

## UNDERSTANDING AND OPERATING THE PPBRAE



### Introduction

The ppbRAE parts per billion (ppb) Volatile Organic Compound (VOC) Monitor (Model PGM-7240) is the most sensitive Photo-ionization Detector (PID) on the market. The ppbRAE is a broadband detector, and is able to measure a few ppb of VOCs in real-time. Our patented PID sensing technologies and the unique zeroing gas solution make the ppb-level VOC detection practical.

### Calibration

#### (1) Zero Calibration

Ambient air contains a few 10's to a few 100's of ppb of organic vapors or other UV-ionizable compound. These levels can usually be neglected with conventional ppm level PIDs (e.g. the MiniRAE 2000), but are very significant to the ppbRAE that works down to ppb level. Therefore, an appropriate zeroing scheme and zero gas solution are extremely important for the ppbRAE to perform correctly in the low ppb range.

#### (1.1) Zeroing Scheme

In general, the purpose of zero calibration is to determine the signal for the background where the gas of interest exists. The zero signal consists of the electronic blank plus the signal due to the matrix gas. Ideally, during the zero calibration, both of the electronic blank and the signal due to the matrix should be canceled. Therefore, the matrix gas should be used as zero gas for zero calibration.

When the ppbRAE was introduced, there was some concern as to the availability and variability of portable cylinders of highly pure zero air. Therefore, V1.08 and earlier firmware versions used electronic zeroing to avoid this uncertainty. The electronic zero is the signal when the lamp is off, i.e. the electronic blank. This former zeroing scheme does not cause significant issue when the measurement concentration is in ppm range, because the matrix gas signal is relatively negligible compared with the signal of the gas of interest. However, it was discovered that when the measurement concentration is in

the low ppb range, multiple units have some variability when measuring the same ambient air after the same calibration. This is because the matrix gas signal with the lamp on becomes significant and may vary from unit to unit and the zeroing scheme in firmware V1.08 and earlier version do not cancel it out.

Instead, V1.20 and later firmware versions use zero gas to zero the unit thereby canceling both the electronic blank and matrix gas signal. Therefore, the consistency amongst units at low concentration is markedly improved.

An appropriate zero gas is required for zero calibration with V1.20 and higher version firmware. The lower the concentration of the VOC in the zero gas is, the better the accuracy of the measurement in the low ppb range is. Any zero gas for ppb zeroing preferably has less than 10 ppb total hydrocarbons and must have the same matrix as measurement. For example, if the ppbRAE is used to measure ppb level VOC in air, the instrument must be zeroed with "ultra zero" air that consists of 21% oxygen and 79% nitrogen.

#### (1.2) Zero Gas Sources



RAE Systems has developed the single-use VOC zeroing tube (RAE P/N 025-2000-010, as shown below) as the best and the most convenient provider of "ultra zero" air by purifying the ambient air running through it. Possible ppbRAE zero gas sources are listed below in order of preference:

- 1) Single-use VOC zeroing tube (RAE Systems P/N 025-2000-010);
- 2) Large (>200 scf) laboratory ultra-zero air cylinder (<10 ppb VOC);
- 3) Disposable zero air cylinder (e.g. the 34-L zero air cylinder, RAE Systems P/N 600-0024-000, as shown above);
- 4) Clean outdoor air;
- 5) Multiple-use organic vapor zeroing filter (RAE Systems P/N 490-0006-000, as shown below).



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The figure below summarizes typical results with the various zero sources. It can be seen that the VOC zeroing tube provides the best zero standard. Large or disposable cylinders must use a dedicated regulator to prevent cross contamination if the regulator was also used for span gases. The VOC zeroing tube rules out this issue and offers more portability for field use.

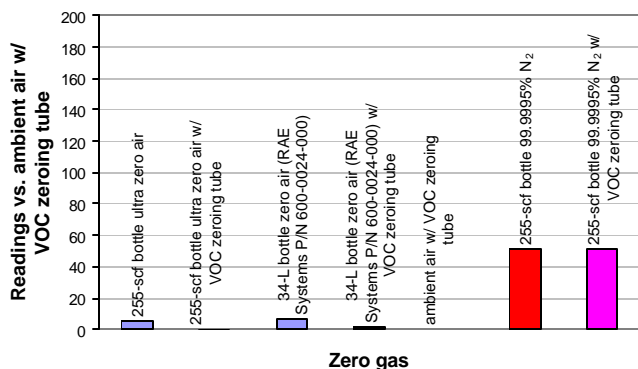


Before the development of the VOC zeroing tube, the multiple-use organic vapor zeroing filter has been a recommended alternative zero gas solution for the ppbRAE. The organic vapor zeroing filter has the following issues: (1) the container is plastic and may absorb and release organic vapors and plasticizers depending on the concentration difference and temperature. (2) The two ends of the filter are open to environment and contaminants can enter the filter. (3) It allows multiple-use and hence makes it difficult to track the functionality status. As the result of the issues listed above, the repeatability and consistency between different charcoal filters is not guaranteed. For this reason the organic vapor zeroing filters should be used only as a last resort when none of the other methods are available, recognizing that they may cause 10's of ppb background to be subtracted. The VOC zeroing tubes get rid of those shortcomings of the conventional charcoal filter. First of all, the container is a glass tube and does not have the issues of plastic container; second of all, the two ends are airtight glass-sealed; third of all, it is single use only.

Clean outdoor air is often a good source of zero air, but there is no simple way of ensuring <10 ppb VOC levels.

Pure nitrogen causes a zero shift from the air baseline and should not be used for zeroing the ppbRAE, even though span gases at >1 ppm in nitrogen are still acceptable for span calibration.

**Zero gas comparison**



The consistency between different VOC zeroing tubes is very good (amongst 5 VOC zeroing tubes, the consistency zeroing from ambient air is about ±1 ppb). The flow resistance of the VOC zeroing tube only causes 30-40 mL/min (ca. 5%) sample flow rate reduction on the ppbRAE. The VOC zeroing tube absorbs largely propane, propene and higher hydrocarbons, but not ethane, ethylene or methane.

**(2) Span Calibration**

A source of 10 ppm isobutylene is connected to the ppbRAE inlet for the span calibration. Preferably the gas is supplied from a Tedlar bag or of cup or “Tee” to avoid pressure and flow rate differences. After both zero and span calibration, the ppbRAE is ready for use. It is easy to check if the ppbRAE after calibration reads correctly or not. In the presence of a known concentration of detectable gas, the ppbRAE should display within a specified accuracy of ±20 ppb or ±10% of readings, whichever is greater.

**Consistency between Different Units**

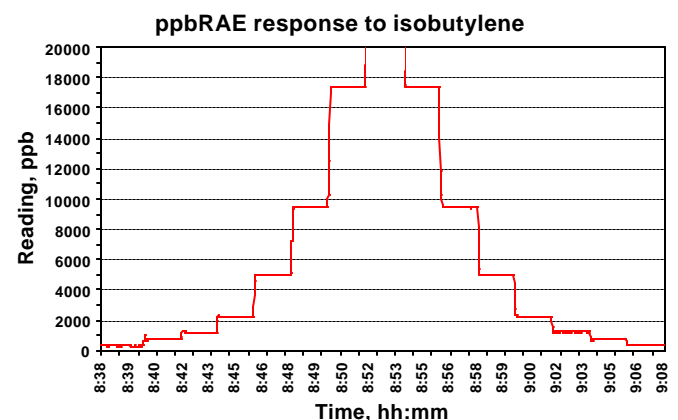
6 ppbRAEs are tested for measurement consistency. The units are zeroed with ambient air from a VOC zeroing tube and span calibrated by 10.0 ppm isobutylene. The table below shows that at a isobutylene standard concentration below 200 ppb, into which the VOC concentration of the ambient air generally falls, a maximum variation of ±10% or ±15 ppb, whichever is greater, can be achieved. Ambient air measurements have greater variability due to sample fluctuations. The sample probes of the units are put together less than 10 cm apart from each other. The continuous monitoring results through 50 sec (2 sec per datum point) are averaged to represent the “true” response to the ambient air. With all the units considered, the average result of each unit presents a maximum variation less than ±10% or ±20 ppb, whichever is greater. This verification shows that the consistency of ppbRAE using the new gas zero scheme (firmware V1.20 and higher version) is an improvement over the former electronic zero (firmware V1.08 and the former versions).

Gas type	Isobutylene standard		Ambient air
	<200 ppb	>200 ppb	
Maximum variation of 6 ppbRAEs	±10% or ±15 ppb	±6%	±10% or ±20 ppb

**Sample Measurements**

The data shown below represent typical performance of ppbRAEs, and should not be treated as the specification.

The following Figure shows the ppbRAE response to various concentrations of isobutylene in increasing and decreasing

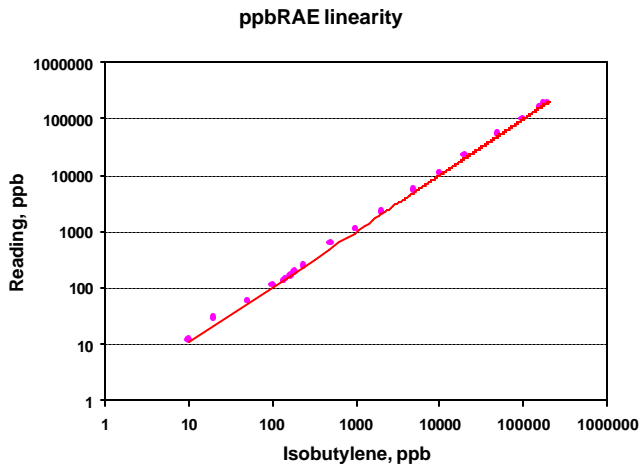


staircase steps of each concentration for two minutes. The response and recovery time of 90% changes is less than 5 seconds. All measurements are accurate and repeatable within

the specification whether switching the gas from low to high concentration or vice versa.

The Figure below shows that the ppbRAE gives a linear response in the range of 10 ppb to 200 ppm. Various concentrations of isobutylene were diluted from the same

change of gas concentrations above the ambient background level.



etup and cylinder. It should be noted that if different cylinders were used, differences in background impurities from cylinder to cylinder could cause a significant error in this kind of ppb level measurement. Inter-connecting tubing and Tedlar bags can also contribute significant error due to absorption at low ppb levels or release of plasticizers or previously adsorbed compounds. The user needs to be extremely cautious to avoid contamination when experimenting at the low ppb levels. An accurate and clean gas distribution and dilution system is recommended when performing this type of evaluation.

### **Semi-volatile or Reactive Chemicals**

Heavy or reactive chemicals (e.g. hydrazine, phenol, methyl salicylate, dimethyl methylphosphonate, etc.) generally cause sample transferring loss due to the adsorption by the internal surface of the sample probe and the barrier (filters) in the sample probe. As a result, the response is slower or not visible for a period of time when the concentration of the chemical is low. Removing all the filters (including the mineral wool filter, the C-filter, and the stainless steel porous disk filter) is recommended for measuring those heavy or reactive chemicals. In such a case, attention should also be paid to calibrate the unit in the same configuration with the filters removed.

### **How to See Incremental Concentration Changes**

In ppbRAE, users have an option to read the real-time data as an incremental value from the background reading. The number shown on ppbRAE will be the amount detected, minus the background when the “Cancel Background” feature is selected. A superscript “+” flashes in the measurement display to indicate that the background is cancelled. The background can be reinstated when the “Show Background” is activated. It should be noted that this feature of the “Cancel/Show Background” applies to the display only. The datalog function continues to record values that include the background whether or not it is shown in the instantaneous reading display. This feature will allow the user to see clearly the incremental