

Understanding And Operating The ppbRAE Plus



Introduction

The ppbRAE Plus parts per billion (ppb) Volatile Organic Compound (VOC) Monitor is the most sensitive Photoionization Detector (PID) on the market. The ppbRAE Plus 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

Zero Calibration

Ambient air contains a few tens to a few hundreds of ppb of organic vapors or other UV-ionizable compounds. These levels can usually be neglected with conventional ppm-level PIDs (e.g., the MiniRAE 2000), but are very significant to the ppbRAE Plus, which works down to the 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.

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. Both the electronic blank and the signal due to the matrix ideally should be canceled. Therefore, the matrix gas should be used as zero gas for zero calibrations.

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; that is, electronic “blank.” This former zeroing scheme does not cause significant issue when the measurement concentration is in the 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 versions 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 among 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.

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-liter zero air cylinder, RAE Systems p/n 600-0024-000, as shown here);
4. Clean outdoor air.
5. Multiple-use organic vapor zeroing filter (RAE Systems p/n 490-0006-000, as shown below).



Figure 1 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 was 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 the environment, and contaminants can enter the filter; (3) it allows multiple-use and hence makes it difficult to track the functionality status. As a result of the issues listed above, the repeatability and consistency among 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 tens of ppb background to be subtracted.

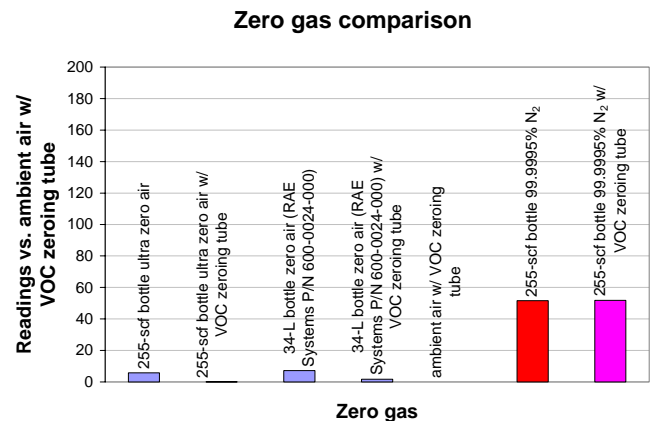
The VOC zeroing tubes get rid of the conventional charcoal filter’s shortcomings. First, the container is a

glass tube and does not have the issues of plastic containers. Second, the two ends are airtight and glass-sealed. Third, it is designed for 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 Plus, even though span gases at >1 ppm in nitrogen are still acceptable for span calibration.

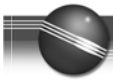
Figure. 1



The consistency between different VOC zeroing tubes is very good (among five VOC zeroing tubes, the consistency zeroing from ambient air is about ±1 ppb). The flow resistance of the VOC zeroing tube only causes 30 to 40mL/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.

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, a cup, or a “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 reads correctly after calibration. 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 Among Different Units

Six ppbRAE Pluses are tested for measurement consistency. The units are zeroed with ambient air from a VOC zeroing tube and span calibrated with 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 $\pm 10\%$ 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 located less than 10cm apart from each other. The continuous monitoring results through 50 seconds (2 seconds 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 $\pm 10\%$ or ± 20 ppb, whichever is greater. This verification shows that the consistency of ppbRAE Pluses using the new gas zero scheme (firmware V1.20 and higher version) is an improvement over the former electronic zero (firmware V1.08 and former versions).

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

Sample Measurements

The data shown in Figure 2 represent typical performance of ppbRAEs, and should not be treated as the specification.

Figure 2.

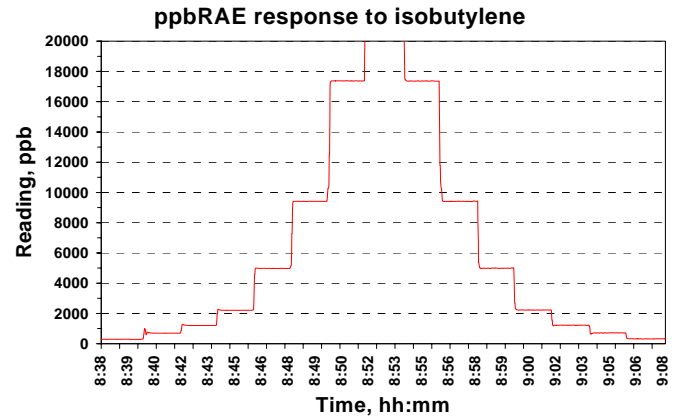


Figure 2 shows the ppbRAE response to various concentrations of isobutylene in increasing and decreasing staircase steps of each concentration for two minutes. The response and recovery time of 90% changes is less than 5 seconds. All measurements are accurate and repeatable within the specification whether switching the gas from low to high concentration or vice versa.

Figure 3 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 setup 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. Interconnecting 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.

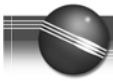
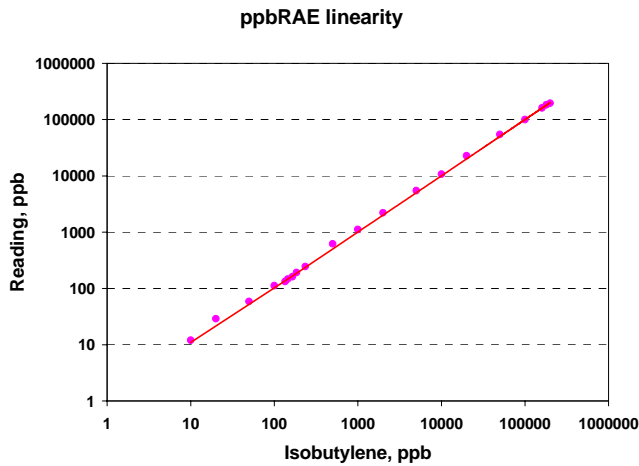


Figure 3.



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 heavy or reactive chemicals. In such cases, attention should also be paid to calibrate the unit in the same configuration with the filters removed.

How to See Incremental Concentration Changes

With a ppbRAE Plus, users have an option to read the real-time data as an incremental value from the background reading. When the “Cancel Background” feature is selected, the number shown on the ppbRAE Plus indicates the amount detected, minus the background. A superscript “+” flashes in the measurement display to indicate that the background is cancelled. The background can be reinstated when “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 regardless of whether it is shown in the instantaneous reading display. This feature allows the user to clearly see the incremental change of gas concentrations above the ambient background level.