

Application Brief AB-066

GASID APPLICATION PERFORMANCE I: EXPERIMENTAL METHODOLOGY AND REPRESENTATIVE RESULTS

Introduction

The GasID is a new infrared analyzer for identifying hazardous gases and vapors at or below IDLH levels. It works by recording the molecular fingerprint of an unknown compound and comparing it to libraries of reference fingerprints. The library hit which best resembles the unknown spectrum is used to identify the compound. For HazMat response, the GasID fills a gap between hand-held meters (CGIs, PIDs, colorimetric tubes, etc.) which only detect gases and vapors at low levels, and higher end instruments (such as GC/MS) which require relatively long analysis times and sophisticated operation. This application note describes how the GasID performance is characterized in the laboratory, and gives results for gases and vapors from various chemical families.



Experimental

Performance Verification. The GasID system was run overnight to ensure full stabilization prior to collecting any data. Each day of analysis, the GasID laser calibration was verified by comparing several peaks in a measured transmission spectrum of polystyrene to the published NIST frequencies. Three baseline noise spectra were also recorded in the absence of any sample.

Gas Generation. Samples were generated using one of two methods, depending on whether the compound was a gas or vapor at standard conditions. Gases were purchased as certified mixtures with nitrogen. The gas concentrations c_{gas} (ppm) of interest were obtained by combining each stock gas having known concentration c_{stock} (ppm) and flow F_{stock} (mL/min) with high purity nitrogen flowing at F_{N_2} (mL/min) through a manifold:

$$c_{gas} = c_{stock} \frac{F_{stock}}{F_{stock} + F_{N_2}} \quad (1)$$

The combined gas flows were passed through the GasID cell, and sample flows were maintained during data collection. For the thermal desorption gas experiments,

the flows were passed directly through the sorbent tube holder, which was subsequently analyzed on the GasID.

Vapor Generation. Vapors of volatile liquids were generated using a closed-loop recirculating chamber. A given volume of liquid (typically several microliters) was injected into the chamber, which had a well-defined volume. The molar vapor concentration c_{vapor} (ppm) was calculated using the sample density d (g/L), molar mass MM (g/mol) and volume V_{sample} (L), as well as the chamber volume $V_{chamber}$ and the molar volume of air (22.4 L/mol):

$$c_{vapor} = \frac{d \times V_{sample} \div MM}{V_{chamber} \div 22.4} \times 10^6 \quad (2)$$

The ambient air and sample vapor were circulated within the chamber loop (which incorporated the GasID cell) to establish an equilibrium sample concentration. The vapor samples were kept static during data collection. For the thermal desorption vapor experiments, a large volume (140 L) chamber was used to simulate a contaminated environment, which was sampled with the GasID sorbent tube holder and hand pump. The tube holder was subsequently analyzed on the GasID.

Spectral Analysis. In all experiments, a new background was collected prior to introducing sample into the GasID cell. The signal was monitored visually to ensure that the spectral peaks had stabilized before collecting each sample spectrum (except for the thermal desorption measurement, which was automated through the GasID software). Following each analysis, the GasID cell was flushed with either dry air or nitrogen for several minutes to ensure it was clean. All spectra were recorded at 4 cm^{-1} resolution and 128 co-added scans, and at least three replicate spectra were recorded for each sample at each concentration. Atmospheric water vapor and carbon dioxide were compensated prior to all calculations.

Calculations

Limit of Detection. In these experiments, the limit of detection (LOD) is defined as the lowest concentration of sample that produces a single peak in the infrared spectrum whose absorbance value is three times the baseline noise level.

Table 1. Detection and Identification Limits for Representative Gases and Vapors.

Compound	Chemical Family	IDLH (ppm)	LOD (ppm)	LOI (ppm)	TDF ₀
Acetone	Ketone	2500	4.2	24	4.8
Ammonia	Base	300	8.9	60	×
Benzene	Aromatic	500	1.2	95	5.7
Hexane	Hydrocarbon	1100	1.8	10	5.6
Hydrogen Chloride	Acid	50	18	140	×
Isopropanol	Alcohol	2000	5.2	26	3.7
Methylene Chloride	Alkyl Halide	2300	4.9	23	4.9
Propane	Hydrocarbon	2100	8.8	33	×

× = compound not trapped well by TD sorbent.

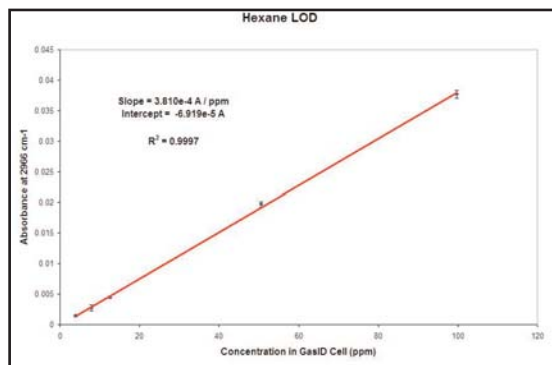


Figure 1. LOD determination using the maximum spectral absorbance values of a compound over a range of concentrations.

In other words, it's the lowest concentration at which a compound can be seen, but not necessarily identified. The LOD for each sample was determined by averaging the maximum peak absorbance values at each concentration and performing a linear regression fit of the absorbance versus concentration data (Figure 1). The slope m (A/ppm) and intercept b (A) of the fit were used with the baseline noise level N (A) to calculate the LOD:

$$LOD = \frac{3N - b}{m} \quad (3)$$

The noise levels were determined by averaging the peak-to-peak absorbance values from 1150 – 1050 cm^{-1} in the baseline noise spectra for each day.

Limit of Identification. Though LOD is a good measure of absolute sensitivity, it is not the best metric for determining the GasID analytical performance. Therefore, the limit of identification (LOI) is defined at the lowest concentration of sample that produces an entire spectrum which matches its corresponding library spectrum with at least 0.95 similarity. In other words, it's the lowest concentration at which a user can confidently identify a gas vapor. The LOI for each sample was determined by searching each experimental spectrum against all 5,500 GasID library spectra, and plotting average similarity versus concentration (Figures 2). The point at which a given curve intersects the similarity of 0.95 (as determined by visual inspection) is reported as the LOI for that sample.

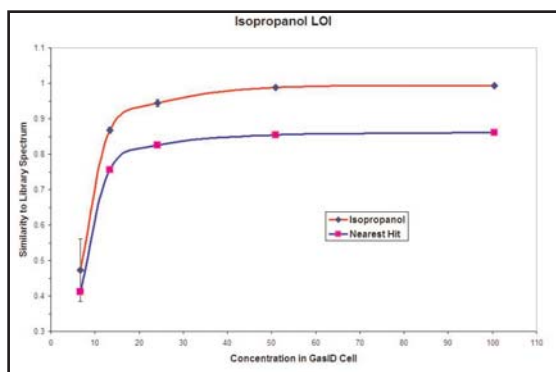


Figure 2. LOI determination using spectral similarity values of a compound over a range of concentrations. Isopropanol (red) has a LOI of 26 ppm and its nearest hits (blue) have much lower S values, indicating good discrimination of Isopropanol across the concentration range.

Thermal Desorption Factor. When an environment is sampled with a collection device such as a Tedlar™ bag, the compound concentration inside the bag is the same as its concentration in the environment. This type of device does not provide any preconcentration of the sample. Therefore, the LOI values reported here are the concentrations one should be able to identify when simply capturing a volume of contaminated air. This sampling is best for relatively high concentration

environments, inorganics, and other compounds which are not trapped well by thermal desorption tubes. When an atmosphere is sampled by thermal desorption (TD), the sorbent acts as a filter that selectively captures the contaminating compound. In this manner, the sample is preconcentrated by an enhancement factor, and the concentration in the GasID cell is actually higher than in the environment. This sampling is ideal for relatively low level organic contaminants, such as VOCs.

In these experiments, the ability of the GasID sampling device to preconcentrate compounds is described by the thermal desorption factor (TDF). Mathematically, the TDF is the ratio of the maximum spectral absorbance of a compound A_{TD} following TD sampling of an environment of a given concentration, compared to the maximum absorbance of the compound A_{calc} at the same concentration with no TD enhancement:

$$TDF = \frac{A_{TD}}{A_{calc}} \quad (4)$$

A_{calc} values were determined for a given compound using its LOD fit equation and the environmental concentrations (within the combined gas flow or vapor chamber). Since the TDF is dependent on concentration, it was determined at three different compound ppm values, and a linear fit was performed to model the $f(c)$ relationship (Figure 3). The TDF values

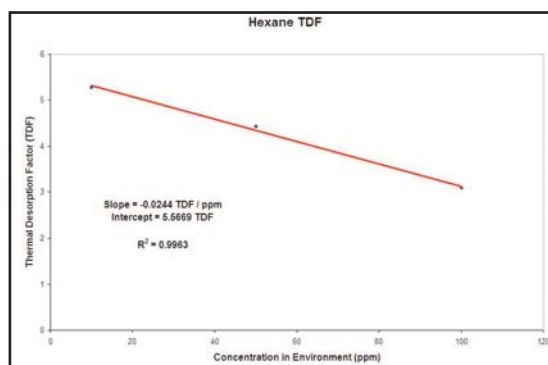


Figure 3. TDF values over a range of concentrations. The TDF represent the highest attainable TDF value as the concentration approaches zero.

reported here represent the highest possible enhancement factors as the compound concentrations approach zero ppm (where TD sampling is most useful):

$$TDF_0 = \lim_{c \rightarrow 0} f(c)$$

For example, if an environment is contaminated with acetone ($TDF_0 = 4.8$, see Table 1) and is sampled with the GasID TD device, the acetone in the GasID cell will be up to five times more concentrated than in the environment. One must remember that the true TDF of a compound at any given time is dependent on many things, including sample dispersion in the environment, atmospheric conditions, and sampling parameters. In this study, the default GasID parameters were used, including a pump rate of 200 mL/min, 10 min sampling time, 150 mg of Tenax TA™ sorbent, and a desorption temperature of 200 °C.

Results

Table 1 summarizes the LOD, LOI and TDF results for all the compounds studied here. These gases and vapors were chosen to represent a variety of chemical families and IDLH levels. Additional results will be published as more compounds are characterized by the methodology described in this note.