Standard Practice for
Testing Nitrogen/Phosphorus Thermionic Ionization Detectors for Use In Gas Chromatography[1]

This standard is issued under the fixed designation E1140; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε¹ NOTE—Editorial corrections were made to Footnote 3 in November 2010.

1. Scope

1.1 This practice covers testing the performance of a nitrogen/phosphorus thermionic ionization detector (NPD) used as the detection component of a gas chromatographic system.

1.2 This practice applies to an NPD that employs a heated alkali metal compound and emits an electrical charge from that solid surface.

1.3 This practice addresses the operation and performance of the NPD independently of the chromatographic column. However, the performance is specified in terms that the analyst can use to predict overall system performance when the detector is coupled to the column and other chromatographic components.

1.4 For general chromatographic procedures, Practice E260 should be followed except where specific changes are recommended in this practice for the use of a nitrogen/phosphorus (N/P) thermionic detector.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific safety information, see Section 5, Hazards.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *CGA Standards:*[3]

CGA P-1 Safe Handling of Compressed Gases in Containers

CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium

CGA V-7 Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures

CGA P-12 Safe Handling of Cryogenic Liquids

HB-3 Handbook of Compressed Gases

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of gas chromatography and its various terms, see Practice E355.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *drift*—the average slope of the noise envelope expressed in amps/h as measured over ½ h.

3.2.2 *linear range*—range of mass flow rates of nitrogen or phosphorus in the carrier gas, over which the sensitivity of the detector is constant to within 5 % as determined from the linearity plot.

3.2.3 *minimum detectability*—the mass flow rate of nitrogen or phosphorus in the carrier gas that gives a detector signal equal to twice the noise level.

3.2.4 *noise (short term)*—the amplitude, expressed in amperes, of the baseline envelope that includes all random variations of the detector signal of a frequency greater than one cycle per minute.

3.2.5 *selectivity*—the ratio of the response per gram of nitrogen or phosphorus in the test substance to the response per gram of carbon in octadecane.

4. Significance and Use

4.1 Although it is possible to observe and measure each of the several characteristics of a detector under different and unique conditions, it is the intent of this practice that a

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complete set of detector specifications be obtained at the same operating conditions, including geometry, flow rates, and temperatures. To specify a detector's capability completely, its performance should be measured at several sets of conditions within the useful range of the detector. The terms and tests described in this practice are sufficiently general so that they may be used under any chosen conditions.

4.2 Linearity and speed of response of the recorder should be such that it does not distort or otherwise interfere with the performance of the detector. Effective recorder response should be sufficiently fast so that its effect on the sensitivity of measurement is negligible. If additional amplifiers are used between the detector and the final readout device, their characteristics should first be established.

5. Hazards

5.1 *Gas Handling Safety*—The safe handling of compressed gases and cryogenic liquids for use in chromatography is the responsibility of every laboratory. The Compressed Gas Association (CGA), a member group of specialty and bulk gas suppliers, publishes the following guidelines to assist the laboratory chemist to establish a safe work environment. Applicable CGA publications include: CGA P-1, CGA G-5.4, CGA P-9, CGA V-7, CGA P-12, and HB-3.

6. Application

6.1 The N/P thermionic detector is an element-specific ionization detector that is essentially a major modification of the flame ionization detector (FID). As in the normal FID, it measures increase in ionization current passing between two electrodes, one of which is polarized relative to the other. Usually these are the inorganic salt source and the collector, with one often being at ground potential.

6.2 The mechanism of the detector will only be discussed briefly in this practice partly because full understanding of the detector is not presently available and partly because the substantial differences in bead chemistry, detector geometry, and bead heating mechanism prevent a singular view being given.

6.3 The addition of a heated alkali metal compound in the detector area causes enhancement of the response for carbon-nitrogen and carbon-phosphorus bonds. In addition, the selectivity of response can be further enhanced when the bead is electrically heated. Lower hydrogen and air flow rates that diminish the normal flame ionization response for hydrocarbon compounds can be used. This selective enhancement allows the NPD to be used for the detection of very small quantities of nitrogen- and phosphorus-containing compounds without interference from the signal of other molecular species.

6.4 The selective response to C-N and C-P bonds means that the detector is not suitable for permanent gas or elemental nitrogen or phosphorus analysis in the true definition of the term. It should be noted, however, that some volatile inorganic phosphorous compounds do give a strong response with this detector, comparable to that of organophosphorus compounds.

7. Detector Construction

7.1 There is a wide variation in the method of construction of this detector. It is not considered pertinent to review all aspects of the different detector designs available, but to consider one generalized design as an example and recognize that many significant variants may exist. Examples of significant differences may exist in bead chemistry and method of heating, space jet and collector configuration, potential applied across the cell, its polarity, and the flow rates and composition of the three gases used.

7.2 An essential part of the N/P thermionic detector is the presence, in the active area of the detector, of an inorganic material containing an alkali metal, often rubidium. The inorganic material may be a salt or silicate. It is usually, but not necessarily, present in bead form and may be combined with other components for mechanical support, such as a ceramic core.

7.3 The inorganic salt mixture is usually connected to, or supported by, a wire of platinum or other noncorrosive material. In some designs the bead is heated by passing a current through this wire; in others, the bead is heated by hydrogen combustion, for example, the burning flame itself.

7.4 The carrier gas (usually helium or nitrogen) flows through a jet as in normal FID practice and mixes, prior to leaving the jet, with a small volume of hydrogen. Combustion gas (usually air) is fed around the jet in some manner and then moves over or around the bead before exiting from the detector. It is worth noting that if this mixture is lean enough, due to low hydrogen flow, there will be insufficient fuel to maintain a true flame.

8. Equipment Preparation

8.1 The detector shall be evaluated as part of a gas chromatograph using injections of liquid samples that have a range of component concentrations.

8.1.1 The detector shall be operated with carrier gas type and hydrogen and oxidizer gas flow rates as recommended by the manufacturer of the equipment. No attempt will be made in this practice to guide the selection of optimum conditions, except to state that because selectivity and sensitivity of the NPD are very dependent on the hydrogen flow rate, several flow rates (in the range of 1 to 8 mL/min for the electrically heated bead detector) should be tested for optimum detector performance.

8.1.2 The complete set of performance specifications must be determined at the same operating conditions, since the absolute sensitivity and noise vary independently over a wide range depending on the operating conditions. Once selected, the operating conditions should not be changed during the determination of the detector characteristics.

8.1.3 Detector stability over the course of the evaluation is essential for meaningful results. This may be monitored by checking the bead temperature, the heating current, gas flows, and other parameters during the evaluation as dictated by the instrument manufacturer. (Some electrically-heated beads tend to lose sensitivity continuously with operating time and require increasing the bead heating current to recover lost sensitivity.)

8.2 *Column*—Any column that fully separates the sample components without causing overload or sample adsorption may be used. One suitable column is a 4 ft by 2 mm glass column packed with 100/120 mesh deactivated chromosorb W coated with 2 wt. % dimethyl silicone oil.

8.3 *Gases*—With N/P thermionic detectors it is of critical importance that all gases are pure and that the gas lines are not contaminated with oils, solder flux, etc. The use of well conditioned molecular sieve traps in all lines helps to achieve this purity. If the chromatograph is fitted with in-line chemical filters after the gas regulators and flow controllers, they also should be well conditioned to ensure that no contaminants reach the column from elastomeric diaphragms contained in these parts.

NOTE 1—To condition a molecular sieve 5A column well, heat the trap with a slow flow of carrier gas at 350°C for a minimum of 2 h.

8.4 *Gas Connections*—All gas tubing and connections should be made of cleaned copper or stainless steel, including all ferrules and joints within the system. Vespel and graphite ferrules may be used for GC column connections provided that they are sufficiently conditioned after installation. These steps will minimize contamination problems.

9. Sample Preparation

9.1 A solution containing three compounds dissolved in isooctane should be used, with great emphasis placed on the purity of all chemicals and particularly the solvent. Blank runs should be made on the solvent to ensure that no interfering peaks elute at the same time as the compounds of interest, which would invalidate the results. The three test compounds are azobenzene for nitrogen response (15.38 % nitrogen), malathion for phosphorus response (9.38 % phosphorus), and octadecane for specificity (84.95 % carbon). Azobenzene and malathion should be mixed in an appropriate ratio to allow comparable peak heights under the isothermal conditions used. Typical ratios are between 0.5 and 2.0, depending on detector construction and operating conditions. Concentration limits between 1 µg/L and 1 mg/L are recommended initial values. The octadecane need be checked only at one concentration level for specificity, and the recommended concentration for this should be 1 g/L.

9.2 Because of the toxicity of malathion, it is recommended that a dilute solution be used as the starting material, and that this solution be purchased from one of the special supply houses that routinely make chemical standards. Precautions for handling toxic materials must be followed throughout the dilution sequence as standard good laboratory practice.

9.3 *Sample Injection*—The recommended procedure for accurate injection of liquid samples is the "solvent flush," or Burke injection technique, in which a carefully washed 10-µL syringe is loaded with 1 to 2 µL solvent, 1 µL air, 3 µL sample, and 1 µL air. While time consuming, this procedure allows repeatability of ±2 % or better, and minimizes needle volume effects.

10. Data Handling

10.1 All manufacturers supply an integral electrometer to allow the small electrical current changes to be coupled to recorders/integrators/computers. The preferred system will incorporate one of the newer integrators or computers that converts an electrical signal into clearly defined peak area counts in units such as microvolt-seconds. These data can then be readily used to calculate the linear range.

10.1.1 Another method uses peak height measurements. This method yields data that are very dependent on column performance and therefore not recommended.

10.1.2 Regardless of which method is used to calculate linear range, peak height is the only acceptable method for determining minimum detectability.

10.2 *Calibration*—It is essential to calibrate the measuring system to ensure that the nominal specifications are acceptable and particularly to verify the range over which the output of the device, whether peak area or peak height, is linear with respect to input signal. Failure to perform this calibration may introduce substantial errors into the results. Methods for calibration will vary for different manufacturers' devices but may include accurate constant voltage supplies or pulse-generating equipment. The instruction manual should be studied and thoroughly understood before attempting to use electronic integration for peak area or peak height measurements.

11. Test Substances

11.1 The test substance and the conditions under which the detector sensitivity is measured must be stated. This will include, but not necessarily be limited to, the following: type of detector, detector geometry (for example, source of alkali metal), carrier gas, carrier gas flow rate (corrected to detector temperature), detector temperature, detector polarizing voltage, hydrogen flow rate, air flow rate, method of measurement, and electrometer range setting.

11.2 Azobenzene is the standard nitrogen-containing test substance. Malathion is the standard phosphorus-containing test substance. Measurement of the test substance must be made within the linear range of the detector and at a signal level at least 100 times greater than the minimum detectability (200 times greater than noise level).

12. Test Conditions

12.1 Measure the noise level in accordance with the specifications given in Section 13. Measure sensitivity in accordance with the specifications given in 14.1. Both sensitivity and noise level measurements must be carried out under the same conditions (for example, carrier gas flow rate and detector temperature) and preferably at the same time. When stating the minimum detectability, state the noise level on which the calculation was based.

13. Procedure for Noise and Drift Measurement

13.1 Noise includes fluctuations of the baseline envelope of a frequency less than one cycle per minute. The amplitude of these fluctuations may actually exceed the short-term noise. Such fluctuations are difficult to characterize and are not typically to be expected. They are usually caused by other chromatographic components, such as the column, system contaminants, and flow variations. These other noise contributions may not be derived from the detector itself and are

difficult to quantitate in a general manner. It is, however, important for the practicing chromatographer to be aware of the occurrence of this type of noise contribution.

13.2 Make noise measurements over short periods of time only, based on the expected peak width of the sample peaks; the suggested time interval is one minute for typical peaks (see Fig. 1). This noise corresponds to the observed noise only. The actual noise of the system may be larger or smaller than the observed value, depending upon the method of data collection or signal monitoring from the detector, since observed noise is a function of the frequency, speed of response, and the bandwidth of the electronic filtering circuit measuring the detector signal.

13.2.1 With the attenuator set at maximum sensitivity (minimum attenuation) adjust the detector output with the "zero" control to read near mid-scale on the recorder. Allow at least ½ h of baseline to be recorded.

13.2.2 Draw two parallel lines to form an envelope that encloses the random noise excursions with a period less than 1 min. Measure the distance between the parallel lines at right angles to the edges of the chart paper. Measure five adjacent one-minute sections and average the values. Express the value as amperes of noise, peak-to-peak.

13.2.3 Measure the net change in amperes of the lower line on the envelope over ½ h and multiply by two. Express the value as amperes per hour drift.

14. Performance Evaluation

14.1 *Sensitivity (Response)*—Sensitivity (response) of the NPD is the signal output per unit mass of nitrogen or phosphorus in the test substance, in accordance with the following relationship:

$$S = A_i/m \qquad (1)$$

where:

S = sensitivity (response) in amperes × seconds/gram, A · s/g
A_i = integrated peak area in A·s, and
m = mass of nitrogen or phosphorus in the test substance, g.
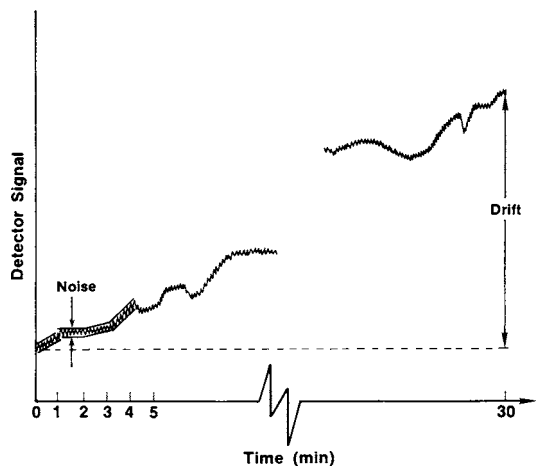

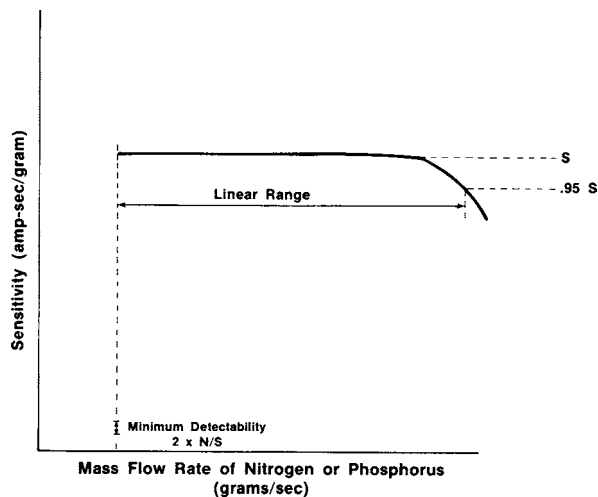**FIG. 1 Noise and Drift**

FIG. 2 Linear Range and Minimum Detectability

Sensitivity measurements should be made under the same conditions as noise measurements.

14.2 *Selectivity*—Selectivity can be calculated as sensitivity for nitrogen (or phosphorus) divided by the sensitivity for carbon, as calculated in 14.1.

14.3 *Minimum Detectability*—Minimum detectability can be determined from the measured sensitivity and noise level values as follows:

$$D = 2N/S \qquad (2)$$

where:

D = minimum detectability, g/s,
N = noise level, A, and
S = sensitivity of the detector, A · s/g.

14.4 *Linear Range:*

14.4.1 The linear range of the NPD is the range of mass flow rates of nitrogen or phosphorus over which the sensitivity of the detector is constant to within ±5 % as determined from the linearity plot. This range must start at the calculated minimum detectability.

14.4.2 *Method of Measurement*—Use the test sample and injection technique described in Section 8 to determine the detector sensitivity over a range of mass flow rates. Initial concentration limits of 1 μg/L and 1 mg/L of azobenzene for nitrogen or malathion for phosphorus are recommended, but lower or higher concentrations may be needed to adequately define the limits of linearity.

14.4.2.1 For each sample, calculate the detector sensitivity in accordance with 14.1. Determine the mass flow rate by dividing the mass of *N* or *P* injected by the peak base width, as shown in the following equation:

$$\text{Mass flow rate} = \qquad (3)$$

$$\frac{(\text{Volume injected}) \, (\text{Concentration of test substance}) \, (\% \, N \text{ or } P)}{\text{Peak base width}}$$

$$\frac{m}{} = \frac{(\text{Volume in } \mu L) \, (\text{Concentration in g/L}) \, (15.38 \text{ for } N \text{ or } 9.38 \text{ for } P) \, (10^{-8})}{(\text{peak width in } s)}$$

TABLE 1 Typical Values for Nitrogen/Phosphorus Thermionic Ionization Detector Performance Characteristics

Performance Characteristics	Typical Values	
	Nitrogen mode	Phosphorus mode
Sensitivity, A · s/g N(P)	0.1–1.0	1–10
Selectivity, g N(P)/S	$1 \times 10^3 - 5 \times 10^4$	$1 \times 10^4 - 5 \times 10^5$
Minimum detectability, g N(P)/s	$5 \times 10^{-14} - 2 \times 10^{-13}$	$1 \times 10^{-14} - 2 \times 10^{-13}$
Linear range	$10^3 - 10^5$	$10^3 - 10^5$
Noise, A	$1 \times 10^{-14} - 1 \times 10^{-13}$	$1 \times 10^{-14} - 1 \times 10^{-13}$
Drift, A/h	$5 \times 10^{-13} - 5 \times 10^{-12}$	$5 \times 10^{-13} - 5 \times 10^{-12}$

Plot the sensitivity versus the mass flow rate for *N* or *P* for each test sample. This graph is called the linearity plot; a typical example is shown in Fig. 2.

14.4.3 The linear range may be expressed by giving the linearity plot itself, with the minimum detectability indicated on the plot.

14.4.3.1 The linear range may also be expressed as the ratio of the upper limit of linearity (obtained from the linearity plot (Fig. 2)) to the minimum detectability (both measured for the same test substance) as follows:

$$LR = \dot{m}_{max}/D \qquad (4)$$

where:

LR = linear range of the detector,
$\dot{m}_{max}$ = mass flow rate at the upper limit of linearity, as obtained from the linearity plot, g/s, and
D = minimum detectability, g/s.

If the linear range is expressed by this ratio, the minimum detectability must also be stated.

14.4.3.2 The linear range may also be expressed by giving the lower limit of linearity and the upper limit of linearity (for example, from 1×10^{-14} g/s to 1×10^{-10} g/s).

14.4.3.3 As another alternative, the linear range may be expressed by giving the linearity plot itself, with the minimum detectability indicated on the plot.

15. Standard Values

15.1 Detector characteristics measured at optimum conditions recommended by the manufacturer may be expected to fall within the typical range of values listed in Table 1, which also indicates the way these values should be expressed. All data refer to azobenzene, malathion, and octadecane as test substances.

16. Keywords

16.1 flame ionization detector (FID); flame photometric detectors (FPD); gas chromatography (GC); nitrogen/phosphorus detectors (NPD); packed columns; supercritical fluid chromatography (SFC); thermionic detectors

APPENDIXES

(Nonmandatory Information)

X1. CORRECTION OF FLOW RATE TO DETECTOR TEMPERATURE

X1.1 Because the carrier gas flow rate is usually measured at ambient (room) temperature, it has to be corrected to the conditions at the detector. The correction is made using the following equation:

$$F_f = F_o \, (T_f/T_a) \, (P_f/P_a) \, [1 - (P_w/P_a)] \qquad (X1.1)$$

where:

F_f = corrected flow rate, mL/min,
F_o = flow rate measured at column or detector outlet at ambient temperature, mL/min,

T_f = flask temperature, K,
T_a = ambient temperature, K,
P_w = partial pressure of water at ambient temperature, torr,
P_a = ambient pressure, torr, and
P_f = flask pressure, torr.

X1.2 The factor $[1 - (P_w/P_a)]$ is only used if a wet (for example, soap bubble) flowmeter is used for the measurement.

X2. LIST OF SYMBOLS AND ABBREVIATIONS

A	=	ampere
A_i	=	integrated peak area, A × s
D	=	minimum detectability, g/s
g	=	grams of a test substance
gC	=	grams of carbon atoms
gN	=	grams of nitrogen atoms
h	=	hour
gP	=	grams of phosphorus atoms
LR	=	linear range of the detector

m	=	mass of a test substance, g, gC, gN, or gP
$\dot{m}$ =	=	mass flow rate, g/s, gC/s, gN/s, or gP/s
$\dot{m}_{max}$	=	mass flow rate at upper limit of linearity, g/s, gN/s, or gP/s,
N	=	noise level, A
NPD	=	nitrogen phosphorus thermionic ionization detector
S	=	detector sensitivity (response), A · s/g
s	=	second