



Study on P2O5 analysis by ICP-OES for the AAPFCO Conference, Sacramento CA, July 2014

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Experimental

- Radial ICP OES (Arcos)
- Cyclonic Chamber with Seapray nebulizer, 1.8mm injector
- 1450 W, 14 L/min Coolant, 1.2 L/min Aux, 0.8 L/min Nebulizer, (+ 0.2 L/min Aux)
- Standard Calibration
- Empirical Calibration
- Varying Internal Standards
- Various Calibration standards (P, **PO4**, PPO4)
- Digestion concerns (P volatility)



Optional Gas adapter (laminar flow to force sample into plasma and avoid external cooling of plasma).





Anatomy of an active plasma stream

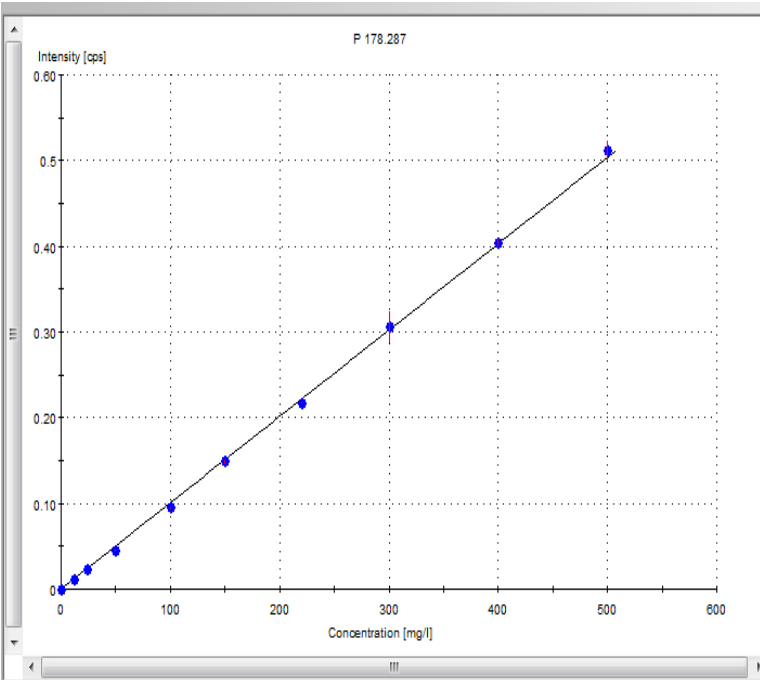


- High Na matrix to show the plasma has a “skin depth effect” which causes much of the sample to pass around the plasma and not completely through the plasma.
- Additional gas option forces the sample stream through the plasma.



Accuracy controls

1. Linearity : An ICP (all ICP's) typically have +/- 2% error in the calibration curve. What does that mean? Using the exact same conditions, intro system and solutions...each time you calibrate, the accuracy of the curve can vary up to 2%. So, on a 50% check solution a range of 49-51% is expected.
2. Adding empirical calibration controls can reduce this to 0.5% or less.
3. Additional gas flow (intro system) can produce a more consistent sample delivery with less plasma effects (efficiency/cooling/EIE).
4. Internal Standard selection and error from using a Blank.
5. Wavelength averaging.



Coef. A0: -0.021276
 Coef. A1: 992.52
 Coef. A2: --
 Coef. A3: --
 Matr. Corr.: No
 Matrix Conc.: --
 Line Range: 0.0212 mg/l - 600 mg/l
 Line Info:
 BEC: 0.393 mg/l
 DL: 0.0212 mg/l
 Std.Error: 3.95 mg/l
 Corr.Coeff.: 0.99986
 Dist.Factor: Factors defined in Conc/Conc

Detection Limit: [mg/l] Lock
 Conc. Min: [mg/l] Lock
 Conc. Max: [mg/l] Lock

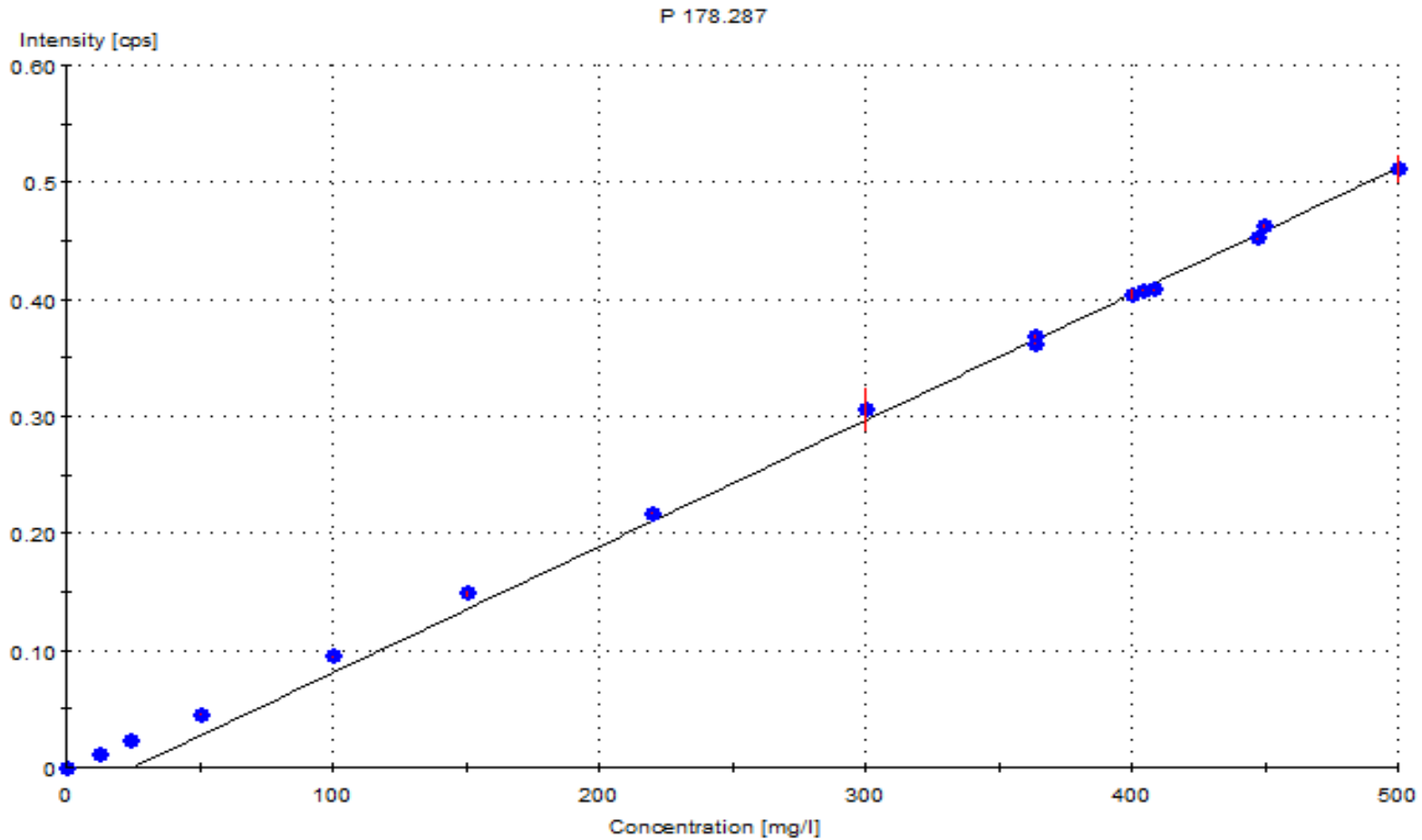
Dist. Ele.	Type	Factor	Use	Lock

Display Name	Type	Int. Standard
Ar 404.442	Monitor	
K 766.491	Analyte	Sc 361.384
P 178.287	Analyte	Sc 361.384
P 213.618	Analyte	Sc 361.384
Sc 361.384	Reference	

Standard	Use	Weight	Int.	IEC Delta	Cert.Conc. [mg/l]	Calc.Conc. [mg/l]	Diff. [mg/l]	Rel.Diff. [%]
BLANK	<input checked="" type="checkbox"/>		1	0.0000	0.0000	0.0000	1.7811e-007	1.7811e-007
STD1	<input checked="" type="checkbox"/>	8.333e-008		0.0117	0.0000	12.0000	11.5839	-3.47
STD2	<input checked="" type="checkbox"/>	4.167e-008		0.0239	0.0000	24.0000	23.6784	-1.34
STD3	<input checked="" type="checkbox"/>	2e-008		0.0460	0.0000	50.0000	45.6800	-8.64
STD4	<input checked="" type="checkbox"/>	1e-008		0.0956	0.0000	100.0000	94.8685	-5.13
STD5	<input checked="" type="checkbox"/>	6.667e-009		0.1492	0.0000	150.0000	148.0413	-1.31
STD6	<input checked="" type="checkbox"/>	4.545e-009		0.2179	0.0000	220.0000	216.2465	-1.71
STD7	<input checked="" type="checkbox"/>	3.333e-009		0.3068	0.0000	300.0000	304.4798	1.49
3A	<input type="checkbox"/>		0	0.3693	0.0000	363.7680	366.5403	0.76
3B	<input type="checkbox"/>		0	0.3629	0.0000	363.7680	360.2119	-0.98
STD8	<input checked="" type="checkbox"/>	2.5e-009		0.4053	0.0000	400.0000	402.2443	0.56
5A	<input type="checkbox"/>		0	0.4083	0.0000	404.2940	405.2685	0.24
5B	<input type="checkbox"/>		0	0.4089	0.0000	408.3370	405.7767	-0.63
7B	<input type="checkbox"/>		0	0.4531	0.0000	447.2140	449.6531	0.55
7A	<input type="checkbox"/>	...	0 ...	0.4638	0.0000	449.9020	460.3247	2.32
STD9	<input checked="" type="checkbox"/>		2e-009	0.5121	0.0000	500.0000	508.2179	1.64



Curve biased based on Empirical Weighting (Magruder)





Method defined calibration with Additional Gas

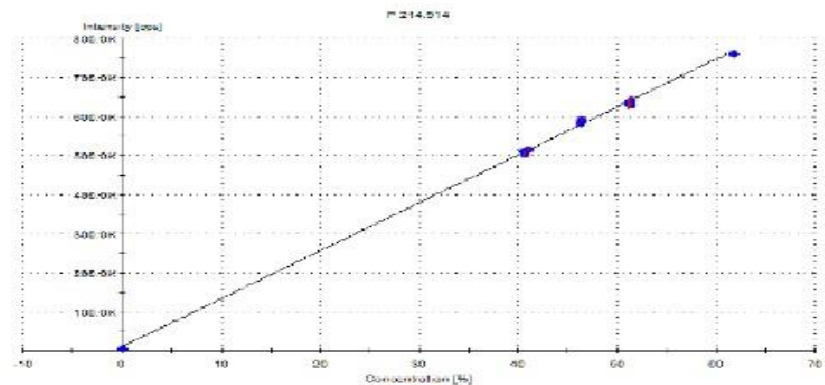
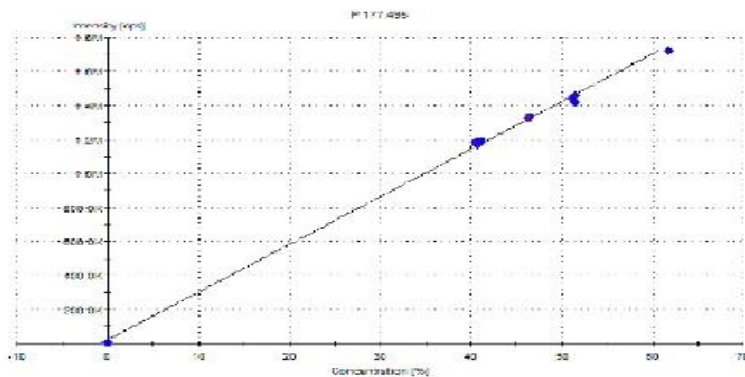
Sample		P2O5	Expected
		%	%
10B		! 0.012	0
7B		51.62	51.34
5B		46.029	46.32
3B		40.54	40.94



Empirical Calibration Results (Blank + 4 Standards)

Empirical Calibration

Sample	P 138.147 %	P 168.599 %	P 169.403 %	P 177.495 %	P 178.287 %	P 214.914 %	P205 Ave %	Expected %
10A	< -0.281	< -0.324	< -16.868	< -0.658	< -0.854	< -0.267	! -3.209	0
9A	60.597	60.589	61.887	60.667	58.873	61.106	60.62	61.67
8A	52.064	51.46	51.721	51.369	51.749	51.487	51.642	51.34
7A	49.65	50.612	50.237	49.898	50.797	50.513	50.285	51.34
6A	51.255	51.351	51.237	50.745	50.974	50.822	51.064	51.06
5A	47.489	47.472	46.528	47.024	47.931	47.345	47.298	46.32
4A	47.203	46.708	45.785	46.623	46.879	46.61	46.635	46.22
3A	40.564	41.235	41.491	41.896	41.925	41.278	41.398	40.94
2A	41.064	40.588	40.957	41.562	41.091	40.812	41.012	40.48
1A	40.325	40.238	40.087	40.803	40.563	40.223	40.373	40.56



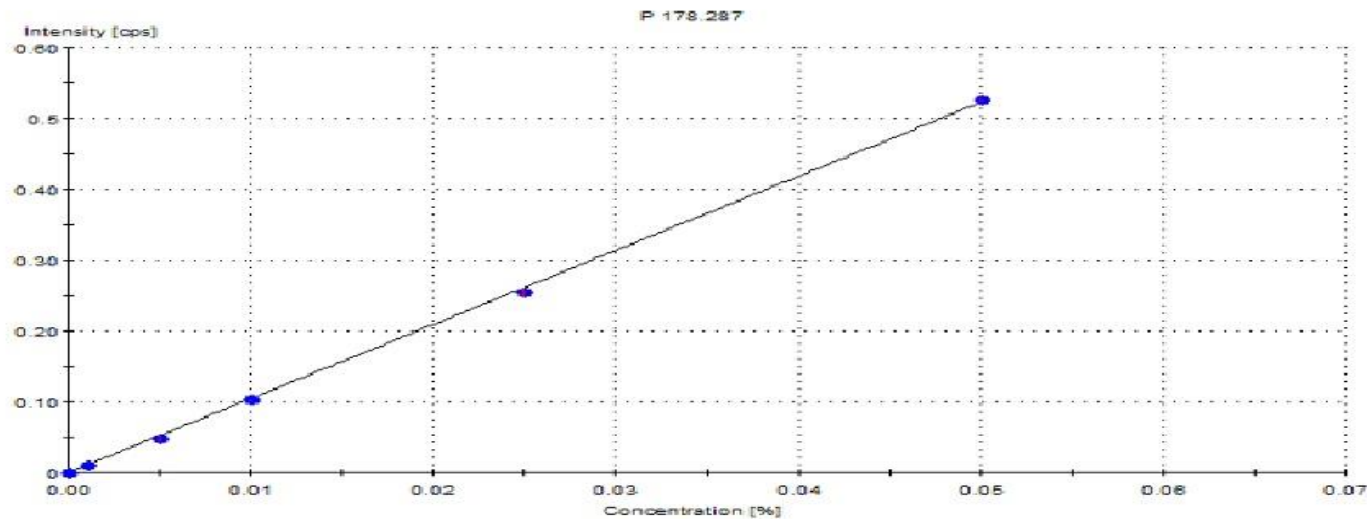


Traditional without Additional Gas (lower trend)

Traditional Calibration

Sample	P 138.147 %	P 178.287 %	P 213.618 %	P 214.914 %	Average %	Expected %
10A	< -0.697	< 0.028	< 0.031	< -0.094	0	0
7A	50.673	50.701	50.718	51.097	50.79725	51.34
5A	45.786	46.129	45.782	45.365	45.7655	46.32
3A	39.248	40.197	40.085	39.953	39.87075	40.94

Calibration = 0, 10, 50, 100, 250, 500ppm Phos



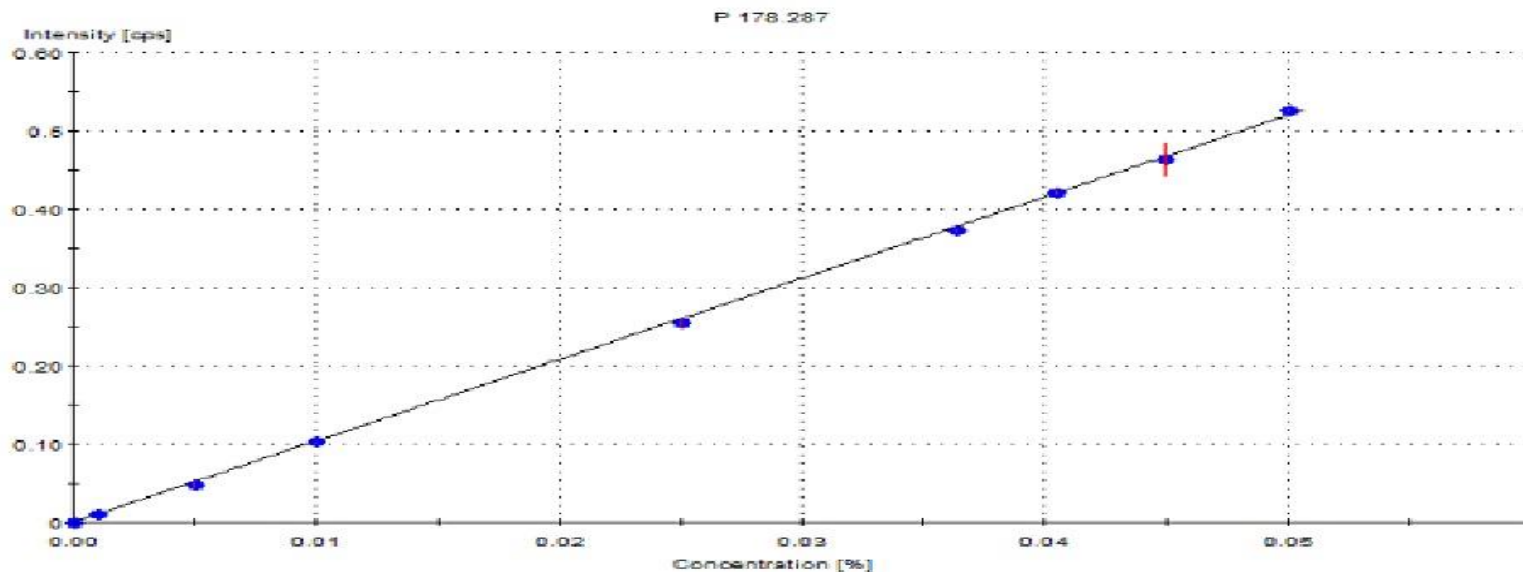


Traditional with partial Empirical (closer to expected)

Traditional Calibration combined with Empirical

Sample	P 138.147 %	P 178.287 %	P 213.618 %	P 214.914 %	P2O5 Ave %	Expected %
10A	< -0.622	< 0.028	< 0.031	< -0.094	0	0
7A	51.624	51.045	51.157	51.563	51.34725	51.34
5A	46.214	46.443	46.179	45.778	46.1535	46.32
3A	39.199	40.47	40.432	40.317	40.1045	40.94

Calibration = 0, 10, 50, 100, 250, 500ppm Phos + 4 Empirical Stds





Other Phosphorus based calibrations

PPO4 calibration gave a biased higher than expected results.

Needs to be re-worked and confirmed.

PO4 – precipitates in the presents of high salt matrices, not suitable for this application.

PP04 Calibration

Sample	P205 Ave %	Expected %
10A	0.021	0
7A	52.051	51.34
5A	46.758	46.32
3A	41.793	40.94



Comments and recommendations

1. Additional carrier gas seems to help accuracy.
2. In a traditional calibration the biggest limiting factor is the ICP's linear error (2%).
3. Empirical calibrations help accuracy and long term precision....!
Wt./Wt. Dilution
0.5012g/0.5g
4. Calibration standards (species) affect accuracy as does digestion!
5. Internal standard, wavelength selection, and averaging also help accuracy.
6. Varying tubing sizes and dilution rate helps based on specific instrumentation more than on the methodology.



Comparison of different techniques (Xepos ED-XRF)

Sample #	Identification	XRF Results as %P2O5	Error	Expected
1	Magruder 2011-07 10-40-0	41.51	0.03	40.56
2	Magruder 2013-01 12-40-0	40.31	0.03	40.48
3	AFPC 2013-07 11-40-0 MAP-S	39.51	0.03	40.94
4	Magruder 2012-03 18-46-0 DAP	49.01	0.03	46.22
5	Magruder 2013-10A 18-46-0 DAP	47.85	0.03	46.32
6	Magruder 2013-03 10-50-0 MAP	53.32	0.03	51.06
7	Magruder 2013-11A 11-52-0 MAP	49.37	0.03	51.34
8	Magruder 2013-11A 11-52-0 MAP	48.82	0.03	51.34
9	Magruder 2013-05 12-61-0 Reagent MAP	58.37	0.04	61.67
10	Magruder 2010-02 32-0-10	0.01942	0.00051	0

4grams of sample was weighed into 32mm XRF cup
 cups used 4 micron polypropylene as the window
 Sample were run again TurboQuant powders program
 300s per measurement condition (4 target conditions used)
 sample chamber was purged with He



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