



Association of
American Plant
Food Control
Officials

SPECIAL GUEST EDITOR SECTION

Determination of Phosphorus and Potassium in Commercial Inorganic Fertilizers by Inductively Coupled Plasma-Optical Emission Spectrometry: Single-Laboratory Validation

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**Validation Support for AOAC
2015.18 Using Magruder Data
(DRAFT)**

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Question and assessment:

- *Can we use existing ICP-PK Magruder data in lieu of conducting a full collaborative study?*
- **Assessment:**
 1. *Reviewed Available Phosphate & Soluble Potash data since 2016*
 2. *Identified 21 samples*
 3. *Compared data from the common methods*
 4. *Compared data to the AAPFCO IA*
 5. *Provided an evaluation of ICP PK data*



Interchangeability between indicators

Can navigate between stdev, %RSD, Investigational Allowance (IA) and Horwitz ratios

1. *Magruder report provides **method stdev***
2. *IA = **analyte stdev** x 2.33*
 - *2.33 = 99% confidence interval, one-tail?*
 - *note: analyte = all method data for that analyte*
 - *combining “pulls-down” better method(s) and “pulls-up” poorer method(s)*
3. *Solve for **analyte stdev** = IA / 2.33*
 - *example for Guar = 50; Avail Phosphate analyte stdev = 1.07 / 2.33 = 0.4592*

Guar % (<i>use Mean</i>)	Avail. Phosphate IA	Sol. Potash IA
50	1.07	1.66

OP No. 72 p. 52



Interchangeability between indicators

4. Generate an **IA ratio**, which compares the **method stdev** to the **IA stdev** (i.e. $\text{method stdev} / \text{IA stdev}$)

- If stdev from the method < stdev from the IA; IA ratio will be < 1
- If stdev from the method > stdev from the IA; IA ratio will be > 1

– Can also use the Magruder method %RSD

- $\text{RSD} = \text{stdev} / \text{mean} \times 100$

- **References:**

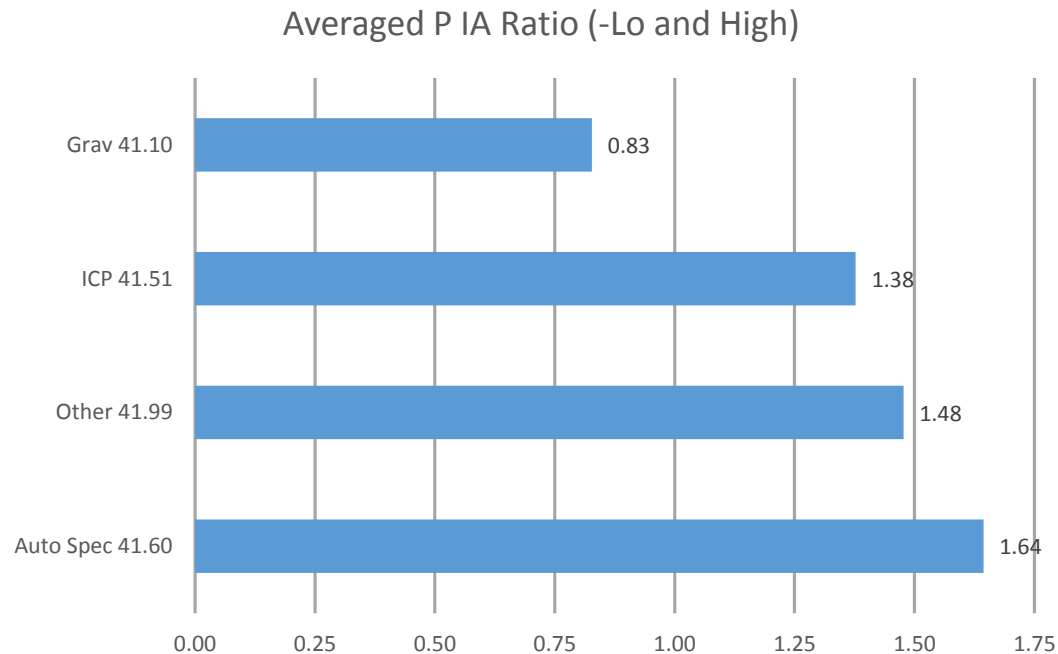
- http://www.magruderchecksample.org/presentations/2018S_IAsVsRSDObservations.pdf
- http://www.magruderchecksample.org/presentations/2018W_NewIAMetrics.pdf

– Can compare to Horwitz (i.e. AOAC historic variability)

- calculate Horwitz predicted %RSD = $2C^{-0.15}$ and solve for stdev



IA ratio for available P₂O₅ by method

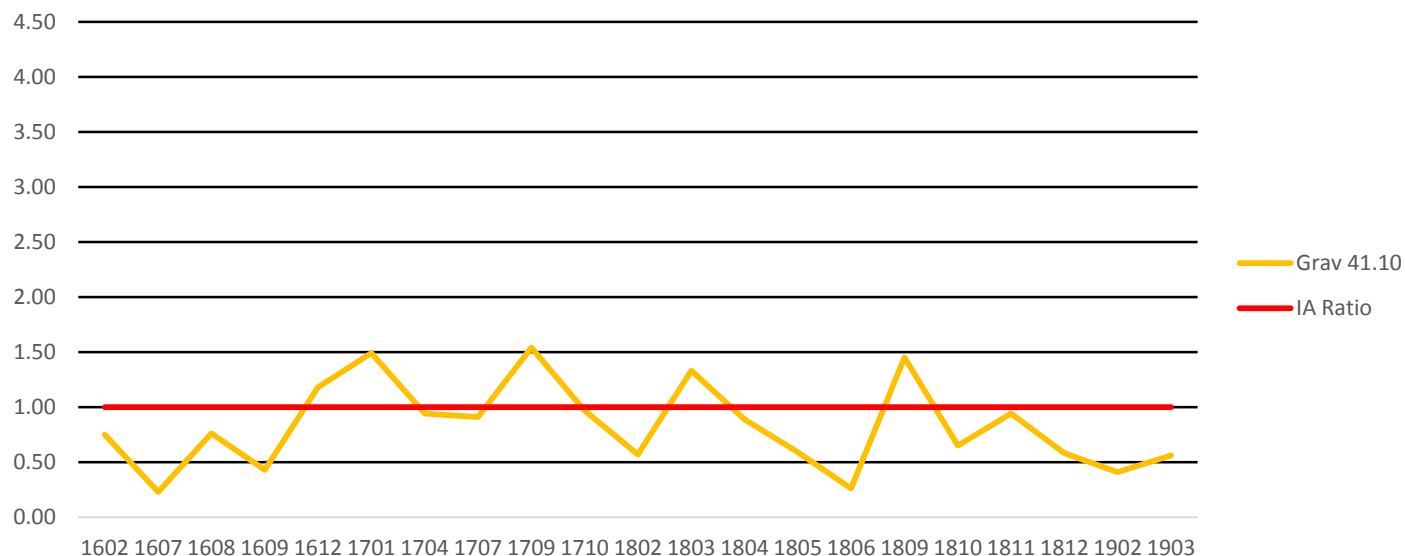


- ***On average, Grav 41.10 method produced IA ratios < 1***
 - *one of the methods used to help establish the IA*
- ***ICP 41.51 was second best method, but with averaged IA ratios above 1***
 - *therefore some data variability above the IA*



IA Ratios for P₂O₅ by Method

P IA Ratio Grav Method 41.10

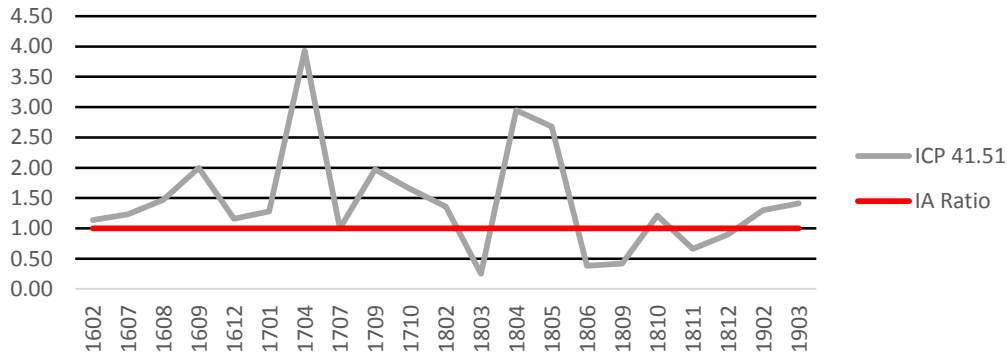


Interpretation

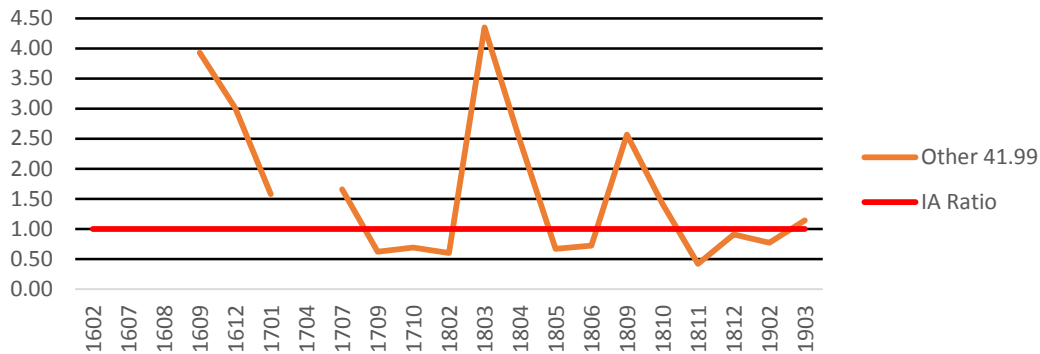
- *Magruder sample ID on X-axis, IA ratio value on the Y-axis*
- *Want most, or preferably all, data to fall below IA ratio of 1*
- *More an indicator of variability/reproducibility than accuracy*
- *Gravimetric IA ratios approaching ideal*
 - *averaged IA ratio = 0.83, with 81% of data ≤ 1*
- *(1803 = 3-1-2; 1809 = 3-1-3); (1701 = 18-46-0; 1709 = 12-40-0)*



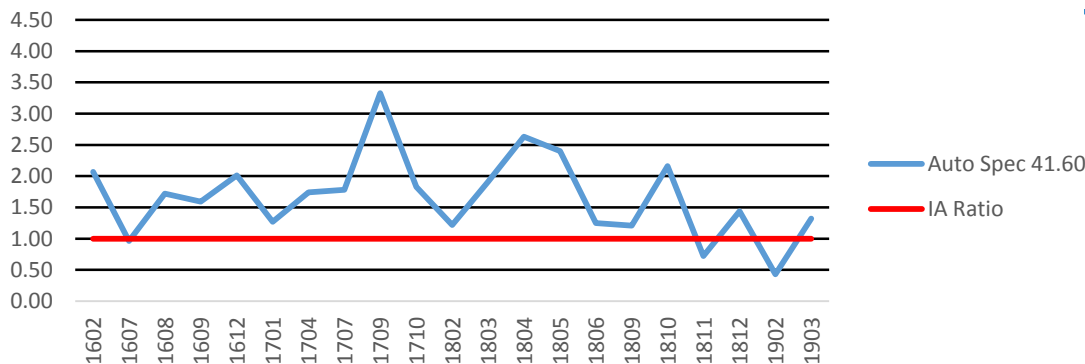
P IA Ratio - ICP 41.51



P IA Ratio - Other 41.99



P IA Ratio - Auto Spectrophotometer 41.60



ICP

- Avg IA ratio = 1.38
- Several values > 1
- Average is approaching the IA, but more variable
- 1704 & 1804 = 15 and 24% P₂O₅
- 1609, 1709 & 1805 ≥ 40% P₂O₅
- Trending in right direction?

Other

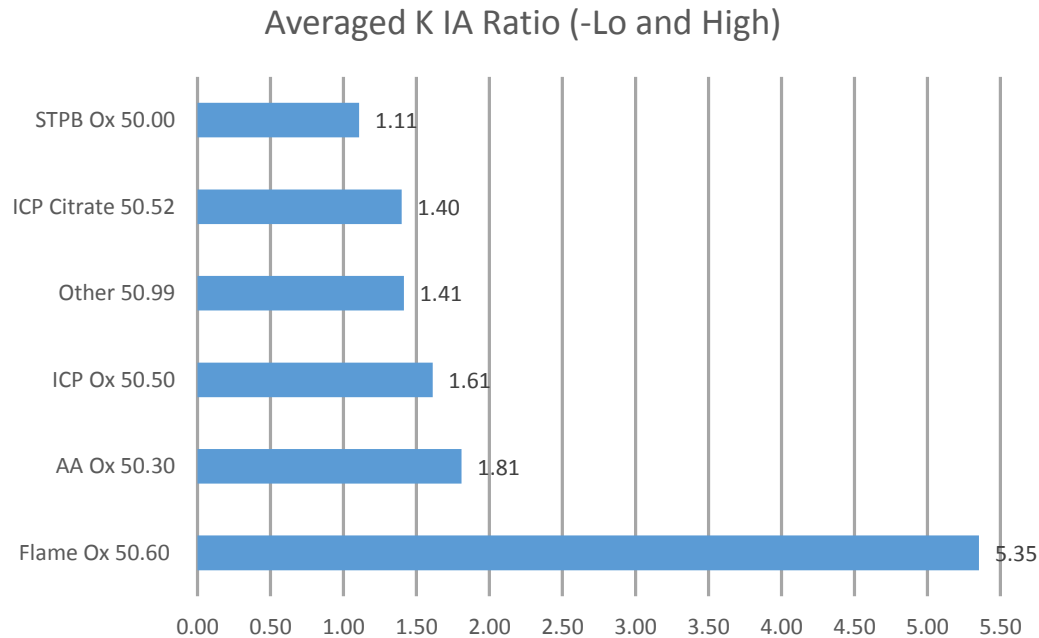
- Avg IA ratio = 1.48
- Several values > 1
- Not one single method

Auto Spec

- Surprise?
- Avg IA ratio = 1.64
- Most values > 1
- 41.60 is collaborated official method



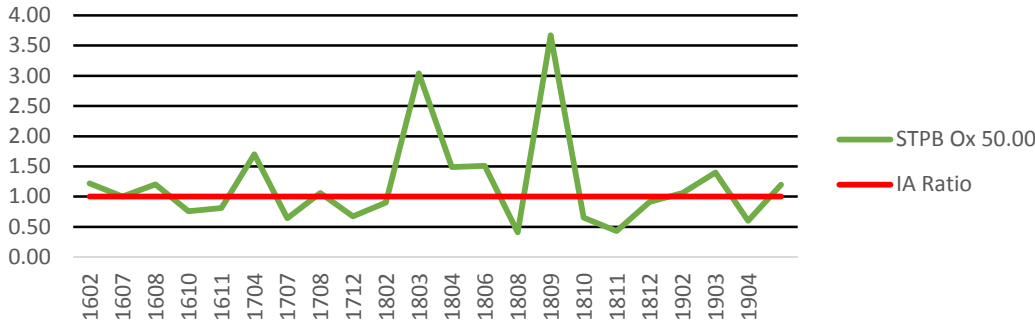
IA ratio for soluble K_2O by method



- ***On average, the STPB oxalate produced IA ratios close to 1***
 - *one of the methods used to help establish the IA*
- ***ICP citrate 50.52 was the second best method, but with averaged IA ratio above 1***
 - *therefore some data variability above the IA*



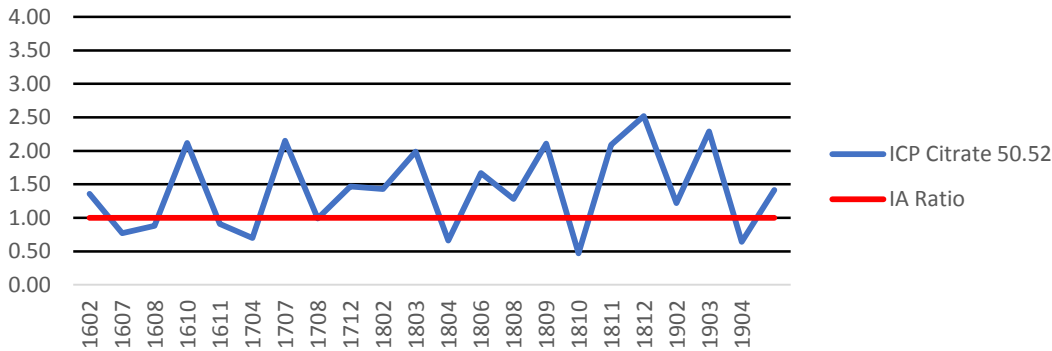
K IA Ratio - STPB Oxalate



STPB Oxalate

- *averaged IA ratio = 1.1*
- *Several values near 1*
- *More variable with low guarantees*
 - 180311 = 2% K₂O
 - 180911 = 3% K₂O
- *Otherwise, close to ideal*

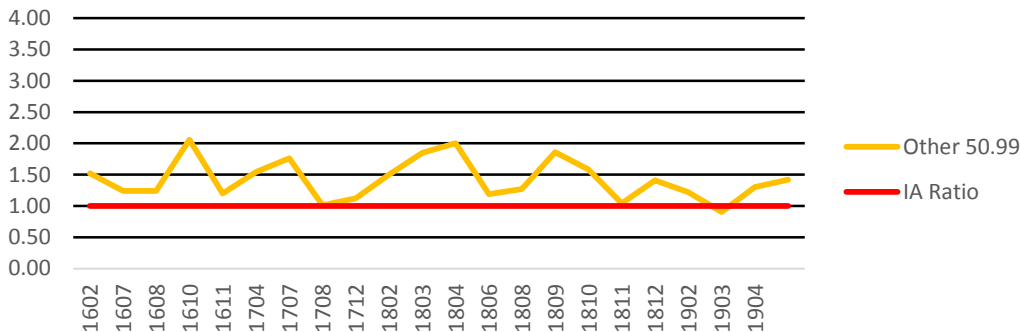
K IA Ratio - ICP Citrate



ICP Citrate

- *Avg IA ratio = 1.40*
- *Data is quite variable*
- *Several values > 1*

K IA Ratio - Other

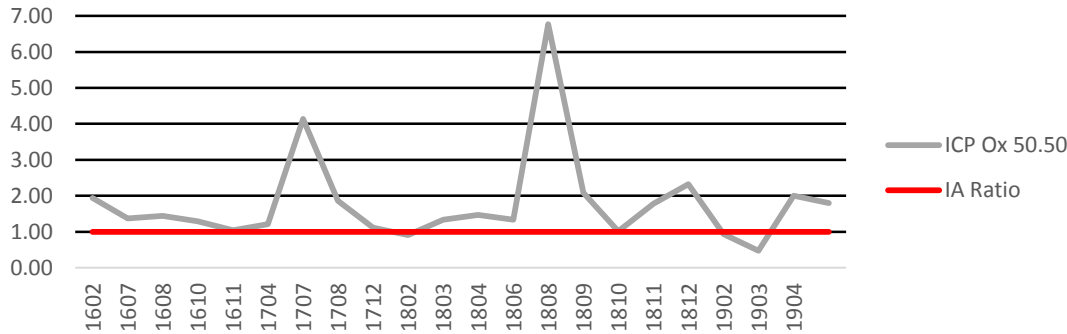


Other

- *Avg IA ratio = 1.41*
- *Not a single method*
- *IA ratio consistently between 1 to 2*



K IA - ICP Oxalate

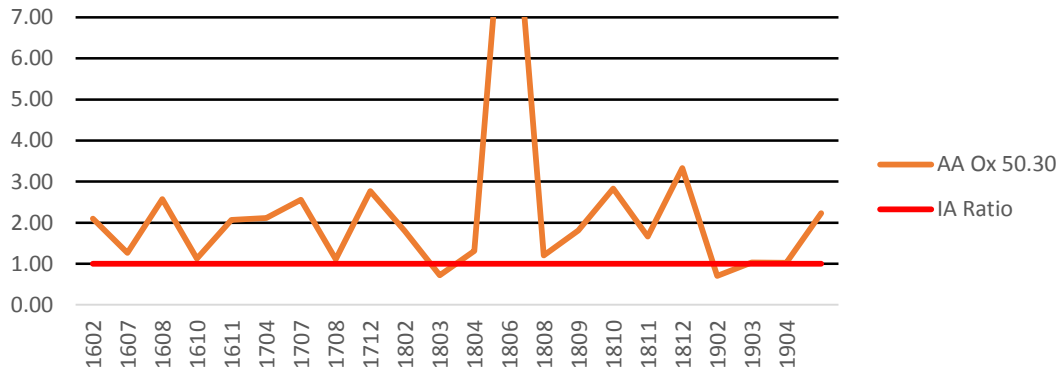


note changes in Y-axis scale

ICP Oxalate

- Avg IA ratio = 1.61
- Oxalate is more difficult ICP matrix than citrate
- 180812 = 0-0-60

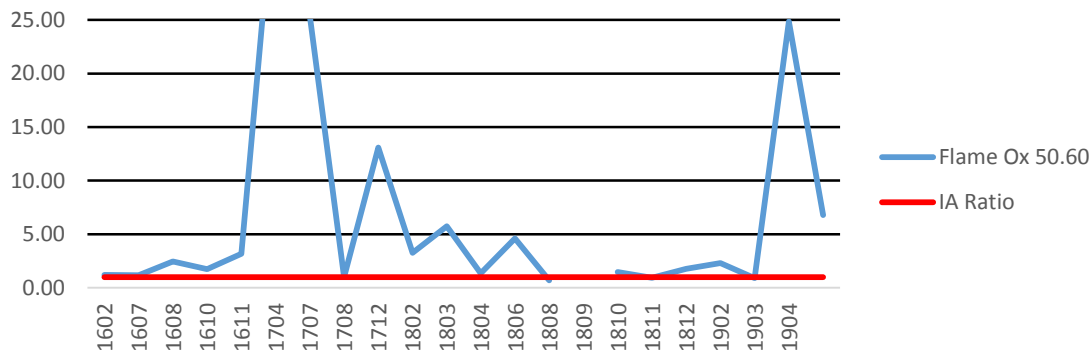
K IA Ratio - AA Oxalate



AA Oxalate

- Avg IA ratio = 1.81
- 5 to 6 labs reporting
- Data is quite variable
- Most values between 1 - 3
- 1806 = SRN, 6% K₂O

K IA Ratio - Flame Oxalate

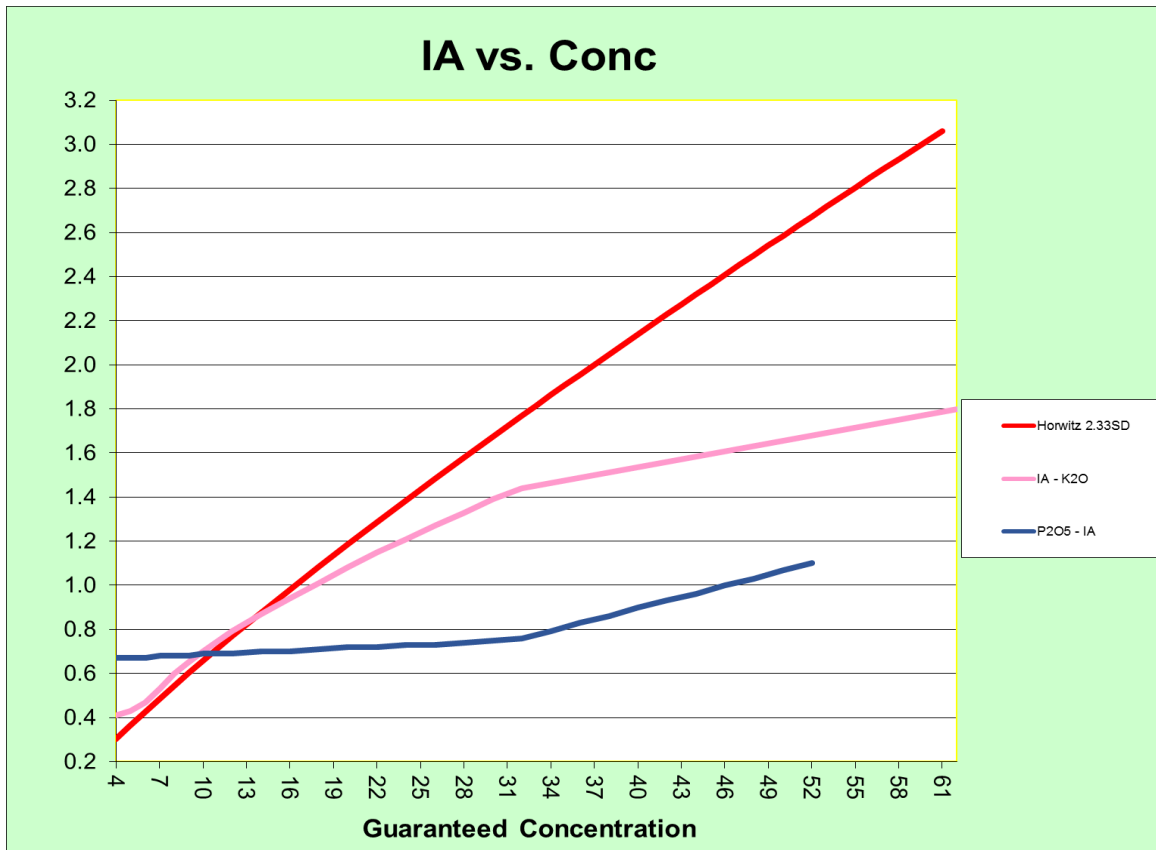


Flame Oxalate

- Avg IA ratio = 5.35
- Yikes!
- Data is highly variable
- Only 3 to 5 labs reporting



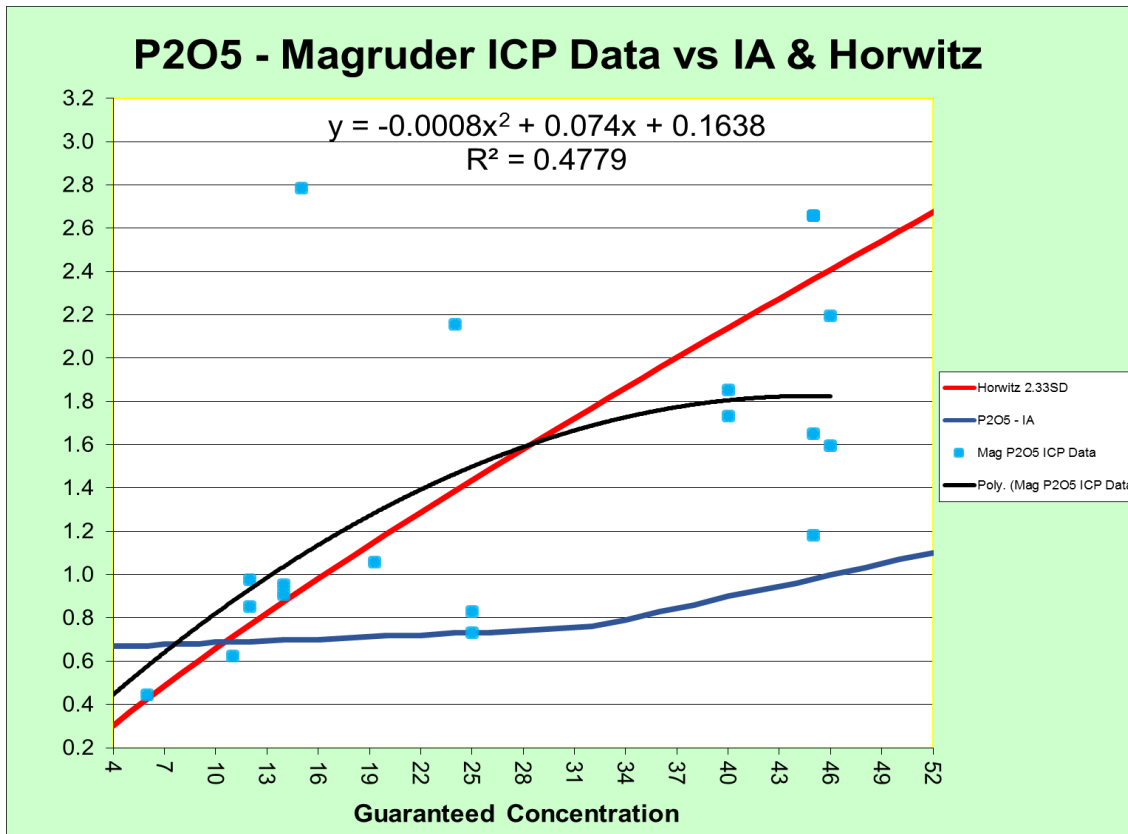
What about Horwitz?



- *Solve Horwitz predicted RSD for stdev, then multiply by 2.33 for “universal” IA estimate*
- *K₂O IA similar to Horwitz at lower conc; below Horwitz at high*
- *P₂O₅ IA is unusual, mostly well below Horwitz & relatively flat*



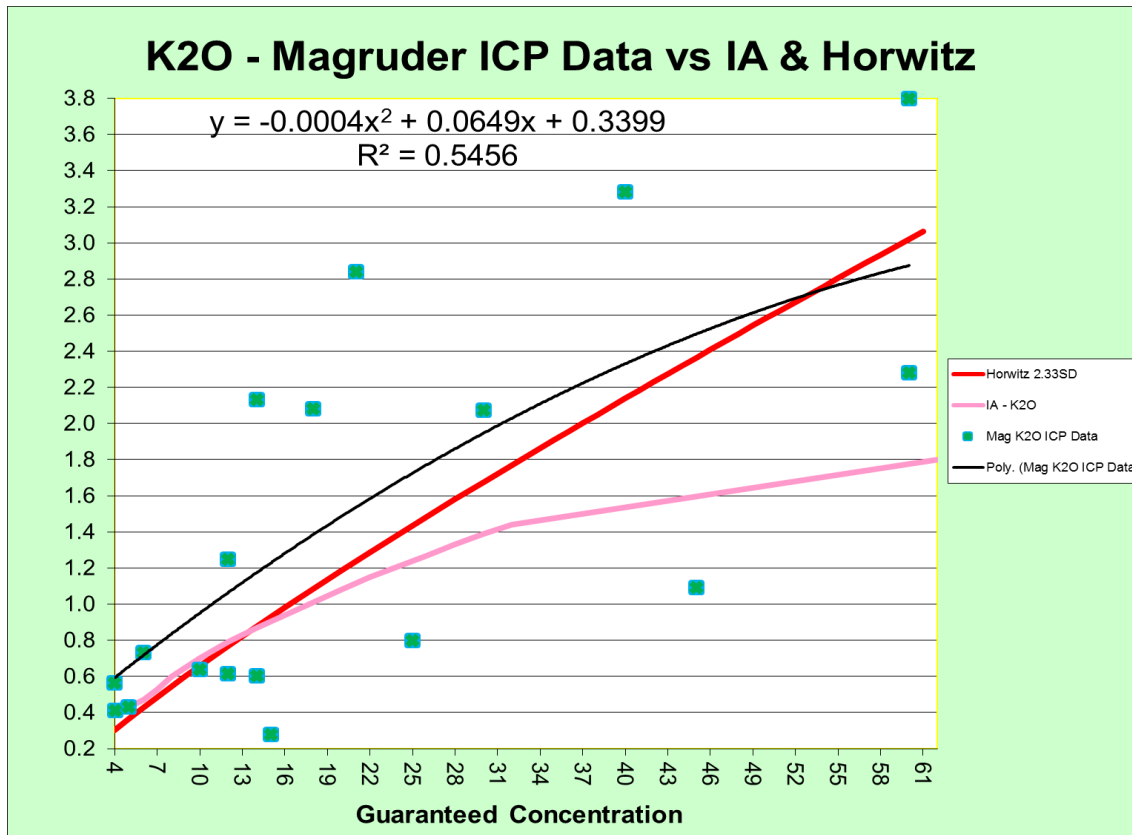
Magruder ICP-P stdev vs. IA & Horwitz?



- *Stdev from Magruder ICP direct available P₂O₅ data*
- *Multiply by 2.33 to put on IA scale, then calculate trend line*
- *Horwitz PRSD solved for stdev, then multiplied by 2.33*
- *On average, ICP-P data is more similar to Horwitz than to the IA*
- *Data still quite variable*



Magruder ICP-K stdev vs. IA & Horwitz?



- *Stdev from Magruder ICP citrate K₂O data*
- *Multiply by 2.33 to put on IA scale, then calculate trend line*
- *Horwitz PRSD solved for stdev, then multiplied by 2.33*
- *On average, ICP-K data is more similar to Horwitz than to the IA*
- *Data still quite variable*



Summary (Good)

- 1. Currently, ICP citrate is the second best P & K method***
 - some other “official” methods are worse*
- 2. Several Magruder P & K samples/guarantees***
 - probably enough to satisfy reviewers*
- 3. Wide range of concentrations and matrices***
- 4. Participants likely state, industry, commercial, private and possibly international labs?***
- 5. Duplicates, so have estimate of repeatability***
- 6. Data is similar to Horwitz, so acceptable***
HorRat values are likely
- 7. Would save LOTS of time***



Summary (Bad)

- 1. ICP PK data sometimes exceeds the AAPFCO IA**
 - *If becomes official, may need to improve variability or increase IA?*
 - *Relegate to screening method, or not a BPM?*
- 2. Accept data as is, without opportunity for improvement**
 - *No practice samples*
 - *Can't work with collaborators to improve accuracy or precision*
 - *Can't un-invite under performing lab(s)*
- 3. Fixed data format/sources vs. dynamic**
 - *Magruder – may have different labs and/or different numbers of labs reporting for any given sample*
- 4. Statistical challenges?**
 - *Used robust statistics, so not sure about raw statistics*
 - *May be less than 8 labs reporting sometimes, which may eliminate tests for outliers*
 - *Note < 7 eliminates robust statistics*
- 5. May not meet ISO criteria?**



Conclusions

- *Quicker and easier completion of collaborative study, so the good may outweigh the bad*
- *Data likely better if did traditional collaborative study of selecting samples, collaborators, evaluating “pre-screening” sample data and providing training*
 - *A historical bias?*
- *Data will most likely meet AOAC validation criteria*
- *Some data may not meet AAPFCO’s IA criteria*
- *Look to AOAC for some guidance on data handling*
- *Looking to AAPFCO Magruder committee for recommendations*
- *Acknowledge: Andy Crawford, Frank Sikora, Harold Falls*

