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Comparison of universal chromatographic detectors for trace gas analysis

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Abstract

Various performance parameters of three detector systems used in trace level gas analysis, helium ionization detection (HID), discharge ionization detection (DID), and gas chromatography–mass spectrometry (GC–MS), have been compared. The detectors were compared for sensitivity, sample matrix effects, and stability. While detection limits were roughly comparable for all three detectors, both GC–MS and DID out-performed HID in various matrix effects and stability tests. Furthermore, HID demonstrated non-linear behavior over a relatively small concentration range.

1. Introduction

The analysis of sub-ppm level impurities in high purity gases has gained great interest in the last several years, especially in the semiconductor industry. Much of this analysis is done chromatographically, and almost every conceivable chromatographic detector is used for these analyses. The most active area for this application involves detectors that respond universally to impurities other than the carrier. While the thermal conductivity detector and the ultrasonic detector both fall into this category, their detection capabilities are generally limited to the low ppm level, and they will not be considered further. The helium ionization detection (HID) system has gained wide acceptance in this application because of its excellent sensitivity [1,2]. HID uses a tritium source of beta emission for ionization, the ions are accelerated by an electrical potential, and detected by a standard electrometer configuration [3–5]. Although much work has been done on the ionization process [6,7], the exact mechanism is not well understood. A common misconception is that ionization occurs through a "simple" Penning ionization. However, this fails to explain a number of unusual behaviors of this detection system. When carrier gas of sufficient purity is used, both positive and negative peaks result. The contribution of various impurities in the carrier may cause all positive peaks, enhance sensitivity, or suppress detection entirely [8–12]. A complex associative ionization mechanism has been proposed which more closely matches these observed behaviors [13]. Still, HID is a useful and widely accepted analytical tool for gas analysis.

Two other detection systems, discharge ionization detection (DID) and mass spectrometry (GC–MS), are beginning to be used more exten-

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sively in these applications. DID employs a DC helium corona discharge, supported by a separate gas flow from the carrier, as its ionization source. The detector is configured in a two-cell arrangement, with the discharge cell connected to the detection cell by a windowless aperture. The carrier flows into the detection cell, where it is ionized by the discharge and detected by a standard electrometer configuration [14–16]. Although photoionization has been claimed as the ionization mechanism, other pathways such as electron impact probably contribute to ionization.

The standard mass spectrometer has often been used as a detector for the chromatographic analysis of molecular impurities in many gases [17–21]. The advent of porous layer open tubular (PLOT) columns with many standard stationary phases used in gas analysis have made direct interfacing of the column to the mass spectrometer possible, allowing analysis of lower molecular weight impurities such as oxygen and nitrogen without the sensitivity losses associated with these analytes using other interface types (*e.g.*, jet and membrane separators) [22–35]. This development has placed GC–MS in the group of methods available for trace level gas analysis.

A comparison of various performance criteria is in order for these detectors. While sensitivity is an important consideration, it is not the only aspect of detector performance that must be considered. Response linearity is consideration when accurate quantitation is important. The effects of a sample matrix on the detector are significant. Finally, detector stability over time is important with respect to baseline drift and response. This consideration is especially important when the analysis is conducted continuously in an on-line application. A comparison of these parameters for these detectors is presented here.

2. Experimental

A Valco (Houston, TX, USA) 3000 gas chromatograph with dual helium ionization detectors was used for the HID part of the comparison. This instrument contains all components (columns, valves, fittings, and detectors) inside a helium-purged housing held at slightly positive pressure. This instrument, because of this configuration, is limited to packed columns. The plumbing configuration is such that heart-cutting and backflushing can be done, although only direct injection with a 1 ml sample loop is used here. Two ten-foot (1 ft. = 30.48 cm) Hayesep A columns were used for all determinations presented here, except the response and baseline recovery studies, and detection limit evaluations where additional chromatographic resolution was needed. Here, a 10-foot molecular sieve was substituted for the second Hayesep A column.

A Tracor (Austin, TX, USA) 540 GC system fitted with a discharge ionization detector was used for DID performance testing, fitted with dual six-port Valco valves, one for sample injection with a 1 ml sample loop, and one for switching a Molsieve 5A PLOT column in and out of series with a PoraPLOT Q column (Chrompack, Rariton, NJ, USA). All determinations were done with the PoraPLOT column only, except the response and baseline recovery studies, and detection limit determinations where additional chromatographic resolution was required. Packed columns were also used in matrix effect portion of the comparison to provide a bridge between the HID and GC–MS data. No helium purging was used for any components in this system.

GC–MS evaluations were conducted on a Hewlett-Packard (Avondale, CA, USA) 5988A quadrupole mass spectrometer equipped with a 5890 gas chromatograph. The mass spectrometer uses a differentially-pumped electron impact (EI) source, which enables it to maintain sufficient source vacuum at relatively high carrier flow (approximately 15 ml/min). This mass spectrometer is only capable of mass determinations down to $m/z = 4$. Therefore no determinations of hydrogen concentration were possible. All valves and fittings are housed in a helium-purged housing. The GC–MS system uses a plumbing configuration similar to that described for the DID system, including the use of PLOT columns. The interface between columns and the

source vacuum consisted of a 5 m × 0.2 μm linear restrictor of deactivated fused silica. Because of the reduced capacity of this restrictor, a 0.2 ml sample loop is used with this instrument. All evaluations discussed here were performed with the PoraPLOT Q column only, except response and baseline recovery studies, and detection limit evaluations where additional chromatographic resolution was required.

Linearity and detection limit evaluations required the preparation of mixtures with ppb level impurities. Due to the uncertainties in stabilities of low ppm mixtures, it was decided that they should be prepared by dynamic blending of mixtures containing higher levels of impurities. A two-stage dynamic blender (Fig. 1) was constructed using mass flow controllers (Omega Engineering, Stamford, CT, USA) to allow dilution over a range of 1:100 to $1:10^6$. This blender used all VCR (Cajon Co., Macedonia, OH, USA) type connections to guarantee a leak-tight system. Dilution gas (helium) was purified with a zirconium-based metal getter manufactured by SAES Getters (Colorado Springs, CO, USA), which reduced each impurity concentration to below detectable levels. Flow from each output

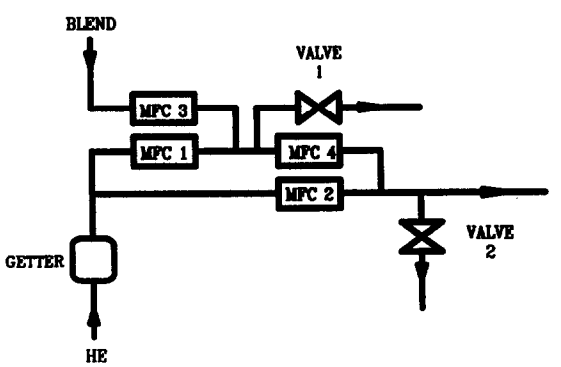

Fig. 1. Schematic diagram of dynamic blender used for preparation of low-level blends. Pure gases or ppm level blends with confirmed compositions are introduced at point marked BLEND. Helium is introduced at point marked HE. MFC 2 and 4 are 1 l/min full-scale electronic mass flow controllers. MFC 1 and 3 are 10 ml/min full-scale mass flow controllers. Valves 1 and 2 are manually adjusted excess flow needle valves. Single stage blender output is from OUTPUT 1 (upper horizontal arrow) and dual stage from OUTPUT 2 (lower horizontal arrow).

port was controlled by venting through an excess flow valve, thereby minimizing active components in the flow path of interest. This blender was used to verify concentrations of individual components in the high-level mixture, using pure gases at the blender input. The high-level mixture was introduced into the blender through a deep-purge regulator, purged with purified helium. It was dynamically blended to appropriate levels for linearity and detection limit evaluations.

3. Useful detection limits and linearity

Detection limits at ppb levels have been reported for all these detectors previously. Often these determinations involved operating conditions that cannot be easily maintained in daily operation because of their contribution to instrument instability. Because of this, an extremely conservative definition for useful detection limits has been chosen. A signal-to-noise level of 5:1 was chosen. DID and HID parameters (*e.g.*, HID polarization voltage, DID discharge current, etc.) were chosen such that the baseline drift over the course of analysis was less than one full scale of electrometer output. GC–MS parameters were chosen such that background signal changed by less than ± 100%. Low level blends were prepared within a factor of two of this value using the dynamic blender described above, and the reported detection limit was extrapolated from this point. Except for the determination of carbon monoxide, chromatographic parameters (*e.g.*, carrier flow, column temperature) were chosen to maximize detection performance while allowing chromatographic resolution of all components determined. All blends were prepared with a helium balance gas, so matrix effects should often be expected to degrade this performance.

Table 1 summarizes the detection limits (in ppbv) as defined above for six common impurities. In all cases except hydrogen, which could not be determined with the instrument used in this study, the GC–MS system showed equivalent or superior detection limits compared

Table 1
Detection limits in ppbv for six common analytes

Analyte	HID	GC–MS	DID
H_2	5	N/A [a]	50
O_2	50	1	10
N_2	10	1	10
CO	25	10	5
CH_4	5	10	5
CO_2	5	0.1	15

[a] N/A = Not analyzed.

to the other two instruments. In fact, GC–MS has sensitivity of 1 ppbv or below in 3 out of 5 analytes evaluated. While HID showed superior performance when hydrogen was the analyte, DID was superior to HID for oxygen determination.

Linearity was evaluated over the range of 10 ppbv to 10 ppmv for several impurities for each detector utilizing dynamic blending. Analytes for each detector were chosen from those for which the individual detector had sufficient sensitivity. Fig. 2a–c summarizes the results achieved for each detector. While both DID and GC–MS demonstrated linear behavior over this range, HID showed significant curvature. The exact concentration–response relationship has not been explored further because it seems likely that several types of expressions could approximate the curvature over such a narrow data range. Because of the relatively small dynamic range of this detector, extending the range of this evaluation is not possible.

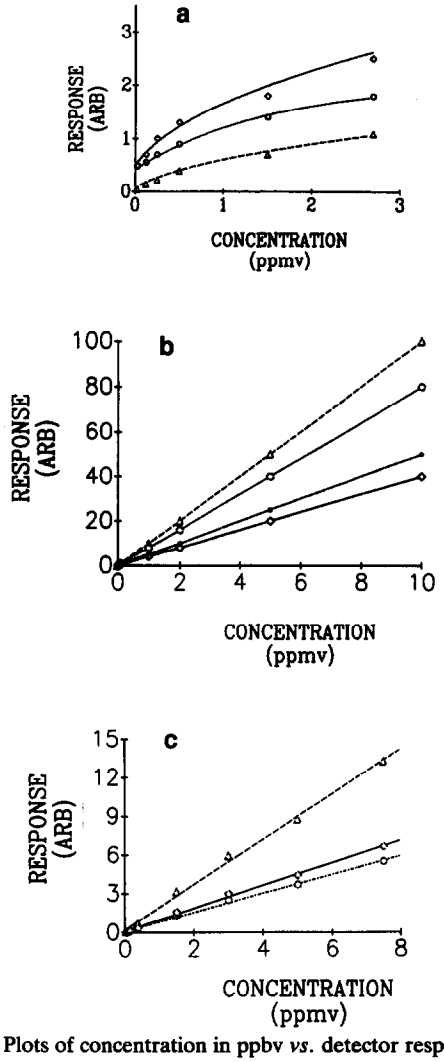

Fig. 2. Plots of concentration in ppbv *vs.* detector response in arbitrary units for the three detectors. Response units are not comparable for the three plots. (a) HID response for hydrogen (△), argon (○), and nitrogen (◇). (b) GC–MS response for oxygen (△), nitrogen (○), methane (◇), and carbon dioxide (●). (c) DID response for nitrogen (◇), carbon monoxide (○), and methane (△).

4. Sample matrix effects

While the above performance parameters are significant, helium is only one of many potential sample matrices of interest to the semiconductor industry. Often it is impossible or impractical to use heart-cutting or backflushing techniques to reduce or eliminate the sample matrix. Therefore it is important to consider the effect of sample matrix on each detector's performance. The first consideration is compatibility with materials of construction of the detector. While this is extremely important, this information is readily available in the literature, and will not be considered further. Other influences of balance gas include the tendency of certain gases (*e.g.*, oxygen) to quench the discharge of the DID

system, making it unusable with these gases. Also to be considered are baseline recovery after introduction of the major sample component, and recovery of detector response during and after the baseline recovery period.

To evaluate baseline recovery, a stable baseline was achieved with each detector with the appropriate parameters adjusted to achieve approximately 0.1 ppmv sensitivity for nitrogen. A sample of high purity argon was injected into each system, and the detector's ability to return to initial baseline was monitored. Fig. 3 illustrates each detector's ability to recover, expressed as a percentage of electrometer output for the HID and DID systems, and as a percentage of background signal at $m/z = 28$ for the GC–MS system. While both the DID and the GC–MS systems recovered within the time to make one analysis (with GC–MS it was almost immediate), over two hours were required for the HID system to recover. Since dead volume within packed columns was a suspected issue, the DID part of the experiment was run with both packed and PLOT columns, and similar results were achieved in both cases.

To evaluate response recovery, detector response to approximately 2 ppmv of nitrogen in helium was measured utilizing the same detector settings as in the baseline recovery study. Then, a sample of high purity argon was injected into each system. Finally, the helium mixture was repeatedly reanalyzed until detector response reached initial response levels. The results in Fig. 4 are plotted as a percentage of initial response. Again, both the GC–MS and DID

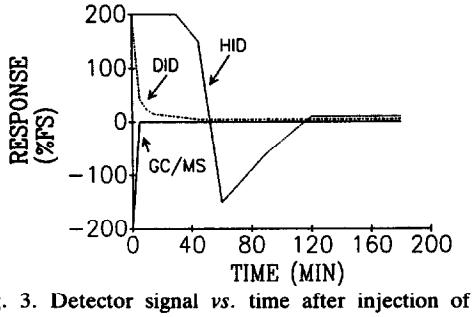

Fig. 3. Detector signal *vs.* time after injection of sample matrix of argon.

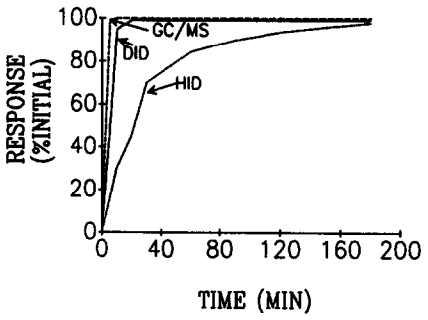

Fig. 4. Detector response *vs.* time to 2 ppmv nitrogen in helium after injection of a sample matrix of argon.

systems recovered within the time required for a single analysis, while the HID system experienced response suppression for a significant period after baseline recovery was achieved.

5. Detector stability

Gas chromatographs are often used as on-line analyzers. They are also used in laboratories where a high sample throughput is important. In both applications, detector stability is an important consideration. Both baseline drift and detector response can be considered as a function of stability. Both were monitored over a five-day period, using the same criteria and detector parameters as were used in the matrix effect evaluation. Fig. 5 illustrates baseline drift of the three detectors over this period. Both the DID and the HID systems show excursions of over 10% during this period, with the HID system showing more extreme excursions both positive and negative directions. Background

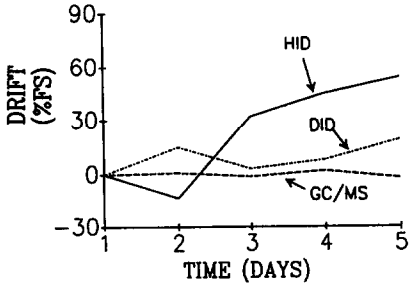

Fig. 5. Baseline drift over five days.

Table 2
Comparison of the detection systems evaluated

System	Advantages	Disadvantages
HID	- Best sensitivity for H_2 - Some identification of impurities	- Poor O_2 sensitivity - Balance gas effects - Stability
DID	- Excellent stability - Excellent sensitivity	- Poor H_2 sensitivity - O_2 balance gas effect
GC–MS	- Most sensitive - Most stable - Least affected by matrix - Positive impurity identification - Limited chromatography necessary	- Cost - $m/z > 10$

signal for the GC–MS system changed little over the five-day period.

Fig. 6 shows the change in detector response to 2 ppmv nitrogen over the same period. The poor response stability of the HID system requires frequent recalibration for on-line use, while both the DID and GC–MS systems demonstrate calibration drift of less than 10% over this period, lending themselves to less frequent calibration. This makes these instruments more amenable to on-line applications.

6. Summary

Table 2 presents a summary of the evaluation discussed here, with pertinent miscellaneous facts. Generally, the DID or GC–MS system should be considered the optimum choice where detector stability is important. Sensitivity of the DID and HID systems is roughly comparable, with each having distinct advantages for specific analytes. While GC–MS provides superior performance for most parameters considered here, the cost of a research-grade instrument as a routine analyzer may be prohibitive in many cases. No one single detector can be shown to be ideal in all situations, however the facts presented here should provide the basic information necessary to choose the right detector for most common gas analysis applications.

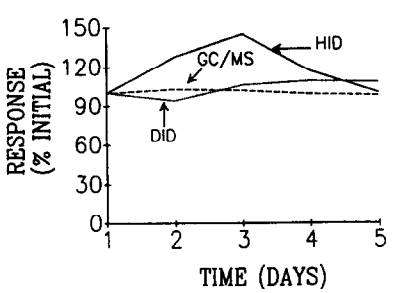

Fig. 6. Detector response to 2 ppmv nitrogen over five days.

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