

Detection Limit Analysis Using the VeraSpec™ Trace Atmospheric Pressure Ionization Mass Spectrometer

Extrel CMS, LLC
Application Note
RAT-105A

Introduction

For many gas purity applications, detection limits of trace (parts-per-billion) and ultratrace (sub-parts-per-billion) level concentrations are required. The best way to achieve these low detection limits is with the application of Atmospheric Pressure Ionization Mass Spectrometry (APIMS). For more than 20 years, quadrupole-based Atmospheric Pressure Ionization Mass Spectrometry (APIMS) has been the research and industrial standard for on-line detection of low-level components of gas mixtures. APIMS instruments can routinely monitor components at the parts-per-billion (ppb) and parts-per-trillion (ppt) level in real time. A quadrupole-based APIMS system can monitor a wide range of gases and gas mixtures while having the stability to provide the long-term repeatability required in most applications.

Experimental

The Limit of Detection (LoD) is calculated using the Extrel VeraSpec Trace APIMS by flowing a calibration gas and bulk gas through a flow controller then into the API source. The source uses a Corona Discharge of 5 kV to ionize the bulk N_2 . The ionized bulk gas then ionizes the analytical gas. All wetted surfaces are heated to optimize the adsorption/desorption rates of molecular layers on the stainless steel inlet and source surfaces. Once ionized, the ions then pass through a small aperture, through a declustering region (2.5×10^{-6} torr), then through a 19 mm quadrupole mass filter, and are collected by a pulse-counting electron multiplier (1.7×10^{-7} torr). A schematic of the system can be seen in Figure 1.

The calibration gas contains 1.2 ppm CO_2 with a balance of N_2 , and is controlled by a mass flow controller at the rates of 1.0, 0.8, 0.6, 0.4, 0.2 scc/min. The bulk gas used is an adiabatic expansion of liquid nitrogen controlled to 2 L/min by a mass flow controller, achieving a dilution factor of 2,000 to 1. The mass spectrometer is set to a slow scan, allowing 30 seconds of dwell (measurement) time for each mass. It should be noted

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Experimental *continued*

that every precaution has been made to optimize the signal-to-noise in this system. This noise reduction includes:

1. Replacing the electron multiplier;
2. Connecting braided ground straps to all components including the data system, quadrupole power supply, both analog and counting preamplifiers, and the chamber itself;
3. Adjusting the counting preamplifier discriminator level carefully;
4. Cleaning the API source needle with a 10KV corona;
5. Tuning all optics carefully with special attention to pole bias, the quadrupole housing, and faraday plate.

In addition, the inlet system is under constant heat and continuous flow of bulk gas. This constant gas flow allows all wet surfaces to off-gas and come to equilibrium. The bulk gas is then run through a getter-based purification system. The Lower Detection Limits (LDL) of Carbon Dioxide (m/z 44) is used for the LoD calculations.

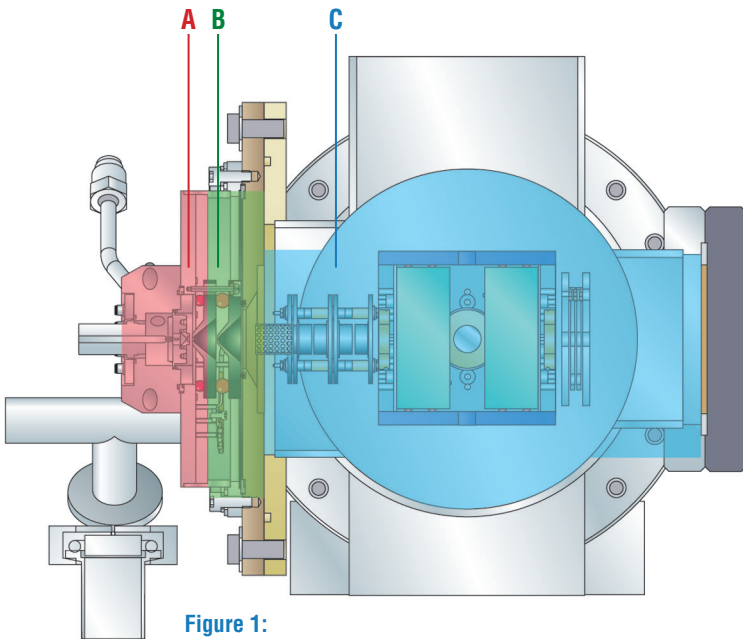


Figure 1:
Schematic of APIMS System.
A. Corona Discharge Region (~1 atm)
B. Declustering Region (2.5 x 10⁻⁶ Torr)
C. Quadrupole Region (1 x 10⁻⁷ Torr)

Results and Discussion

Detection limits are calculated using the following formula:

$$LDL = \frac{t * \sigma_{bl} * \left(\frac{N_1 + N_2}{N_1 * N_2} \right)}{\left(\frac{X_1 - X_{b2}}{X_1 - X_{b1}} \right)}$$

Equation 1:
Mathematical equation for Limit of Detection

The t value in the equation is 2.58 for a 99% confidence level over an infinite number of measurements. Twenty-five measurements are used for N₁ and N₂ as an adjustment for the degrees of freedom. Below are the actual calculations imported from MathCAD Software:

$$a=1.2 \quad t=2.58 \quad N_1=25 \quad N_2=25$$

$$CO_{21}=912 \quad CO_{22}=4406.5 \quad \Delta CO_2 = \frac{(CO_{22} - CO_{21})}{(0.24 - 0.12)} \sigma_{CO_2} = 77$$

$$CO_{2LDL} = \frac{\left(t * \sigma_{CO_2} * \frac{N_1 + N_2}{N_1 * N_2} \right) * 1000}{\Delta CO_2} \quad CO_{2LDL} = 0.546 \text{ ppt}$$

Equation 2:
MathCAD calculations for Lower Detection Limit (LDL)

The raw data used for these calculations are below:

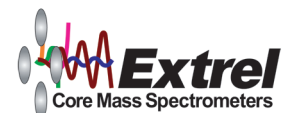
0.2 scc/min Sample in 2 L/min N₂

	m/z 44	m/z 45
Average	81729	2468
Stdev	6920	277
RSD	8.5%	11.2%
Adj. Average (cps)	912	28
Adj. Stdev (cps)	77	3
Calc. Conc. (ppb)	0.120	0.001

0.4 scc/min Sample in 2 L/min N₂

	m/z 44	m/z 45
Average	394822	7077
Stdev	18952	813
RSD	4.8%	11.5%
Adj. Average (cps)	4406.5	79.0
Adj. Stdev (cps)	211.5	9.1
Calc. Conc. (ppb)	0.240	0.002
Delta (cps/ppb)	29120	42869

Table 1: Results of Resolved Peak Experiment



Results and Discussion *continued*

In the previous tables, the Average figure is actually the average of 25 measurements of the area under the curve of each peak. This value is converted to counts-per-second (cps) by dividing the number by 128 (Merlin Automation's specific conversion factor) and 0.7 (peak width at half max). This same adjustment is performed to put all values in terms of cps. The Delta calculation is the change in peak intensity, divided by the change in concentration, to give a result in cps/ppb. The acquisition begins with a sample flow of 0.2 scc/min with each step going up by 0.2 scc/min. This equates to a $\Delta[\text{CO}_2]$ of 120 ppt. Therefore, following the isotope ratio of ^{12}C to ^{13}C of 1.1%, this gives a calculated $\Delta[\text{CO}_2]$ at m/z 45 of approximately 1 ppt.

The calibration curves for m/z 44 and m/z 45 are plotted for linearity and shown.

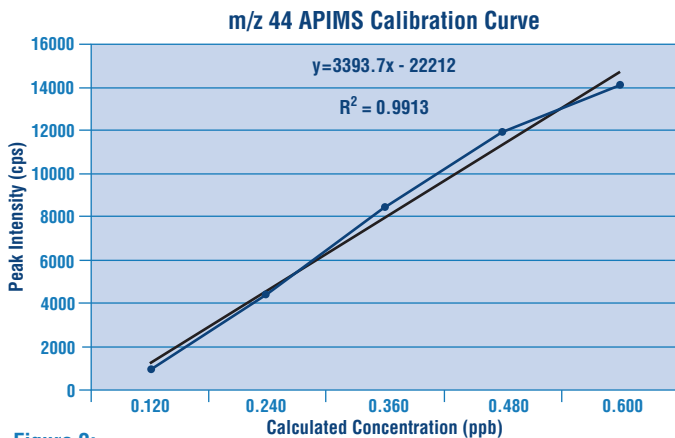


Figure 2:
Calibration curve for m/z 44

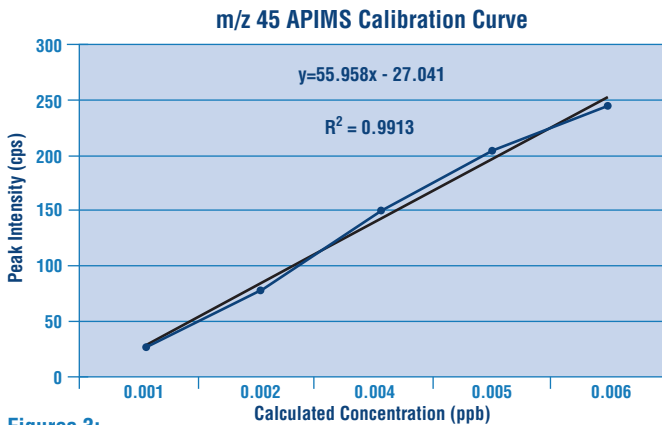


Figure 3:
Calibration curve for m/z 45

The isotope ratio between m/z 44 and 45 calculated from the above data is approximately 3%. This error could come from several sources including:

1. An interfering peak at m/z 45 from a protonated CO_2 ;
2. An interfering background peak at m/z 45;
3. A tail from m/z 44 bleeding into m/z 45.

These possibilities were investigated in the following steps:

1. An interfering peak at m/z 45 from a protonated CO_2 is discounted. The best source of a proton would be from protonated water, which would easily be seen at m/z 19. Since there is no significant peak at m/z 19, it is doubtful that CO_2 would be able to protonated enough to impact the data significantly.
2. An interfering background peak at m/z 45 can be investigated by calculating the isotopic ratio from the difference between two data points. (e.g. using data from the previous experiment, $\Delta\text{m/z } 45$ divided by $\Delta\text{m/z } 44$ gives an isotopic ratio of 1.47 %.) Therefore, it is very feasible that a background peak may skew the data.
3. Narrowing the resolution of the quadrupole may eliminate a tail from m/z 44. After performing this test, the complete calibration curve is rerun. It should be noted that 50 data points are taken at each calibration step ($N=50$).

Results and Discussion *continued*

0.2 scc/min Sample in 2 L/min N₂

	m/z 44	m/z 45
Average	216345	5930
Stdev	10243	960
RSD	4.7%	16.2%
Adj. Average (cps)	2415	66
Adj. StDev (cps)	114	11
Calc. Conc. (ppb)	0.120	0.001

0.4 scc/min Sample in 2 L/min N₂

	m/z 44	m/z 45
Average	402952	8176
Stdev	15962	1025
RSD	4.0%	14.3%
Adj. Average (cps)	4497.2	91.2
Adj. StDev (cps)	178.2	11.4
Calc. Conc. (ppb)	0.240	0.002
Delta (cps/ppb)	17356	20884
LDL (ppt)	5.09	0.54

Table 2: Results of Resolved Peak Experiment

$$a = 1.2 \quad t = 2.58 \quad N_1 = 50 \quad N_2 = 50$$

$$CO_{21} = 2415 \quad CO_{22} = 4497.2 \quad \Delta CO_2 = \frac{(CO_{22} - CO_{21})}{(0.24 - 0.12)} \quad \sigma CO_2 = 114$$

$$CO_{2LDL} = \frac{(t \cdot \sigma CO_2 \cdot \frac{N_1 + N_2}{N_1 \cdot N_2}) \cdot 1000}{\Delta CO_2} \quad CO_{2LDL} = 0.678 \text{ ppt}$$

Equation 3: LDL of Resolved Peak Experiment

The isotope ratio calculates to approximately 2.7%. While this ratio is closer to the natural abundance, it is still inaccurate. Considering the above possibility of an interfering background peak at m/z 45, the Δ_{45}/Δ_{44} for the narrowed resolution experiment can be examined. This yields an isotopic ratio of 1.20%. Since the isotopic ratio should be ~1.18% (1.1% from ¹³C and 0.04% from each of the ¹⁸O isotopes), better results are obtained by narrowing the resolution and considering the deltas of the two data points. Evidence of a slight tail is seen from m/z 44 in the first set of data, and some contribution at m/z 45 from a background peak. Therefore, a lower detection limit is not calculated from the m/z 45 peak. Using this isotope peak would give an artificially low detection limit. The resultant calibration curves from this experiment are seen in Figures 4 & 5.

m/z 44 APIMS Calibration Curve

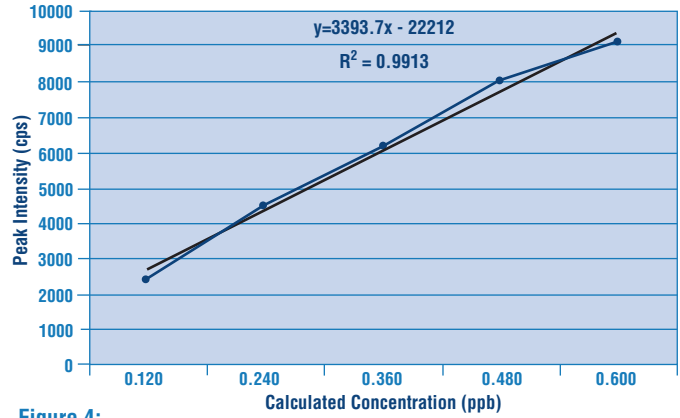


Figure 4: Resolved Peak Experiment: m/z 44 calibration curve

m/z 45 APIMS Calibration Curve

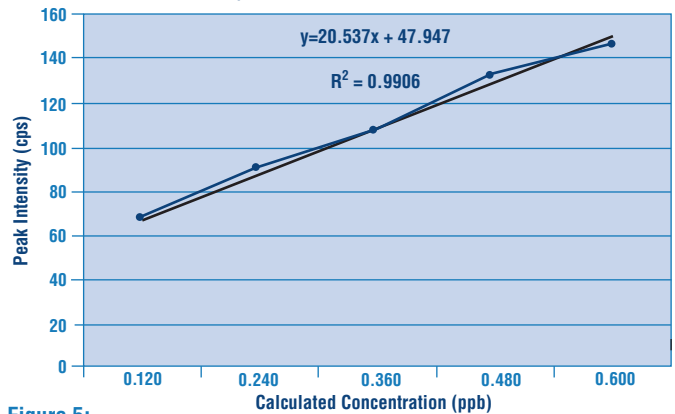


Figure 5: Resolved Peak Experiment: m/z 45 calibration curve

Conclusion

The flexibility and precision of the Extrel VeraSpec Trace enables the researcher to focus the instrument on the specific application. It also allows the researcher to go beyond simple process monitoring into troubleshooting and fundamental research. The VeraSpec Trace system uses the proven and reliable Corona Discharge API source to achieve soft ionization that is ideal for monitoring trace level molecules. The high signal transmission of the 19 mm rod tri-filter quadrupole mass filter provides the highest possible sensitivity and reproducibility for most applications.