MEASURING PID CORRECTION FACTORS FOR VOLATILE COMPOUNDS WITH RAE SYSTEMS INSTRUMENTS

This Technical Note details how to develop Correction Factors (CFs) for new compounds measured by MiniRAE 3000, MultiRAE, AreaRAE, ToxiRAE Pro PID and other RAE Systems instruments with photoionization detectors (PIDs). Correction Factors are used to allow measurement of a large variety of compounds while calibrating with only a single standard gas, commonly isobutylene.

Ideally, CF is independent of the type of instrument and lamp size, as long as the PID lamp energy is the same. However, the correction factors may vary, depending on the following factors:

• PID lamp and sensor design for individual models and variability between instruments of the same models.

• Gas delivery ducts and sensor plates differ for single-sensor instruments (MiniRAE, ToxiRAE Pro) and multi-sensor ones (MultiRAE, AreaRAE) due to design and polymeric materials used.

• Reactive gases may either react or be adsorbed by gas plates. As a result, gases may not reach a PID sensor with the same concentration of VOCs as in the tested atmosphere.

Due to these reasons, CFs for different types of instruments may differ for some gases, as shown in Table 1.

CFs

Chemical	Mini RAE 3000	MultiRAE Pro	ToxiRAE PID Pro	Mini RAE 2000
Hexane	5.1	3.4	3.9	4.3
Benzene	0.5	0.5	0.5	0.5
NH3	9.5	51.4	35.9	9.7
NO	5.6	20.1	15.1	5.2
MEK	1.0	1.0	1.0	0.9

Table 1. CFs measured with different instruments.

The matrix of the gas has important effects on the PID response. Aside from the basic components of air, matrix gases including water vapor can affect the response of a PID. PIDs are commonly calibrated using a dry calibration gas and then used to measure in ambient air with various degrees of relative humidity. CFs listed in RAE Systems Technical Note TN-106 are measured in dry air and apply only to this condition. High humidity may cause a quenching effect resulting in the PID under-reporting actual gas concentrations. A correction factor measured with room air (usually 45% to 55% RH) is more representative of the actual use conditions. For most accurate measurement results, RAE Systems recommends that instruments be calibrated using the actual target gas and in environmental conditions that are as close to the conditions of the actual atmosphere being measured (in terms of humidity, temperature, and pressure).

Correction Factor Definition

The correction factor is defined as the response of isobutylene (IBE)-calibrated PID to an equal concentration (ppmv) of the compound of interest (Gas Y):

$$CF = \frac{\text{Instrument's IBE Response x Gas Y Concentration (ppmv)}}{\text{IBE Concentration (ppmv) x Gas Y Instrument Response}}$$

Thus, the higher the correction factor, the lower the sensitivity to the compound of interest. To account for any drift during the measurements, one can make isobutylene measurements before and after the sample measurements and take the average response to the isobutylene standard.

Tested Gas Concentrations

It is essential to prepare representative sample gas for accurate CF estimation. The gas concentration is always a trade-off between chemical properties of gas, gas preparation equipment, and instrument accuracy.

For CF estimation, it is preferable to use at least 50 to 100 ppmv for MiniRAE 3000, MultiRAE, or ToxiRAE Pro PID and at least 5 to 10 ppmv for a ppbRAE 3000 and MultiRAE Pro. Manufacturers usually supply gas blended with air or nitrogen with uncertainty of 2% to 10%.

To prepare gas from liquid or solid, only a small amount of chemical is necessary, as shown in Table 2.

Chemical	Concentration, ppm	Volume, µL
Acetone	100	6.6
Bromoform	100	7.9
Chlorobenzene	100	9.2
Dibromochloromethane	100	7.7
Dichloroethane	100	7.4
Ethanol	100	5.3
IPA	100	6.9
Proplyene Glycol	100	6.6
	38	2.5
	23	1.5

Table 2. Liquid volume vs. gas concentration.

Liquid and Gas Sample Preparation

In the case of liquids, extra care should be taken to manage the uncertainty due to sample preparation. Microliter syringes (e.g., Hamilton) are recommended to ensure precise liquid volume (5 µL, 10 µL). Uncertainty calculations for liquid volumes while using small syringe volumes are shown in Table 3.

Syringe Volume	Liquid Volume, µL	Syringe Volume, µL	Uncertainty, %
10 µL	10	0.2	2
	5		4
	2		10
5 µL	5	0.1	2
	2		5
	1		10

Table 3. Uncertainty % vs. liquid volume.

Denver Instruments balance XE-100A, used for solid chemicals, provides repeatability measurements of 0.0001 g (calculated based on STD, or standard deviation), which translates to values in Table 4.

Chemical Weight, g	Repeatability, %
0.002	88.9
0.0035	93.9
0.005	95.8
0.006	96.6
0.009	97.7

Table 4. Chemical weight vs. repeatability.

Low vapor pressure chemicals are able to create low concentrations of their vapors in the air. In this case, aforementioned uncertainties in gas preparation are even higher. To mitigate their effects, two glass jugs with high volume are recommended (e.g., 5 gallons and 12 gallons). Another approach is to prepare and measure at least two different concentrations of a gas.

Method for CF Development with RAE Systems instruments

CF accuracy depends on a gas quality, measurement conditions, and accuracy of PID instruments.

- Standard gas quality and their blend uncertainty is the prerogative of the supplier.

- Gas from liquid or solid depends on the chemical quality and factors discussed in previous paragraph.

- Gas from liquid and solid is prepared in the air at ambient conditions 45% to 55% RH and 20° to 23° C.

To calculate CFs accurately, a procedure based on statistical analysis was developed. Table 5 shows two statistical correction factor calculations with two instruments types (five units of each type) to determine CF accuracy stated for RAE Systems instruments.

In the first experiment, five instruments were tested with 100 ppm equivalent IBE, and the mean and STD were calculated. In this experiment a statistical accuracy for 95% confidence level (2σ for one-tailed normal distribution) of CF was calculated to be ±13.6% for MiniRAE 3000 (A1) and ±13.3% for MultiRAE Pro (A2) was achieved.

To further improve statistical accuracy for a 95% confidence level of CF, another gas concentration of 100 ppm IBE equivalent was prepared and tested with five MiniRAE 3000 and five MultiRAE Pro instruments to yield 10 data points for CF calculation. In this case, a statistical accuracy for 95% confidence level of CF was calculated to be ±9.9% for MiniRAE 3000 (B1) and ±9% for MultiRAE Pro (B2). This procedure yields better than 10% statistical accuracy for CF measurements with RAE Systems equipment.

	MiniRAE 3000		MultiRAE Pro	
	A1	B1	A2	B2
	106.7	107.6	101.4	103.2
	98.2	97.2	91.6	94.2
	103.2	98.2	102.1	101.1
	95.4	97.6	103.1	101.9
	95.8	99.1	102.8	100.0
Mean 5	99.9		100.2	
STD 5	4.9		4.8	
Mean 10		99.9		100.1
STD 10		4.4		4.0
95% conf. range	99.9± 13.6	99.9± 9.9	100.2± 13.3	100.1± 9.0

Table 5. CF accuracy calculation based on statistics.

CF Measurement Using Gas Standards

If a cylinder of standard gas in dry air is available, simply calibrate the instrument with isobutylene. For instruments with an option of 3-point calibration (MiniRAE 3000, ppbRAE 3000, MultiRAE, and MultiRAE Pro), use ambient air for zero, and 10 ppm and 100 ppm isobutylene.

For instruments with 2-point calibration (MultiRAE Lite, ToxiRAE Pro PID, RAEGuard PID family):

• If the concentration of the target gas is less than 50 ppm, use 10 ppm standard gas for calibration.

• If the concentration of the target gas is above 50 ppm, use 100 ppm standard gas for calibration.

A T-type tubing connection in between the gas cylinder and instrument is recommended. After calibration, perform a bump test with standard gas and measure the test gas in the same way to calculate the CF.

CF Measurement for Liquid and Solid Samples

If the target gas is to be prepared from a liquid or solid sample, proceed as follows:

• Obtain a large vessel such as a 5- or 12-gallon glass jug.

• Calibrate its volume. One simple way to do this is to fill the bottle with water and measure the difference in weight with an accurate balance (each kg of water equals 1 liter of volume) or simply fill a jug with water using a calibrated beaker (syringe) and calculate the amount.

• Use a magnetic stirrer with a stirring bar covered by PTFE to aid in mixing.

• Bore two holes in the cap to insert the instrument influent and effluent sample lines. Use PTFE tubing for these lines to minimize losses due to adsorption. To avoid gas dilutions during a measurement, use a closed-loop system.

• MiniRAE 3000, ppbRAE 3000, and RAEGuard have inlet and outlet ports with air output adapter. Simply attach them to tubing to closed loop. Because the MultiRAE has no air output adapter, add a short piece of PTFE tubing to the output port and connect the instrument to a jug with tubing to close the loop.
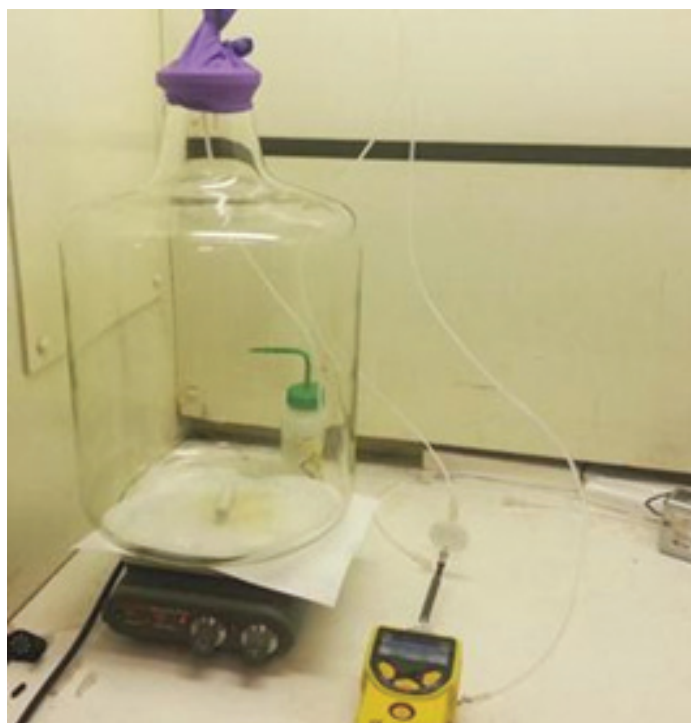
- For a ToxiRAE Pro, use the plastic cap from the kit. Attach the cap with tubing to an additional external pump with a power supply to deliver gas from a jug to an instrument.
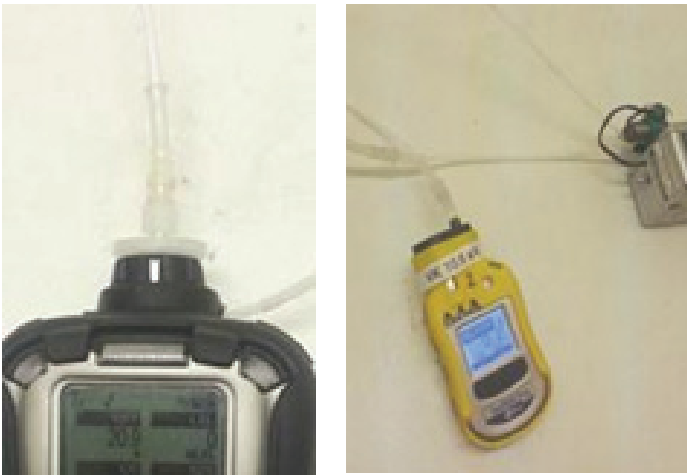
Connecting MultiRAE Pro and ToxiRAE Pro PID to the jug tubing.

- Calibrate and bump test the PID instrument with standard isobutylene gas, as described earlier.

- Using a microliter syringe, inject a volume of liquid calculated to the jug wall and seal the jug to give the desired concentration:

$$\text{Concentration (ppmv)}$$
$$= \frac{24.4 \left(\frac{L}{mol}\right) \text{x Volume injected(uL)xLiquid density} \left(\frac{g}{mol}\right) \text{ x } 10^6}{1000 \left(\frac{mg}{g}\right) \text{x Molecular weight} \left(\frac{g}{mol}\right) \text{x Vessel volume (L)}}$$

- Using an XE100A balance, weigh the calculated amount of solid and insert to the jug on a stainless steel or PTFE plate and seal the jug to give the desired concentration:

$$\text{Concentration (ppmv)}$$
$$= \frac{24.4 \left(\frac{L}{mol}\right) \text{x Amount scaled(g) x } 10^6}{\text{Molecular weight} \left(\frac{g}{mol}\right) \text{x Vessel volume (L)}}$$

- Allow time for the liquid (or solid) to evaporate and mix. Assist mixing with magnetic stirring. If the compound has a high boiling point, apply heat (e.g., using a heat gun) to the vessel wall to speed evaporation. Be sure that the chemical has fully evaporated before starting the measurement procedure.

- Connect the instrument to the jug tubing as described above, and perform the CF measurement.

- Record the sample measurement, and remove the instrument.

- Repeat the process with another four instruments of the same series and with a second gas concentration to obtain ten CF values to average. Calculate the CF using the equations above.

- To avoid data distortion due to the VOCs adsorption on the jug walls and tubing, complete the measurement procedure for one gas concentration within five hours from start of measurement.

- After completion, unseal the jug and flush it with fresh air.

- If desired, a known volume of liquid water can also be injected to achieve a desired relative humidity and CF under humid conditions. For such measurements, the sensor must be very clean, or else the readings may drift upward.