Practical Considerations for Quantitative Gas Analysis with Quadrupole Mass Spectrometers

APPLICATION NOTE

Many factors must be considered when comparing the overall suitability of different quadrupole-based gas analyzers for any given application and the list can sometimes appear daunting and confusing. This can be due to inconsistencies in the way that different manufacturers choose to define specifications or, in some cases, omit them altogether. These factors can be categorized into two main areas: (i) inlet interface suitability and (ii) quadrupole mass analyzer suitability. This article aims to remove some of this confusion and define and present those practical specifications which are critical for repeatable and reliable quantitative gas analysis.

(i) Inlet/Interface

The suitability of the inlet and interface determines how well the gas analyzer can capture, condition or transfer the gas sample without altering it and for it to be measured on an appropriate timescale, which could be milliseconds or hours. The inlet and interface can include both the upstream transfer elements and the downstream pumping and gas handling elements.

(ii) Quadrupole Mass Spectrometer

Assuming the inlet and interface are properly designed and equal between systems, then the quadrupole mass spectrometer is the critical element determining the overall precision, stability, and detection limits of the gas analyzer. The quadrupole mass spectrometer includes the ionization method, the transmission characteristics, and the quality of the driving electronics.

Precision, stability, and detection limit are often mis-represented in commercial literature. This mis-representation can be addressed and clarified by directly comparing two different classes of quadrupole analyzers: a 6mm rod diameter, RGA type instrument, typical of many currently on the market, and a higher performance 19mm rod diameter instrument, used in more demanding research and industrial applications. These two systems are compared with nominally identical inlet/transfer conditions, so that only the mass spectrometer performance is under consideration. This presents a direct comparison of the *practical range* of precision, stability and detection limit in each case so potential users of this powerful analytical technique may be better equipped to make meaningful comparisons between different suppliers.

The specifications that will be addressed are:

- Detection Limit (minimum and maximum detectable concentration)
- Speed of Analysis (measurement speed and response time)
- Analysis Precision (repeatability of measurements)
- Analysis Stability (long-term instrument stability)
- Dynamic Range (comparison of largest and smallest detectable signals)

This study will be conducted by assessing and comparing the performance of two instruments, the MAX300-CAT and the MAX300-LG. The MAX300-CAT is typical of the high-end RGA based gas analyzers, based upon 6mm quadrupole rod technology, whereas the MAX300-LG is a higher performing analyzer based on 19mm quadrupole rod technology and more sophisticated electronics. The specifications of each, as they would appear in most commercial literature, is shown below.

MAX300-CAT Instrument Specifications:

- Detectable compounds: Any gas or vapor sample
- Detectors: Faraday/electron multiplier
  - Low detection limit: <10x10^{-14} Torr (<10 ppb)
- Analysis rate: Up to 1000 measurements per second
- Ionization energy control for reduced fragmentation
- Filaments: Dual filament with firmware protection
  - Over-pressure protection provided by built-in Pirani and BA gauges
- Mass range options: 1-100, 1-300 amu

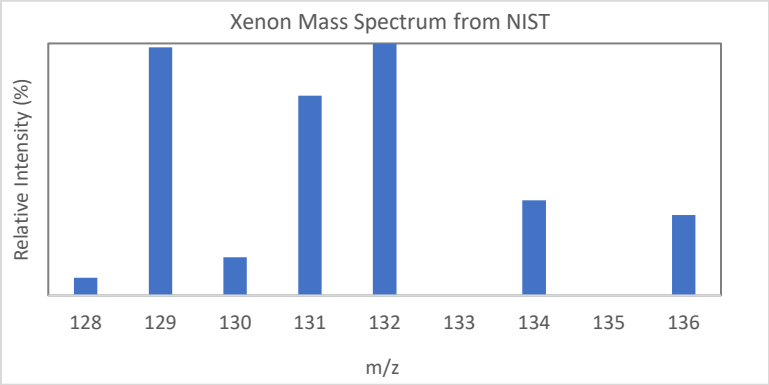
MAX300-LG Instrument Specifications:

- Detectable compounds: Any gas or vapor sample
- Detectors: Faraday/electron multiplier Dual Detector
  - Low detection limit: <1x10^{-15} Torr (<1 ppb)
- Analysis rate: 12,500 measurements per second
- Ionization energy control for reduced fragmentation
- Filaments: Two, one active and one spare
  - Built-in automatic switchover for continuous operation
- Mass range options: 1-250 amu, (1-300, 500 amu, optional)

Detection Limit Comparison

The specified figure of detection limit can be very misleading. Often it will be a calculated figure, or it may reflect data that has been averaged and smoothed for long periods of time to give a best possible case which is often not achievable in practical situations. Nonetheless, the ultimate detection limit is a good starting point to begin to define the practical capabilities of the analyzer.

An effective way to measure the ultimate detection limit is to analyze xenon in air. Xenon occurs naturally in air at approximately 87ppb (parts per billion). It has several isotopes, each with different relative abundancies. The xenon mass spectrum, taken from NIST (National Institute of Standards and Technology), is shown below for reference.



m/z	Relative Abundance	Isotopic Abundance	Concentration in Air (ppb, approx)
128	7	1.91%	1.66
129	98.4	26.40%	22.97
130	15.2	4.07%	3.54
131	79.3	21.23%	18.47
132	99.9	26.91%	23.41
134	37.8	10.44%	9.08
136	31.9	8.86%	7.71

Figure 1: Xenon in Air as Reported by NIST, Spectral and Numerical Form

The two spectra in Figure 2 below are the xenon isotopes in air measured with the MAX-CAT and MAX300-LG analyzers. The data demonstrates a detection limit of ~5ppb for the MAX300-CAT analyzer compared with a detection limit of <1ppb for the MAX300-LG analyzer. These spectra show the ultimate detection limit of each analyzer and were achieved over approximately 1 hour of averaged data collections. It is important to note that the concentration of xenon in air does not change over the analysis time. This scan time may not be possible or practical when measuring other samples. However, most manufacturers utilize similar scan methods for their quoted detection limits.

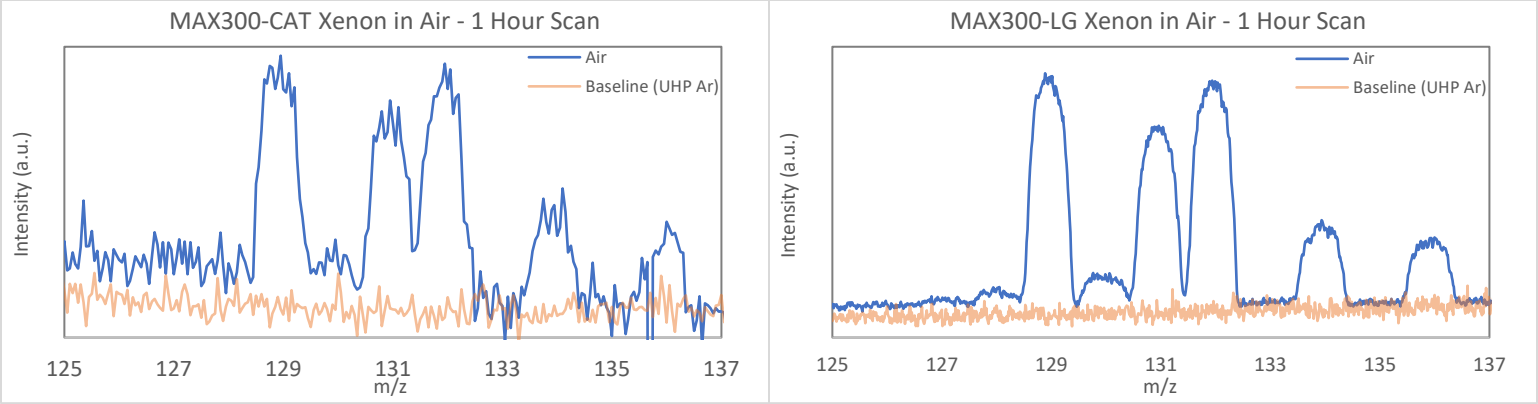


Figure 2: Xenon in Air Spectra Taken with a MAX300-CAT and MAX300-LG

The detection limit and general data quality are influenced by scan speed. This can be seen in the spectra when scan speed is increased to something more practical.

Speed of Analysis

Analysis speed is a key factor in quantitative gas analysis. Applications such as catalysis, reaction monitoring or kinetics, and evolved gas monitoring all require faster capture of process changes than QA/QC applications, while a breath measurement application needs to report quantitative differences on the millisecond scale. Note that this refers to the ability of the analyzer to measure, with the desired level of accuracy, raw signals and then analyze these in a given timeframe, taking into account spectral interferences, in order to output the result of a single analysis. The rate at which an analyzer scans directly influences this data quality. Slower scanning or more averaging yields more repeatable results and lower detection limits.

The following comparison shows the same xenon in air spectra taken at faster effective scan rates and less scan averaging. Each spectrum represents a 10-minute total scan time compared with the previous 1-hour scan time.

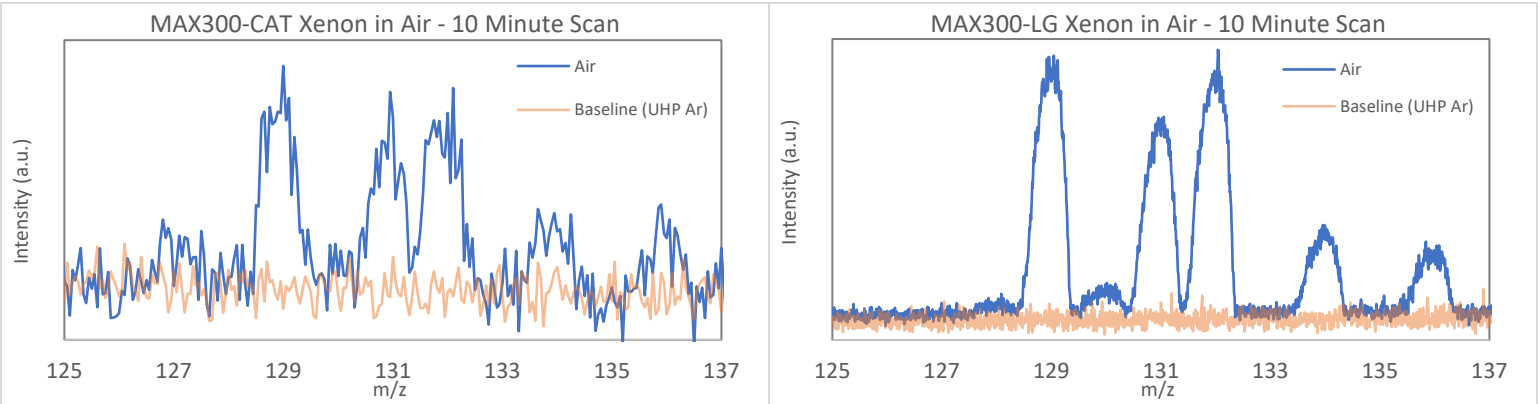


Figure 3: Xenon in air spectra taken with MAX300-CAT and MAX300-LG Using Faster Scan Time

The detection limit of the of MAX300-CAT analyzer has clearly risen, and is now equal to, or greater than 10ppb, compared with ~5ppb previously. The detection limit of the MAX300-LG by comparison is still <1ppb under the same scanning conditions, demonstrating that the higher performing quadrupole/driving electronics copes much better with the demands of practical scanning speeds. This is critical to the implementation of an instrument into an analysis as the ultimate detection limit and the practical detection limit are not necessarily equivalent. The detection limit of an analyzer should not be based on a published value, but instead on a practical demonstration of the data quality at the required scan speed for specific applications and gas mixtures.

This data also shows that the overall quality of the spectrum for the MAX300-CAT has worsened when compared to that of the MAX300-LG. Because of the noise introduced into the spectrum from the MAX300-CAT, the quantitative capability of the data has decreased. This is a measure of the precision of the two analyzers which can be directly compared.

Analysis Precision

Analysis precision (or short-term repeatability) represents the standard deviation of analysis results over short time periods. Repeatability can be improved by slowing analysis scan speed or averaging more scans. The data trends in Figure 4 show the analysis precision of the MAX300-CAT and the MAX300-LG analyzing Xe-132 isotope in air (23.4ppb, approx.) at an approximate scan rate of 3 minutes/scan.

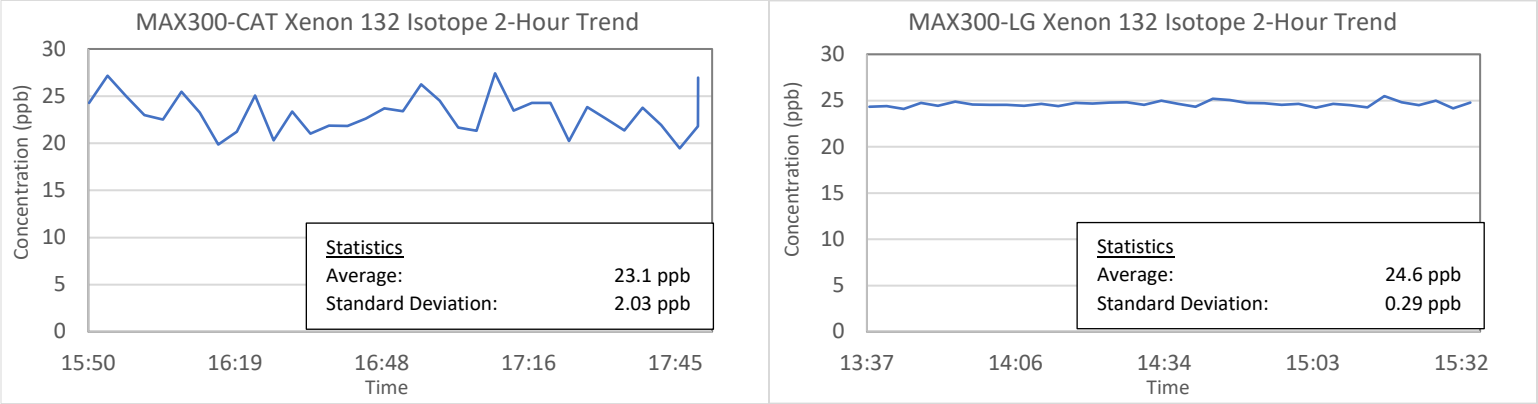


Figure 4: 2-Hour Trend of Xe-132 Isotope on the MAX300-CAT and MAX300-LG

The data obtained by the MAX300-LG is of higher quality than that of the MAX300-CAT, over the same analysis. The comparably large standard deviation of the MAX300-CAT analysis results must be factored in practical quantitative gas analysis. Measurement uncertainty decreases and the analyzer can make more accurate, quantitative measurements with lower standard deviations.

Analysis Stability

Analysis stability is a representation of drift or fluctuations over long-term data collection. It is a critical factor which influences longer analyses such as process control, slow heating TGA and thermal analysis, and air monitoring, but also impacts general instrument operation. Stability allows for accurate results over time, less calibration frequency, and confidence in the day to day repeatability of the analyzer.

The data trends in Figure 5 show the instrument stability comparison between the MAX300-CAT and the MAX300-LG for the major xenon isotopes in air. The data was collected at an approximate scan rate of 3 minutes per scan, over a 36-hour period.

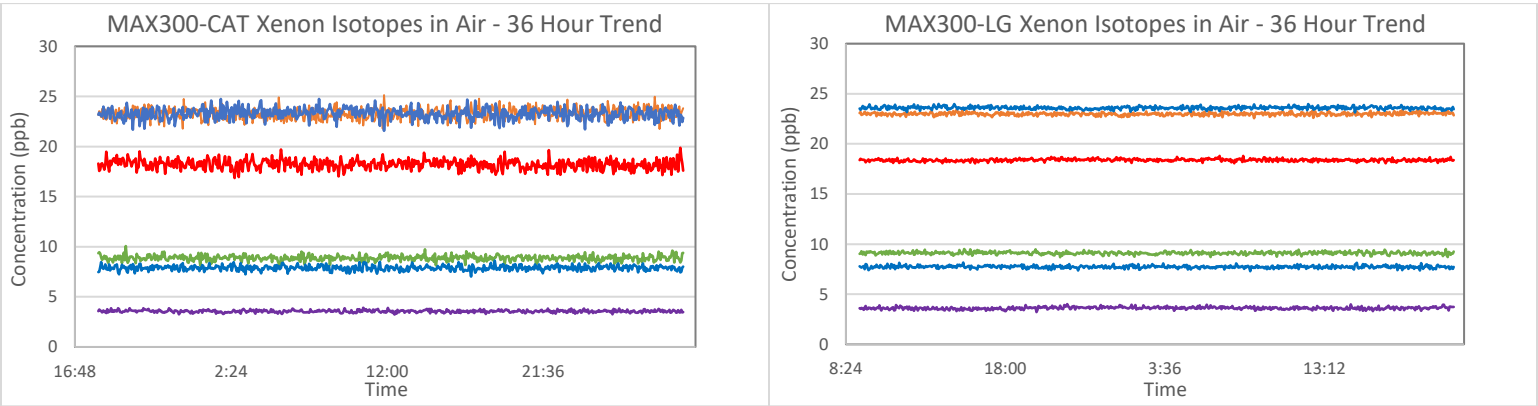


Figure 5: 36-Hour Trend of Xenon Isotopes in Air on the MAX300-CAT and MAX300-LG

	MAX300-CAT	MAX300-LG										
	Xe_129		Xe_130		Xe_131		Xe_132		Xe_134		Xe_136	
Average (ppb)	23.30	23.08	3.57	3.64	18.22	18.38	23.29	23.53	8.89	9.08	7.89	7.71
St. Dev. (ppb)	0.55	0.21	0.12	0.12	0.48	0.13	0.55	0.17	0.27	0.14	0.24	0.14
Rel. St. Dev.	2.37%	0.92%	3.38%	3.20%	2.65%	0.70%	2.36%	0.70%	3.05%	1.50%	3.09%	1.75%
Rel. Drift	0.72%	0.96%	0.52%	0.81%	0.67%	0.31%	0.22%	0.40%	0.29%	0.16%	0.09%	0.33%

Figure 6: Statistical data results from the 36-Hour Xenon Isotopes Experiment

The data above shows that the MAX300-LG's lower detection limits allow for more accurate speciation and quantitation of the low concentration analytes. The stabilities of the both instruments, however, are not affected when increasing the scan rate to a 3-minute scan. Both the MAX300-CAT and the MAX300-LG show no drift (<1% relative) over 36-hours.

Dynamic Range

Large dynamic measurement range is an essential requirement of quantitative gas analysis and becomes especially apparent in applications such as solvent drying, where species must be monitored from high to low concentrations with accuracy and repeatability. A key advantage of the MAX300-LG over other instrumentation is that the detection system (composed of the dual Faraday and Electron Multiplier detector and the fast switching electronics) allows switching between detection mechanisms within a single scan. This means that a wider dynamic range (wider range of concentrations) can be covered in a single analysis. A dilution experiment using a volume filled with ultra-high purity (UHP) argon slowly diluted by UHP nitrogen highlights the instruments' dynamic ranges. The concentration of argon, monitored with respect to time, is shown in Figure 6 for both the MAX300-CAT and MAX300-LG.

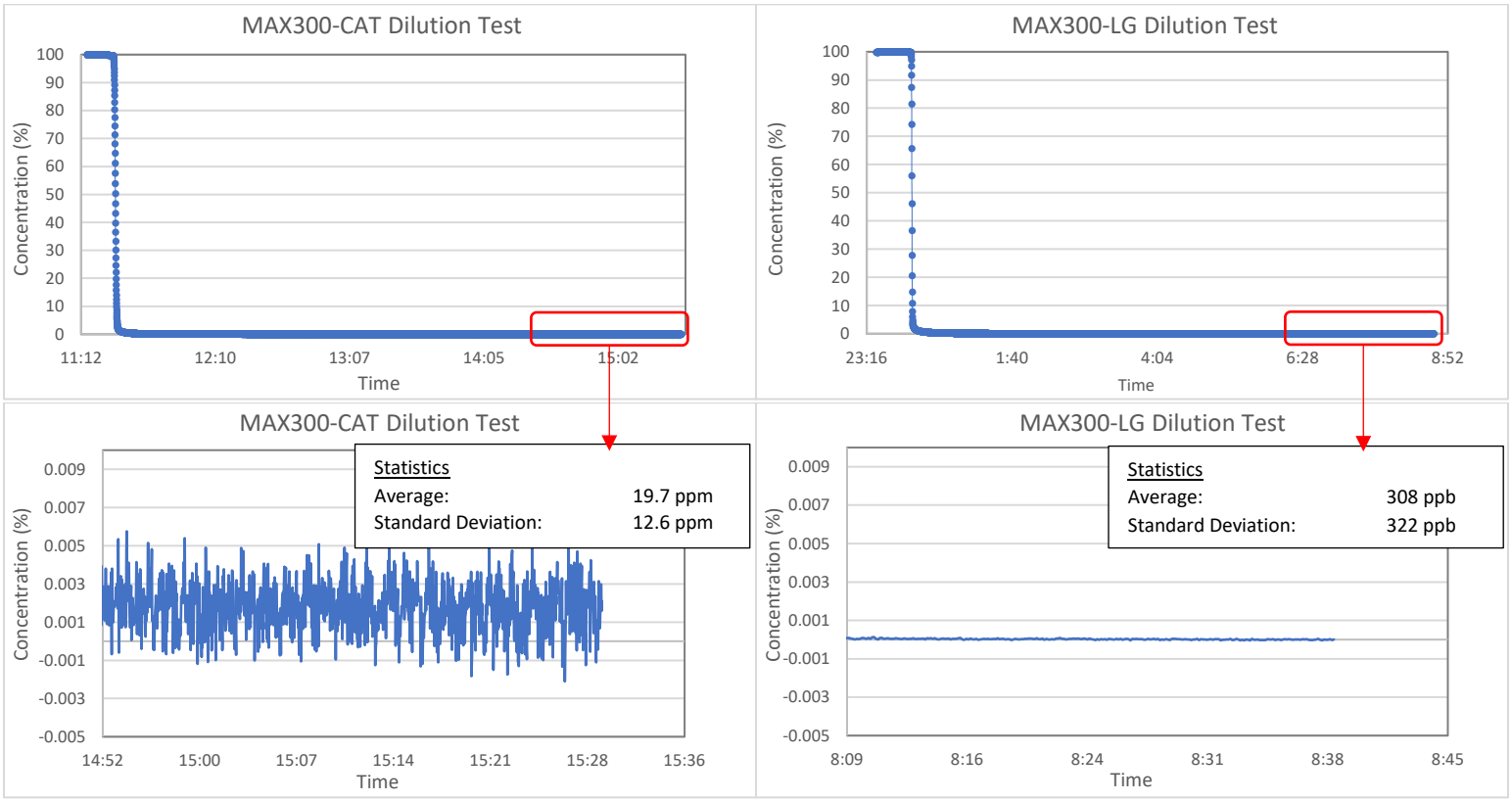


Figure 7: MAX300-CAT and MAX300-LG Dilution Test Results

The above measurement illustrates the importance of the ability of the instrument to operate over the widest dynamic range to produce high quality, accurate quantitative measurements.

An instrument's dynamic range also plays a role in analyses of multiple species of varied concentrations. This affects the ability to accurately and repeatably monitor these component concentrations. Measuring the components in air, including krypton (1.1ppm, approx.) highlights this. An air analysis was conducted on both the MAX300-CAT and MAX300-LG. Figure 8 shows 30-minute trends of the analysis for both the MAX300-CAT and MAX300-LG, using approximately 8 second scans.

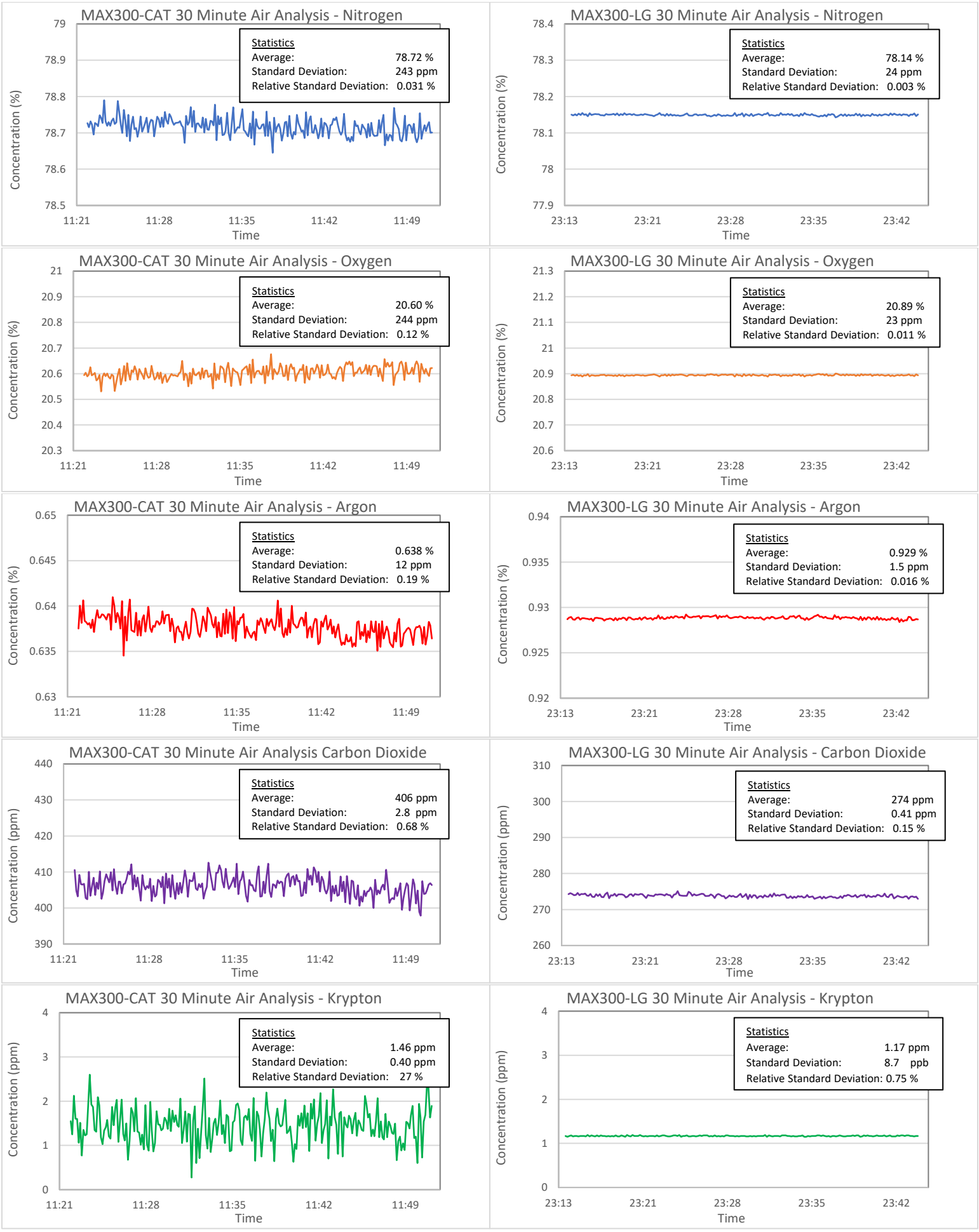


Figure 8: 30 Minute Air Analysis on the MAX300-CAT and MAX300-LG

In conclusion, there are several key factors to consider when comparing the suitability of different gas analyzers for specific applications. While ultimate detection limit is the most prominently highlighted specification, this statistic can be misleading and may not be the most critical instrument capability for a given application. The following all factor into an instrument's performance in various settings:

- Detection limit at different scan rates
- Speed of analyses
- Precision
- Stability
- Dynamic range

The MAX300-CAT, a high-end RGA based gas analyzer using 6mm quadrupole rod technology, can demonstrate low detection limits of approximately 5 ppb, using slow scan speeds. The scan speed on this instrument can be increased to a typical quantitative analysis rate of 2 seconds per component, resulting in an increase of detection limits to 0.5 ppm. The MAX300-CAT has a maximum speed of approximately 2 seconds per component in quantitative scans. While this changes the instrument precision, the stability remains constant. The dynamic range of the MAX300-CAT allows for an analysis range from $1x10^{-6}$ to $5x10^{-13}$ Torr (100% to 0.5 ppm), when scanning at a rate of 2 seconds per analysis component.

The MAX300-LG, a higher performing analyzer based on 19mm quadrupole rod technology and more sophisticated electronics, displays extremely low detection limits of <1 ppb, using slow scan speeds. The scan speed on this instrument can be increased to a typical quantitative analysis rate of 400 milliseconds per component, resulting in a moderate increase of detection limits to <10 ppb. The MAX300-LG has a maximum speed of 5 milliseconds per component in quantitative scans. This instrument has incomparable precision and stability, a result of the large quadrupole and high-performance electronics combination. The MAX300-LG demonstrates a very large dynamic range from the dual detector setup, allowing an analysis range of $1x10^{-6}$ to $<1x10^{-14}$ Torr (100% to <10ppb), while scanning at a rate of 400 milliseconds per component.

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