The Effect of Fuel Air Purity on FID Sensitivity

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Poster Session Report

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Abstract

In the field of capillary gas chromatography, the presence of sensitive detectors and trace analyte samples increases the need for dry, clean fuel gases. Laboratories in an industrial setting often maintain several gas chromatographs in continuous operation. Since large volumes of fuel gases are consumed daily, gas cylinders are changed almost as frequently. Usually the fuel air is of breathing quality and is introduced either directly or after drying via a molecular sieve trap. The objective of this study is to compare flame ionization detector sensitivity vs. air purity under isothermal conditions. This study included air sources as follows: the Parker Balston® Type HPZA-3500 Zero Air Generator, breathing air (cylinder without scrubbers), ultra zero air (cylinder), and filtered house air.

The study proceeded as follows:

1. compared baseline runs taken at 10 minutes, 60 minutes, and 12 hours
2. compared runs of a 50 ppm trace alkane sample, and
3. compared runs of a 1 ppm trace alkane sample for the air sources with the exception of the house air. Finally, both breathing and generated air studies were repeated under optimized conditions and without air scrubbers. This final study also included the filtered house air.

A comparison of the chromatograms for the baseline and the trace component runs showed that both the Parker Balston® Type HPZA-3500 Zero Air Generator and the ultra pure air produced lower signals and better sensitivity: as shown by increased peak area counts. These baseline were also more stable than either the breathing air or the house air. In addition to the lower and stable baseline, the air generator had the advantage of providing a continuous source of air.

Table 1: Chromatographic Conditions

Column	HP-1, 12 m x 0.2 mm, 0.33 µm df
Oven Temperature	110°C
Inlet Temperature	250°C
Detector Temperature	300°C
Split Ratio	28:1
Carrier Gas	0.8 ml/min He
Fuel Gases	30 ml/min H and 300 ml/min Air
Samples	50 ppm and 1 ppm decane, undecane

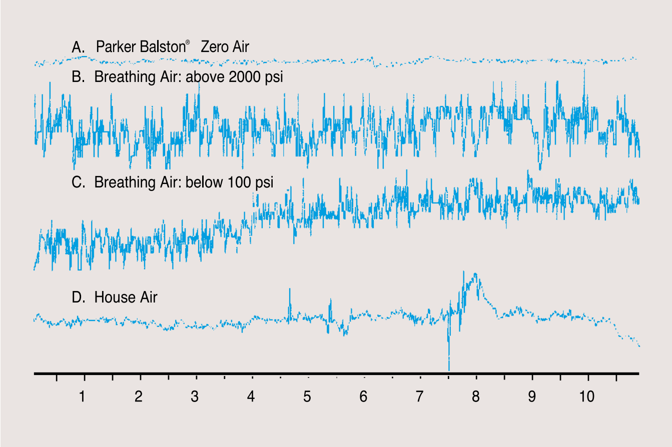

Figure 1: *Baseline Signals – Random spike at 6 min. for Zero Air (A). Baselines are raw data (mA) on equivalent scales*

Introduction

In a previous study, baseline and trace alkane sample data was obtained utilizing a HP 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a 12 meter methyl silicone column (Hewlett-Packard, Avondale, PA). The air sources in that study were the Parker Balston® Type HPZA-3500 Zero Air Generator, an ultra pure air cylinder, and a breathing air cylinder. An improvement in both the baseline and the peak areas was noted for the Parker Balston® zero air, in comparison with the breathing air. In this study, the Zero Air was compared with breathing air at the two specified cylinder pressures of above 2000 psi and below 100 psi and with filtered house air.

For each air source, this study proceeded from a 30 minute baseline run to triplicate runs of each standard: 1 ppm and 50 ppm decane, undecane, and dodecane in iso-octane. Between each air supply, the system was allowed to equilibrate several hours before the baselines were run. Chromatograms showing area counts were generated by a HP 3396A integrator for each run. This peak area data was statistically compared using Statview, a Macintosh statistics software package.

Experimental

A 30 minute baseline and triplicate runs of the 1 ppm and the 50 ppm alkane standard of the air supply were obtained under the conditions listed in *Table 1* for the following air sources:

1. Parker Balston® Type HPZA-3500 Zero Air Generator
2. Breathing Air Cylinder (at pressures above 2000 psi and below 100 psi)
3. House Air via Parker Balston® DXE and BXE filters

The house air was filtered before introduction to the GC due to its potential to damage or contaminate the system by introducing particulate.

Results

Optimized carrier gas flow rate and split ratio were used in order to produce better quantitation. Similar to previous baseline runs, the zero air signal (average signal during blank runs) was lower than either of the other air sources (*Figure 1 and Table 2*). In addition, the zero air undecane peak area counts for both the 50 ppm and 1 ppm standards were significantly larger than those of either the breathing or house air (*Table 2*). Tables 3 and 4 contain the statistical comparisons of the average peak area counts for both the 50 ppm and 1 ppm standards respectively.

Parker Balston® zero air was used as the reference in the paired t value and 2-tail probability determinations. The paired t value critical values at the 97.5 confidence level were 3.18 for 3 degrees of freedom and 4.30 for 2 degrees of freedom. The calculated values in both the 50 ppm and the 1 ppm runs were larger than the respective critical values; therefore, the differences in area counts were not due to random fluctuations. In addition, the 2-tail probabilities were below the absolute critical value of 0.05. This occupance supports the theory of non random differences in area counts as determined by the paired t test. Since both the paired t values and 2-tail probability values were outside their respective critical ranges, the differences in peak areas were not due to random fluctuations[1]. These differences were due to the flame purity.

Table 2: Baseline Data

Air Source	Parker Balston®	Breathing Air > 2000 psi	Breathing Air < 100 psi	House Air
Signal	12	22	18	22

Table 3: Undecane Peak Area Data 50 ppm Standard Data

Mean Area Counts	10878	9784	9181	8206
Standard Deviation	426	194	179	89
Paired t Values	–	3.8	8.75	14.82
Probability (2-Tailed)	–	0.032	0.003	0.001
Degrees of Freedom	3	3	3	3

[1] *Abacus Concepts, Statview II, Abacus Concepts, Inc.: California 1987*

Table 4: Undecane Peak Area Data 1 ppm Standard Data

Mean Area Counts	1744	1629	1531	1404
Standard Deviation	2.1	35.2	20.8	21.1
Paired t Values	–	4.77	19.57	27.06
Probability (2-Tailed)	–	0.041	0.003	0.001
Degrees of Freedom	2	2	2	2

Conclusion

The Parker Balston® Type HPZA-3500 Zero Air Generator has advantages over the conventional sources of air for GC analysis. A lower and more stable baseline signal can be obtained. Due to lower baseline noise, the signal-to-noise ratio is larger, giving rise to higher sensitivity or larger peak areas. A comparison of peak areas for the alkane standards gave similar results. The air generator produced peak areas which were more than 12% of the breathing air peak areas. Not only does the air generator give better baselines. In addition, the air generator also removes the need for frequent cylinder changes, thus saving time.

[1] Abacus Concepts, Statview II, Abacus Concepts, Inc.: California 1987.

Dr. Harold M. McNair is Chairperson of the Chemistry Department at Virginia Polytechnic Institute and State University. Dorothea J. Jeffery and Gregory C. Slack are currently undergraduate students at VPI & SU.

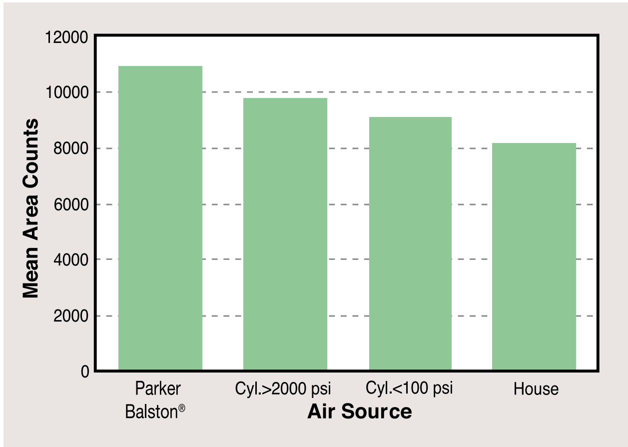

***Figure 2:** Average Area Counts – 50 ppm Undecane.*

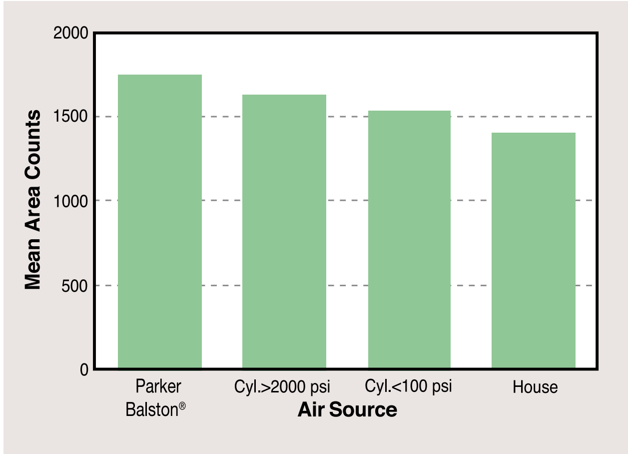

***Figure 3:** Average Area Counts – 1 ppm Undecane.*