Designation: E 1140 – 95 (Reapproved 2005)

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

This standard is issued under the fixed designation E 1140; 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.

## 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 E 260 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]

E 260 Practice for Packed Column Gas Chromatography

E 355 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 E 355.

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 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

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.19 on Chromatography.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from Compressed Gas Association (CGA), 1725 Jefferson Davis Hwy., Suite 1004, Arlington, VA 22202-4102.

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