegative radical".⁵The second reaction theory was surface ionization incorporating a work function, **Figure 4**, defined as the amount of energy required to remove an electron from a surface. "The alkali metal was added to the ceramic source to lower this work function and enable the thermionic emission of charged particles from the heated source more easily. The work function depends on the type and the density of the alkali metal used in the source."⁶ The ionization potentials are equal to the work function required for the reaction. Some alkali-metals used in sources are shown here in relation to their work function:

$$NA > K > Rb > Cs$$

A more detailed rendition of a mathematical modeling of this complex ionization process is presented in Paul Patterson's publication, cited in this text.

The NPD source described in this paper is composed of multiple layers. A fine wire is covered with an alumina ceramic support and cured in a special process by Patterson. The inner layer will minimize the long term corrosion of the hot heater wire. The next set of layers comprise the outer layers of the catalyst (alkali metal additives of rubidium and cesium with strontium to minimize peak tailing of phosphorus compounds). These metals are impregnated in a ceramic matrix and applied layer upon layer. The sources are then conditioned and tested by the manufacturer prior to shipment to Finnigan/Tremetrics.

Optimization of the NPD is simply a three step process. First, the gas flows are properly adjusted, detector base temperature set to 300°C, and the voltage applied to initiate energization of the plasma at the surface of the source. One hour is required for the baseline to stabilize after energization of the plasma. The optimum flow for air is 80 ml/min for Azobenzene and 50 ml/min for Methyl parathion with the Hydrogen at 5 ml/min as shown in **Figures 5** and **6**. The ideal flow for hydrogen with the air at 80 ml/min is 6 ml/min. Hydrogen flows above 6 ml/min will result in ignition of the plasma and a severe drop in sensitivity as shown in **Figures 7** and **8**.

The voltage applied to the source for excitation of the plasma is set by incrementing the voltage by integer amounts until a substantial deflection of the baseline is observed as in **Figure 9**. Application of higher voltages will improve response but shorten source life.

A long term source decay study is shown in **Figure 10** for 1,3-Dimethyl-2-nitrobenzene at 1 ng. A new source was installed and voltage applied at a constant value for the entire time of the study. The decay rate leveled out to < 10 %/day in the third hour and then < 3 %/day for the duration of the study. The stability of 1 ng of Azobenzene is shown in **Figure 11**.

A cross sectional diagram of the detector is shown in **Figure 12**. The source has a -5 volts polarization voltage and the negative ions created are collected above the source by the collector ring. The detector may easily be converted to an FID by switching out the cap and installing a polarizer ring and contact arm as shown in **Figure 13**.

Some representative chromatograms of the NPD are shown in *Figures 14, 15, 16* and *17*. *Figure 16* is a chromatogram provided courtesy of Environmental Consultants, Inc. in Clarksville, Indiana. This chromatogram demonstrates typical sensitivity for a low level standard run for E.P.A. Method 507. *Table 1* shows calibration curves for the 507 method. *Table 2* exemplifies the reliability of the detector for a performance evaluation sample run for laboratory certification. *Table 3* illustrates the long term stability of the NPD for Method 507. Two sources were installed over a two month period and only one continued calibration check standard failed.

The life of the source may be prolonged by setting voltage only high enough to energize the plasma. Whenever the detector is not in use, the voltage should be turned off. The hydrogen flow should never be raised above 6 ml/min to prevent coking up of the source from a hydrogen flame and is routinely run at 4.5 mL/min. A special desensitizing feature enables the operator to temporarily reduce the voltage to the source during the elution of the solvent. When using halogenated solvents, this procedure will prevent unnecessary depletion of the catalyst. A well conditioned column is beneficial as well in lengthening the life of the source. Cyano phases should be avoided, since they would produce a high background and deplete the catalyst.

The specifications for the NPD are listed in *Table 4*. The detector is quite sensitive, stable, linear, and easy to optimize. A self aligning source takes the guesswork out of source replacement. A stability of < 10 %/day decay rate for Azobenzene means less downtime spent calibrating and more time spent running reportable sample injections. A sensitivity in the low picogram range yields low MDL's. A large working range of linearity results in fewer dilutions of samples, *Figures 18 & 19*. A selectivity of 10^5 generates cleaner sample chromatograms, and eliminates the need for extensive sample clean up steps. Longer life of sources results in lower downtime and reduced replacement costs. With operational temperatures to 400°C, the detector will stay cleaner and require less maintenance. This NPD represents a radical breakthrough in NPD technology.

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Notes:

¹ Patterson, Paul. Detectors for Capillary Chromatography: Chemical Analysis Series Vol. 121. John Wiley and Sons. New York, 1992; pp. 139-140.

² pp. 140.

³ pp. 141.

⁴ pp. 147.

⁵ pp. 149.

⁶ pp. 152.

⁷ pp. 159.