



EP-IR Embedded Chemometrics: PCR+™ Accuracy Advantages.

INTRODUCTION

Three chemometrics data treatment methods were applied to the same set of EP-IR spectra for the measurement of Carbon Dioxide (CO₂) between 0 and 5% (50,000 ppm).

They were: (1) polynomial regression; (2) traditional Principal Component Analysis and Regression; and (3) Aspectrics proprietary algorithm "PCR+™."

No significant differences in measurement precision were found between the 3 chemometrics approaches. However, it was unequivocally proved that Aspectrics proprietary PCR+™ algorithm was the most accurate methods to predict CO₂ concentrations over the 0 – 5% range.

MATERIALS & METHODS

Spectrometer:

An Encoded Photometrics InfraRed (EP-IR) spectrometer was used to collect data. This spectrometer was configured with 256 photometric channels covering the 2.5 to 5.0 microns range. Pathlength was 24.2 cm and boxcar average was set to 2048.

Experimental:

Using a gas blender, the instrument was exposed to a series of varying concentrations of CO₂ (see table 1). Spectra were collected to develop quantitative models. Then, a second set of spectra was collected, running the same blender settings programs; the various quantitative models were applied to that data to compute accuracy (bias) and precision (repeatability) of each chemometrics approach.

Table 1: Gas Blender Program

Step #	CO2 (ppm)	Time min	Step #	CO2 (ppm)	Time min
1	0	10	11	4,000	5
2	200	5	12	6,000	5
3	400	5	13	8,000	5
4	600	5	14	10,000	5
5	800	5	15	0	10
6	1,000	5	16	10,000	5
7	0	10	17	20,000	5
8	1,000	5	18	30,000	5
9	1,500	5	19	40,000	5
10	2,000	5	20	50,000	5

Quant Methods Development:

1. Polynomial Regression: this approach, based on the measurement of the fundamental vibration energy absorption band for CO₂ was inspired from the

chemometrics methods currently applied to single wavelength NDIR CO₂ analyzers.

2. PCA / PCR: this approach was based upon the use of both the fundamental vibration energy absorption band of CO₂ and its first overtone. The PCA algorithm used did not rely upon mean centering of the spectral information before PCA treatment.
3. PCR+™: this approach consist of an Aspectrics proprietary algorithm based upon traditional PCA / PCR algorithms, further optimize for the mathematical treatment of EP-IR spectral data.

Accuracy / Precision Evaluation:

Accuracy was tested by calculating the bias, or average of the differences between calculated and reference gas concentrations once a stable concentration had been reached in the gas cell.

Precision (repeatability) was calculated as the standard deviation of population of all calculated results once a stable concentration had been reach in the gas cell.

RESULTS & DISCUSSION

Accuracy:

Table 2 clearly shows the deficiencies of the polynomial model when applied to the prediction of of samples with concentrations greater than 1% (10,000 ppm). We also can observe that the Aspectrics PCR+™ algorithmic approach, which takes into consideration the specifics of the EP-IR unique signal, provides more accurate results than the straightforward application of a PCR algorithm,

Precision:

Table 3 shows that the type of chemometrics models actually matters little as precision remains sensibly the same for all three chemometrics approaches.

CONCLUSION

It has long been known that NDIR instruments using polynomial chemometrics approaches were precise instruments. This was proven again based upon the use of EP-IR spectral information.

However, it also was unequivocally proved that access to multivariate chemometrics approaches such as PCA/PCR improved accuracy (bias) of the measurement.

Moreover, it was proved that the use of a new algorithm -- PCR+™ -- specifically designed to handle EP-IR spectral information output performed best.

PCR+™ is the algorithm of choice used by Aspectrics for all its embedded applications in EPIR pre-calibrated analyzers.



Table 2: Comparison of 3 Chemometrics Approaches – Accuracy (bias)

Blender (ppm)	Polynomial			PCR			PCR+™		
	Calc ppm	Bias ppm	Bias %	Calc ppm	Bias ppm	Bias %	Calc ppm	Bias ppm	Bias %
0	-2	-2	-----	-5	-5	-----	-1	-1	-----
200	212	12	6.1%	200	0	0.0%	203	3	1.3%
400	411	11	2.7%	385	-15	-3.7%	397	-3	-0.8%
600	616	16	2.6%	593	-7	-1.2%	602	2	0.3%
800	811	11	1.4%	796	-4	-0.5%	802	2	0.2%
1000	1002	2	0.2%	991	-9	-0.9%	1000	-1	-0.1%
0	-1	-1	-----	-8	-8	-----	2	2	-----
1000	995	-5	-0.5%	980	-20	-2.0%	994	-6	-0.6%
1500	1482	-18	-1.2%	1474	-26	-1.7%	1501	1	0.1%
2000	1963	-37	-1.8%	1949	-51	-2.5%	2001	1	0.0%
4000	3936	-64	-1.6%	3929	-71	-1.8%	3999	-1	0.0%
6000	6007	7	0.1%	5995	-5	-0.1%	6000	0	0.0%
8000	8067	67	0.8%	8115	115	1.4%	8000	0	0.0%
10000	10093	93	0.9%	10256	256	2.6%	10000	0	0.0%
0	3	3	-----	76	76	-----	1	1	-----
10000	10148	148	1.5%	9864	-136	-1.4%	9960	-40	-0.4%
20000	20935	935	4.7%	20049	49	0.2%	20040	40	0.2%
30000	31438	1438	4.8%	29765	-235	-0.8%	29948	-52	-0.2%
40000	42042	2042	5.1%	39635	-365	-0.9%	40020	20	0.1%
50000	52412	2412	4.8%	50046	46	0.1%	49994	-6	0.0%

Table 3: Comparison of 3 Chemometrics Approaches – Precision (repeatability)

Blender (ppm)	Polynomial		PCR		PCR+™	
	Std Dev ppm	Std Dev %	Std Dev ppm	Std Dev %	Std Dev ppm	Std Dev %
0	0	-----	3	-----	1	-----
200	1	0.32%	3	1.72%	2	0.90%
400	0	0.08%	2	0.52%	1	0.25%
600	1	0.12%	3	0.46%	2	0.32%
800	0	0.05%	5	0.58%	2	0.20%
1000	1	0.05%	3	0.28%	1	0.14%
0	0	-----	2	-----	1	-----
1000	2	0.17%	2	0.23%	3	0.25%
1500	1	0.06%	2	0.12%	1	0.04%
2000	1	0.06%	4	0.20%	2	0.10%
4000	4	0.09%	8	0.21%	5	0.14%
6000	3	0.05%	10	0.17%	5	0.08%
8000	7	0.09%	11	0.14%	6	0.08%
10000	5	0.05%	20	0.20%	5	0.05%
0	0	-----	8	-----	1	-----
10000	12	0.12%	20	0.20%	22	0.22%
20000	23	0.11%	18	0.09%	22	0.11%
30000	69	0.23%	25	0.08%	35	0.12%
40000	80	0.20%	86	0.21%	41	0.10%
50000	72	0.14%	118	0.24%	42	0.08%

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