Avio ICP-OES applications

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Wastewater Analysis with the Avio® 500 ICP-OES and EPA Method 200.7

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Introduction

- Pollution control & prevention is critical for human and environmental health
- Water must be monitored at all stages
- U.S EPA Method 200.7
  - Determination of metals & trace elements in waters and wastes by ICP-OES
  - Variety of implementations
- Focus on wastewaters
  - High elemental concentrations & difficult matrices → perfect for ICP-OES

Sample & Sample Preparation

- Samples: Wastewater Reference Materials
  - Wastewaters C & D (High Purity Standards)
  - Wastewaters Low & High (Inorganic Ventures)
- Sample Preparation
  - Prepare as directed on reference materials
  - No further dilution
- Calibrations
  - External

Element	Standard 1 (mg/L)	Standard 2 (mg/L)	Standard 3 (mg/L)
Ag, Al, As, B, Ba, Be, Cd, Ce, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn	0.5	1	5
Na, Mg, K, Ca	20.5	51	105

- Internal Standards: Sc & Y

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Instrumental Conditions: Avio® 500 ICP-OES

Instrumental Parameters

Parameter	Value
Nebulizer	MEINHARD® Type K
Spray Chamber	Baffled glass cyclonic
Sample Uptake Rate	1.0 mL/min
RF Power	1500 W
Injector	2.0 mm id Alumina
Nebulizer Gas Flow	0.70 L/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	8 L/min
Integration Range	1-10 sec
Sample Uptake Tubing	Black/Black (0.76 mm id)
Internal Standard Tubing	Green/Orange (0.38 mm id)
Drain Tubing	Red/Red (1.14 mm id)
Replicates	4

Low Argon Flows

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Instrumental Conditions: Avio® 500 ICP-OES

Elements, Wavelengths, and Plasma View

Element	Wavelength (nm)	Plasma View
Ag	328.068	Radial
Al	394.401	Radial
As	188.979	Axial
B	249.677	Axial
Ba	493.408	Radial
Be	313.107	Axial
Ca	315.887	Radial
Cd	214.440	Axial
Co	228.616	Axial
Cr	267.716	Axial
Cu	324.752	Axial
Fe	238.204	Radial
K	766.490	Radial
Li	670.784	Radial
Mg	285.213	Radial
Mn	257.610	Axial

Element	Wavelength (nm)	Plasma View
Mo	203.845	Axial
Na	589.592	Radial
Ni	231.604	Axial
P	178.221	Axial
Pb	220.353	Axial
Sb	206.836	Axial
Se	196.026	Axial
Si	251.611	Axial
Sn	189.927	Axial
Sr	421.552	Radial
Ti	334.940	Axial
Tl	190.801	Axial
V	292.402	Axial
Zn	206.200	Axial
Sc (int std)	361.383	Radial
Y (int std)	371.029	Axial

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Results: Linear Dynamic Range

- Highest concentration that will recover within 10% based when analyzed against a normal calibration curve

Elements	Linear Range (mg/L)
Al, Be, Mn, Ti	50
Ag, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li Mo, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Tl, V, Zn	100*
Mg	200
Ca, K, Na	500*

* = highest concentration tested

- Options for extending the linear range
  - Use a less sensitive sample introduction system
  - Vary the torch position
  - Select less sensitive wavelengths
  - Change the viewing height in the plasma

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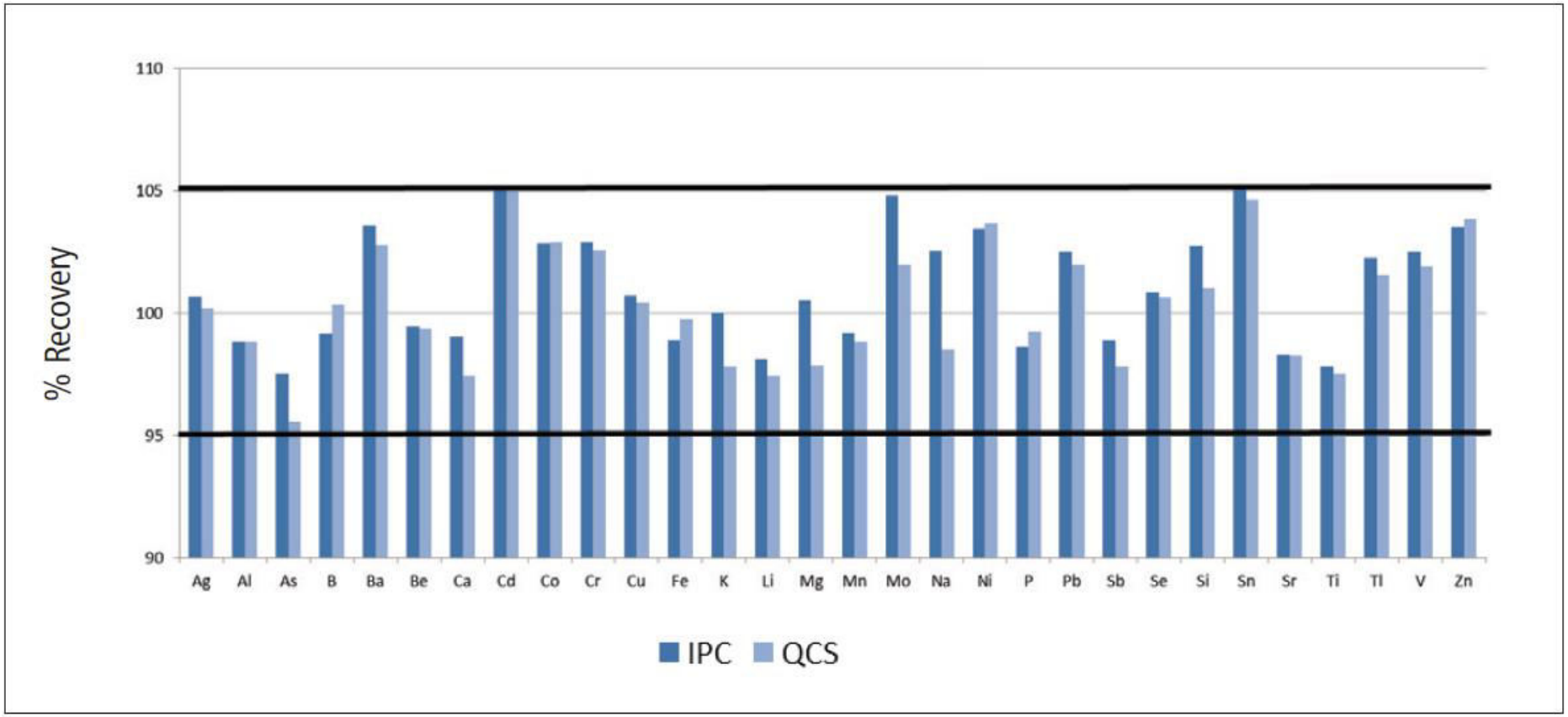
Results: Initial Quality Control

- Initial Performance Check (IPC)
  - Made from same stock solutions as the calibration standards
  - Analyzed after the calibration standards
  - All elements must recover within 5% of their true concentration

- Quality Control Sample (QCS)
  - Made from 2nd source standards
  - Same concentration as the IPC
  - Analyzed after the IPC
  - All elements must recover within 5% of their true concentration

Results: Initial Quality Control

All Elements Recover within 5%



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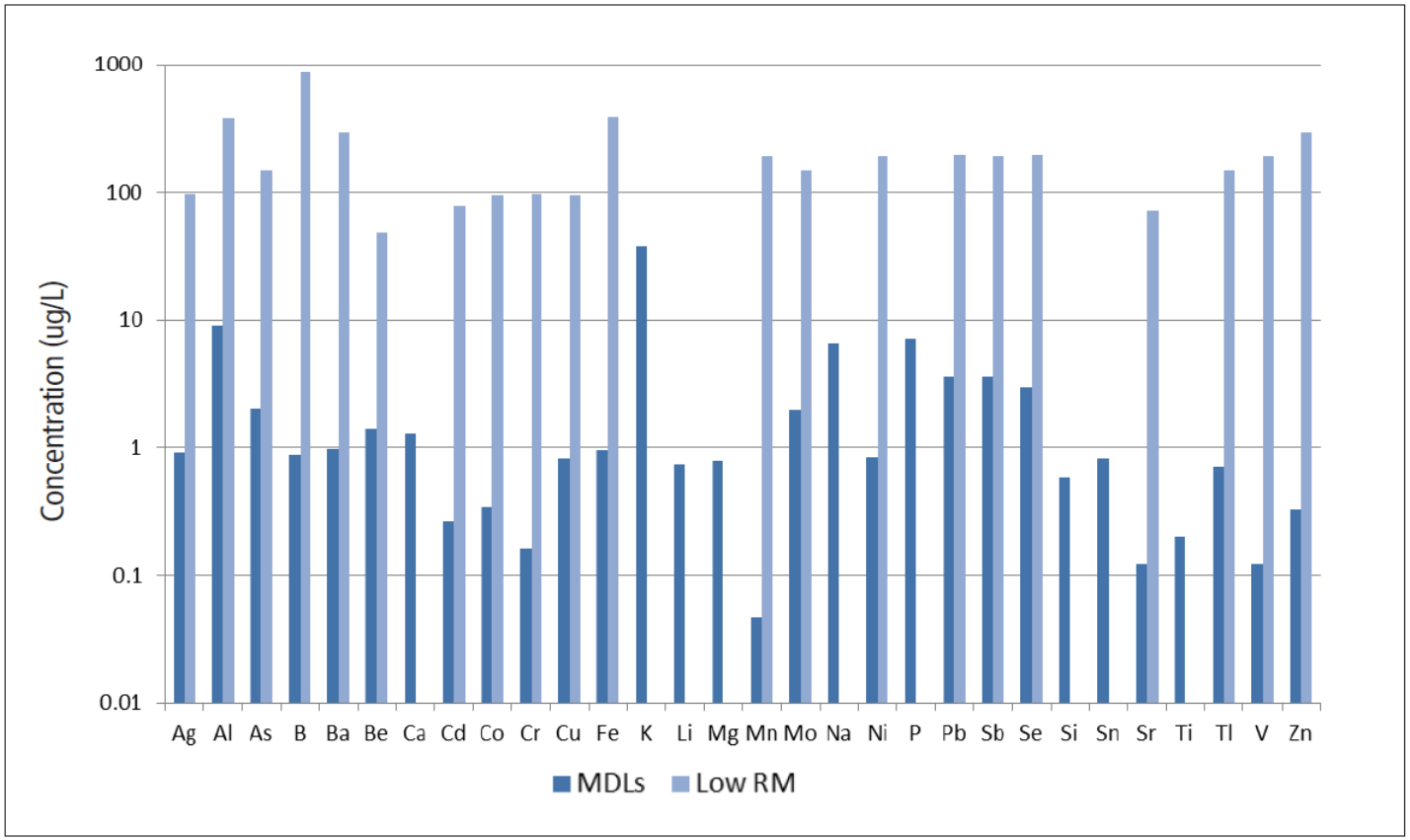
Results: Method Detection Limits

- 3.14 * Standard Deviation of 7 measurements of a blank spiked at 2-3 times the instrument detection limit



MDLs much lower than low reference material

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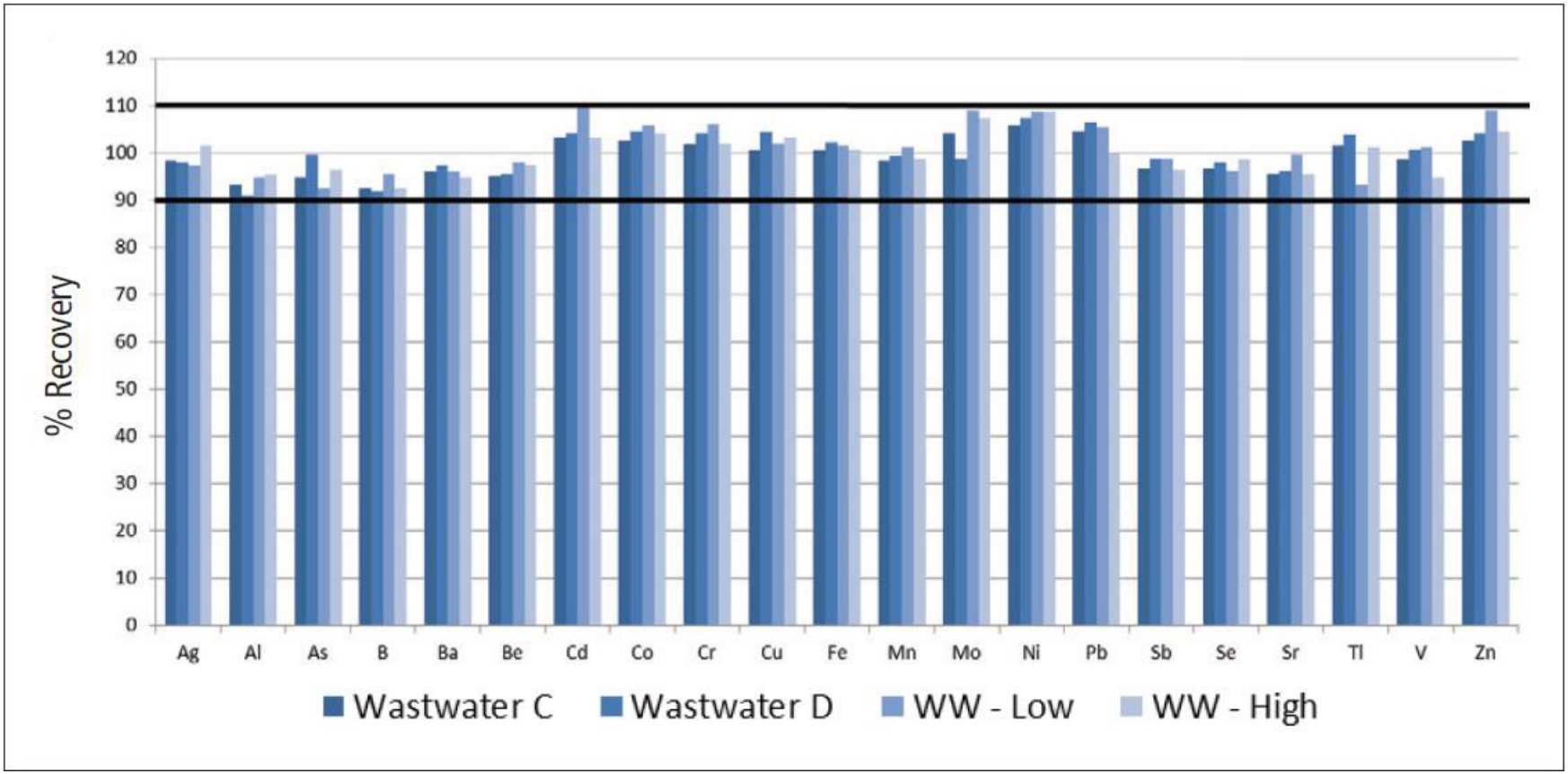
Results: Spectral Interference Check

- Run 300 mg/L Fe + 200 mg/L Al
  - Specified in 200.7
- Look for false positives on analytes
- Confirm that false positives result from contamination and not interferences
- Spectral resolution of Avio 500 allows elements to be measured without the need for IECs

Results: Accuracy

- Run wastewater reference materials



Recoveries within 10% for all elements in 4 different reference materials

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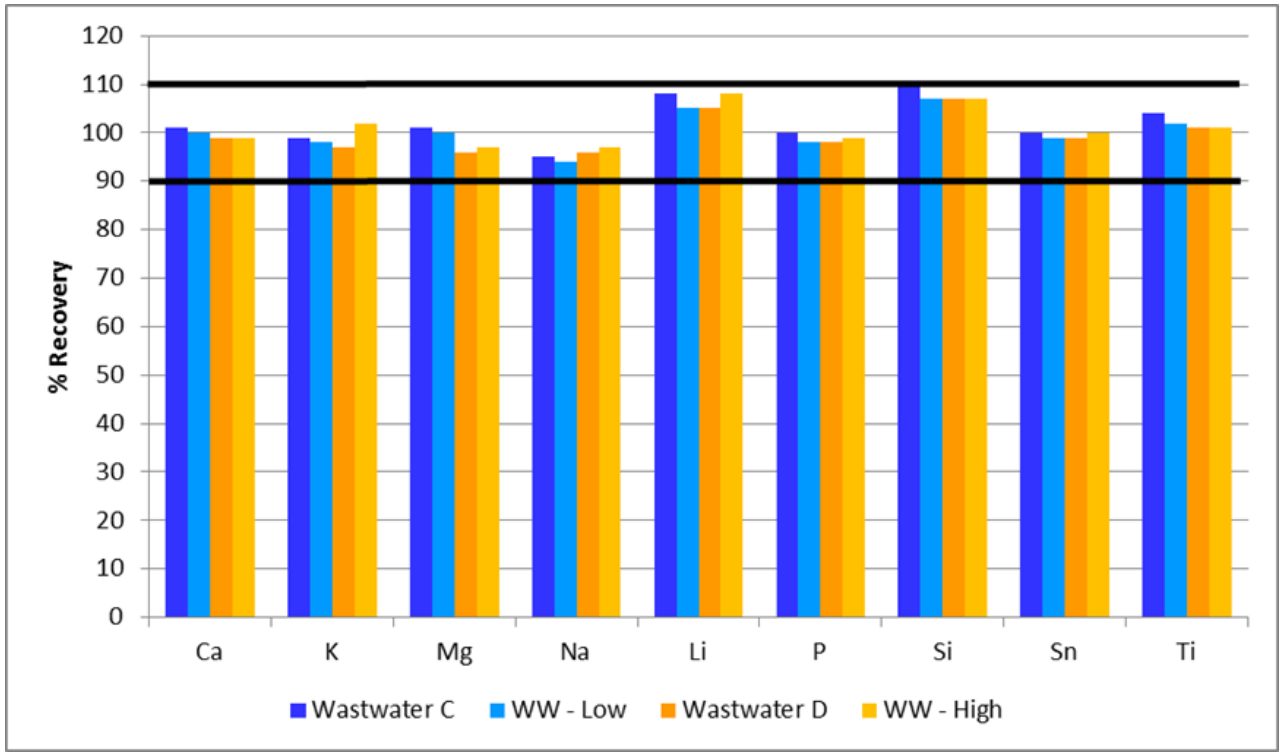
Results: Accuracy

- Elements in EPA 200.7 not certified in the reference materials
  - B, Li, P, Si → Spike at 0.6 and 1.2 ppm
  - Na, Mg, Ca, K → Spike at 75 and 150 ppm



Recoveries within 10% for all elements in 4 different RMs

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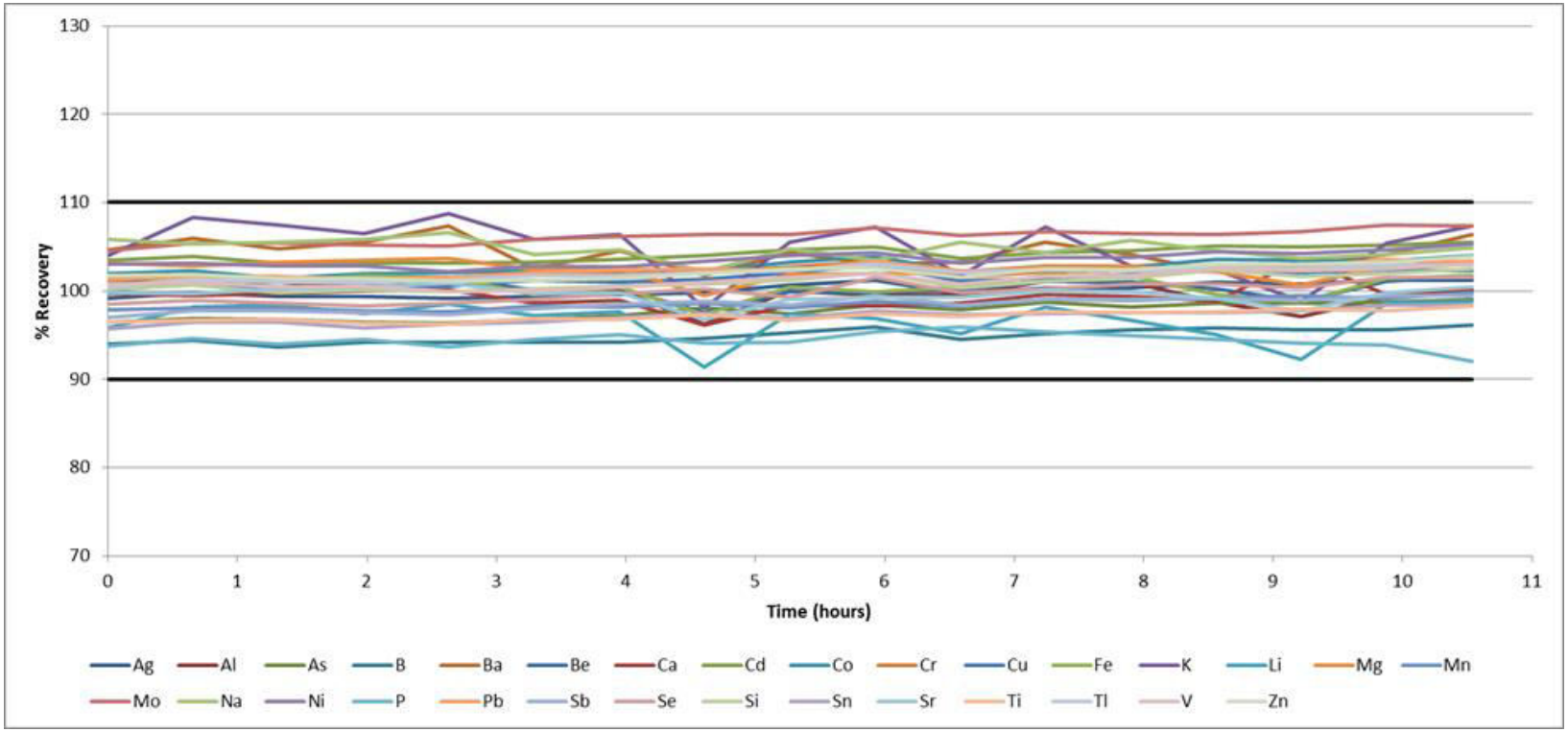
Results: Stability

- Run IPC every 10 samples during a 10-hour wastewater analysis
  - Recoveries must be within 10% of true values



All recoveries within 10% over 10 hours

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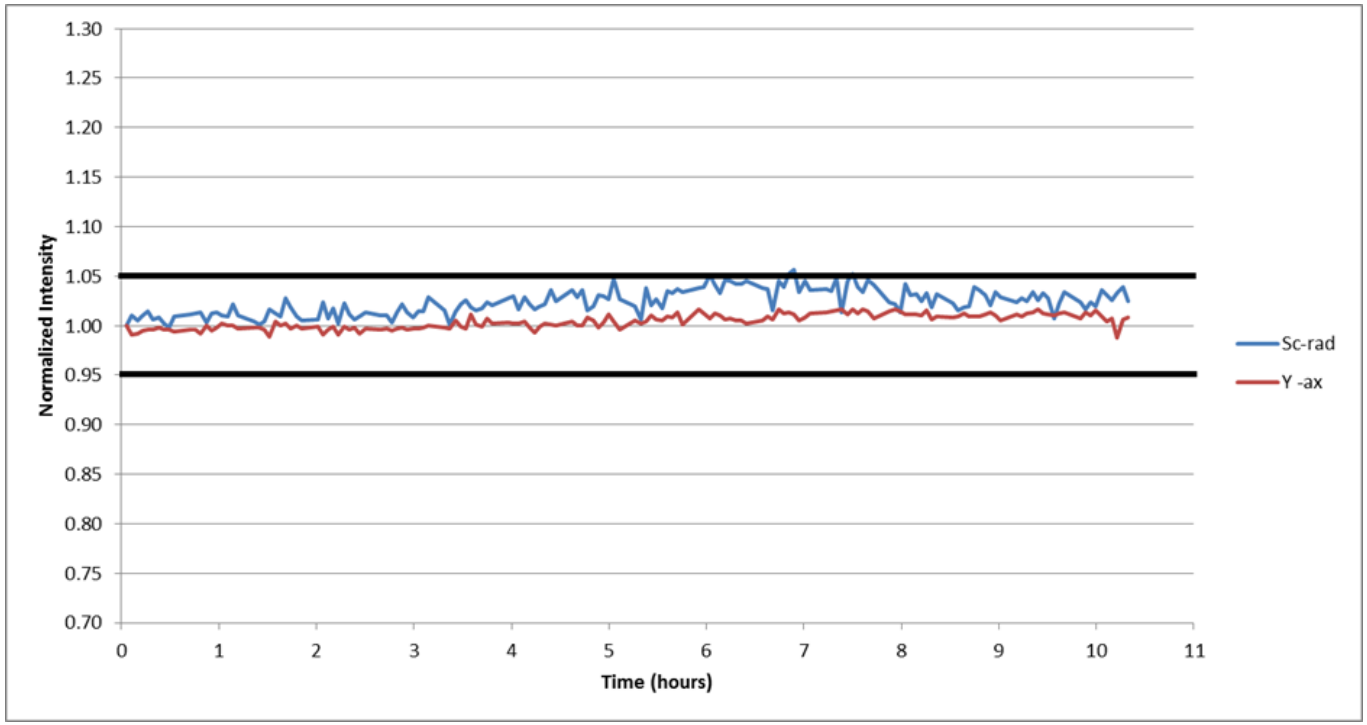
Results: Stability

- Monitor internal standards to check for instrument drift
  - Sc in radial mode, Y in axial mode



Variations of 5% over 10 hours

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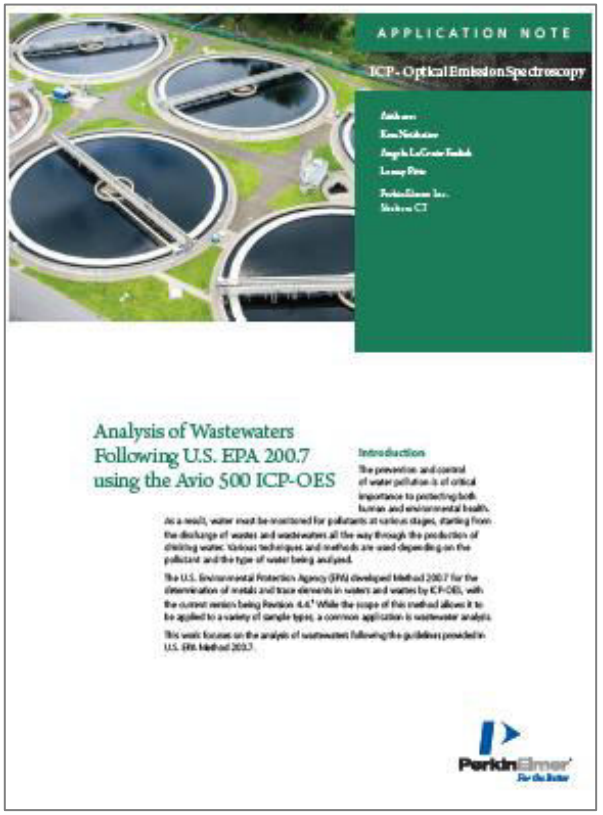
Summary

- The Avio® 500 ICP-OES easily analyzes wastewaters following EPA Method 200.7
- Take advantage of both axial and radial plasma viewing
- Accurate and stable analyses
- Vertical torch and low argon consumption provide a robust, cost-effective way to analyze wastewaters



To download the full application note, visit www.perkinelmer.com/avio500

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Analysis of In-Service Oils Following ASTM D5185 with the Avio 200 ICP-OES

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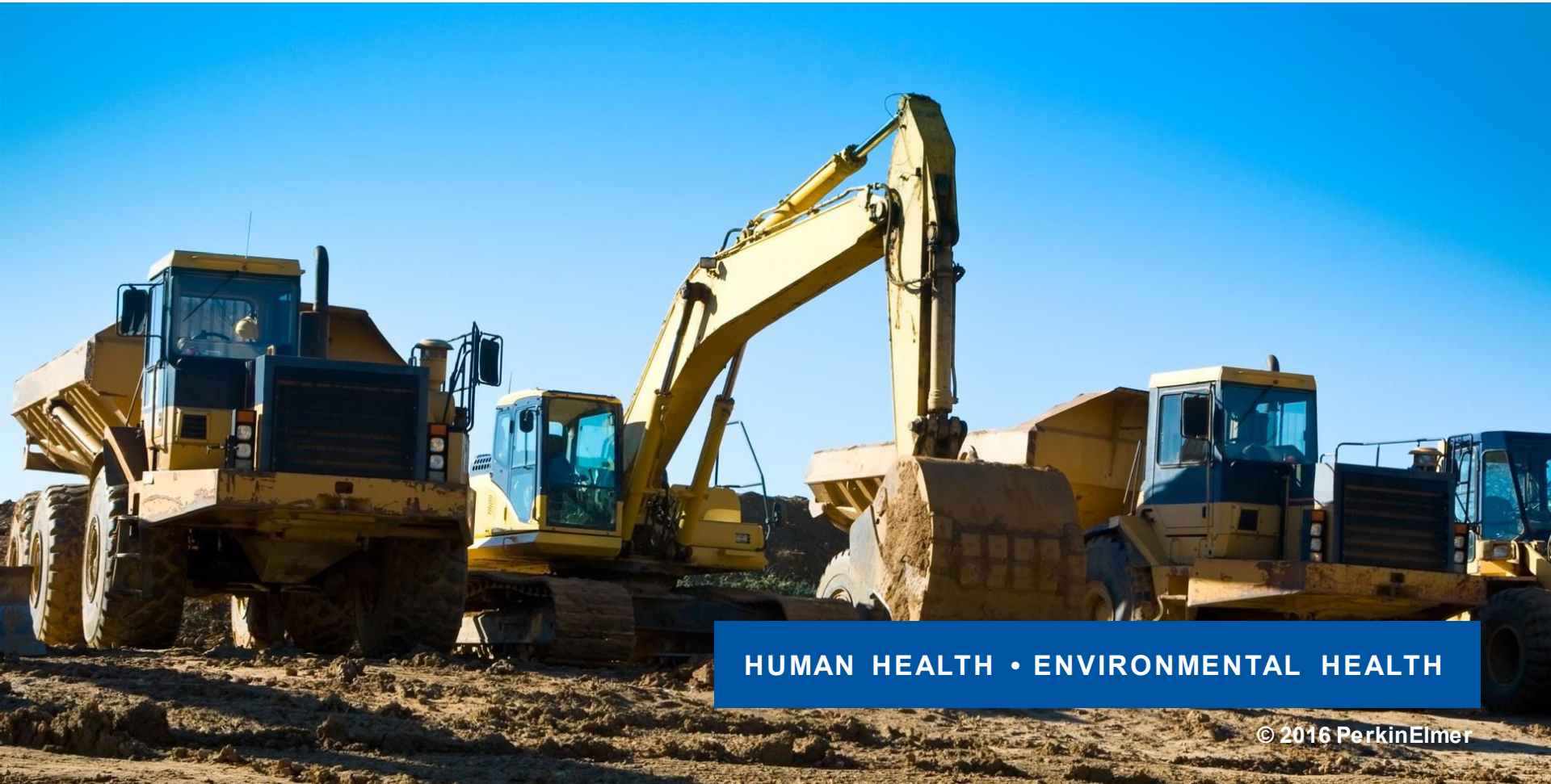

HUMAN HEALTH • ENVIRONMENTAL HEALTH

Introduction

- With heavy machinery, important to monitor its status to prevent breakdown and costly repairs
- Monitor oil & lubricants for metal content
  - Engines, transmissions, gearboxes, and other areas
- Metal content provides information about the conditions of the engine and oil itself
  - Diagnostic for when oil needs changing
- Important elemental concentrations > 1 ppm
  - ICP-OES is ideal technique

Introduction: ASTM D5185 for In-Service Oils

Parameter	Specified by D5185	Common Implementation
Elements	Al, Ba, B, Ca,Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, K, Na, Si, Ag, S, Sn, Ti, V, Zn	Elements important to the components being tested
Sample Preparation	By weight	By volume
Internal Standard	Cd, Co, or Y	Co
QC Frequency	Every 5 samples	Varies between 10-25 samples
QC Limits	± 5%	± 10%

- For high-throughput labs, simultaneous ICP-OES preferred
- For low-throughput labs, the Avio 200 is ideal

Samples & Sample Preparation

- Samples
  - In-Service Oils
- Sample Preparation
  - Dilute10x (by volume) with V-Solv spiked with 40 ppm Co (internal standard)
- Calibrations
  - Blank = 75 cSt base oil
  - Calibration Standards
    - V-23: 50, 100, 500 ppm
    - MA4 for Ca, P, Mg, Zn
- QC
  - 50 ppm V-23 + MA4

Instrumental Conditions: Avio™ 200 ICP-OES

Elements and Wavelengths

Element	Wavelength (nm)
Al	394.401
Ag	328.068
B	249.677
Ba	232.527
Ca	315.887
Cd	228.802
Cr	205.560
Cu	324.752
Fe	259.939
K	766.490
Mg	279.077
Mo	203.845
Mn	257.610
Na	588.995
Ni	232.003
P	214.914
Pb	220.353
Sb	217.582
Si	288.158
Sn	189.927
Ti	334.940
V	292.464
Zn	213.857
Co (internal standard)	228.616

Instrumental Parameters

Parameter	Value
Nebulizer	GemCone™ (modified Babbington)
Spray Chamber	Baffled glass cyclonic
RF Power	1500 W
Torch	3-Slot Avio torch for organics
Injector	1.2 mm ceramic
Plasma Gas Flow	10 L/min
Aux Gas Flow	0.8 L/min
Nebulizer Gas Flow	0.40 L/min
Torch Position	-4
Sample Uptake Rate	2.0 mL/min
Sample Uptake Tubing	Black/Black (0.76 mm id), Viton
Drain Tubing	Red/Red (1.14 mm id), SolvaFlex
Read Delay	18 sec
Replicates	2
Rinse Between Samples	12 sec (fast pump at 6 mL/min)
Auto Integration Range	0.2 - 1.0 sec

Low Argon Flows

Short Integration Times

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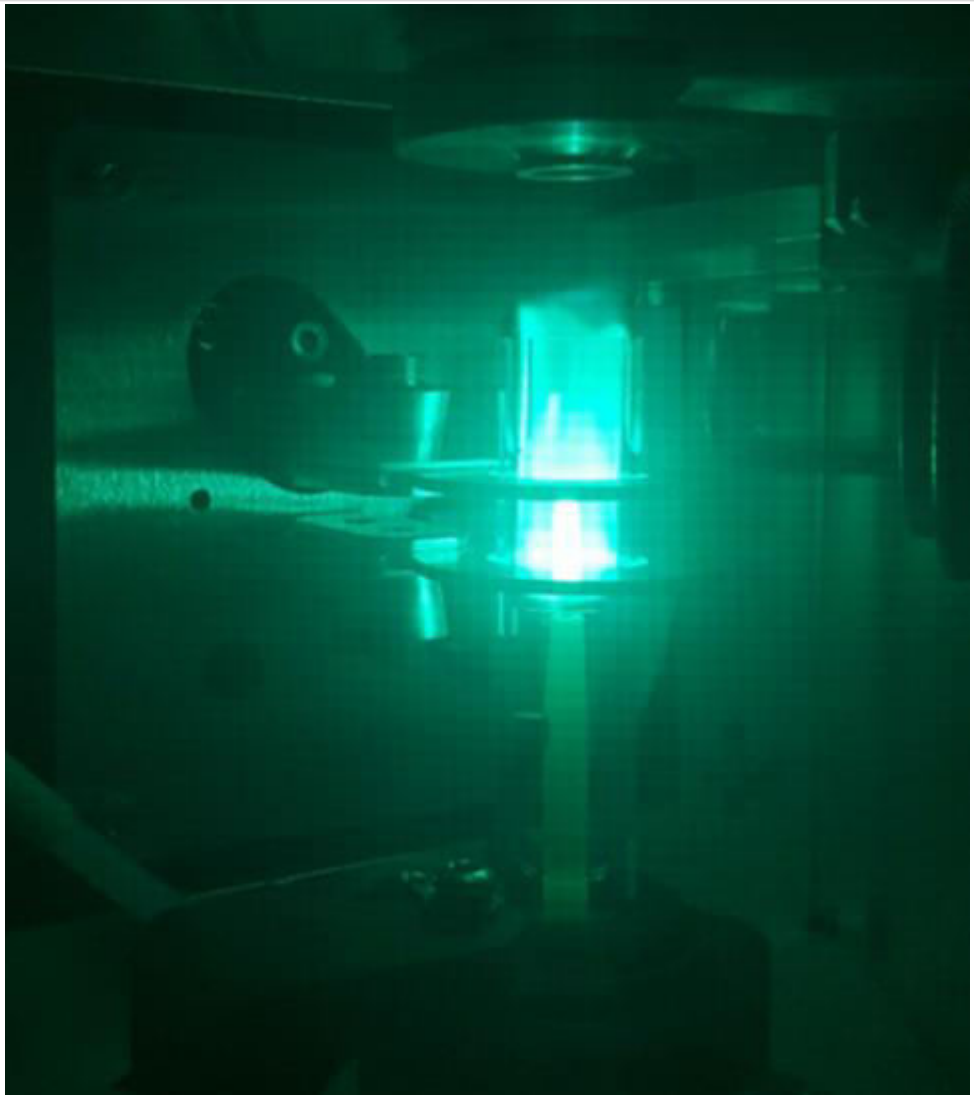
Instrumental Conditions: Avio™ 200 ICP-OES



- Correct Plasma Position
  - Carbon “bullet” just below 2nd flat plate

Results: Typical In-Service Oil Sample

Element	Concentration (ppm)	RSD (%)
Al	16	3.1
Ag	< 0.5*	-
B	81	2.8
Ba	< 0.5*	5.9
Ca	2441	0.21
Cd	< 0.5*	-
Cr	1	2.6
Cu	1	0.26
Fe	27	0.44
K	5	8.0
Mg	17	2.2
Mo	25	0.87
Mn	1	0.69
Na	236	0.44
Ni	2	12
P	847	1.9
Pb	7	0.65
Sb	< 0.5*	-
Si	9	4.2
Sn	< 0.5*	-
Ti	< 0.5*	-
V	< 0.5*	-
Zn	974	2.8

* = lower quantification limit

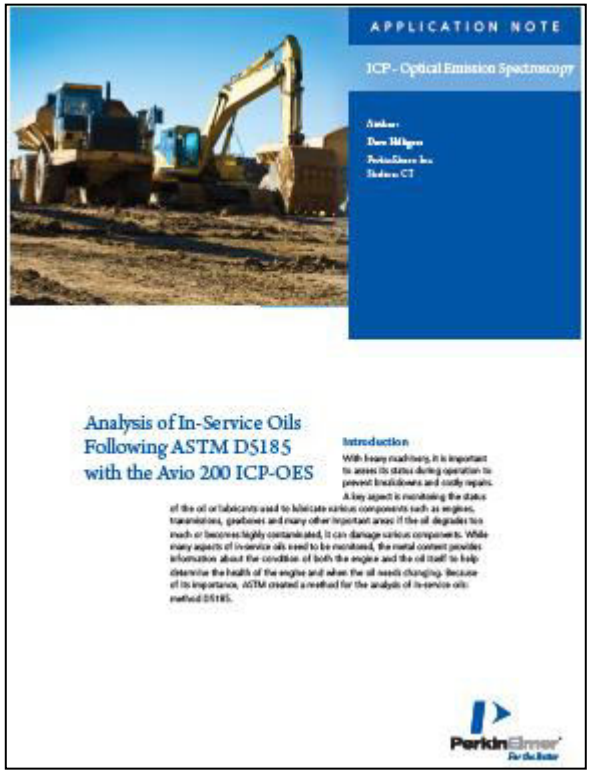
Results: Final QC Sample after 20 Sample Analytical Run

Element	Final QC	
	Concentration (ppm)	% Recovery
Al	50	100
Ag	48	96
B	54	108
Ba	49	98
Ca	45	90
Cd	50	100
Cr	50	100
Cu	50	100
Fe	53	106
K	49	98
Mg	46	92
Mo	49	98
Mn	49	98
Na	49	98
Ni	49	98
P	46	92
Pb	50	100
Sb	50	100
Si	48	96
Sn	49	98
Ti	50	100
V	49	98
Zn	47	94

- All recoveries within 10%

Summary

- The Avio 200 ICP-OES easily analyzes in-service oils following a common implementation of ASTM method D5185
  - Appropriate for low-volume labs
- Benefits of using the Avio 200 ICP-OES
  - Using only 8 L/min of argon, significant cost savings are realized
  - Vertical torch allows excess oil to drain
  - Short integration times allow for faster analyses



To download the full application note, visit www.perkinelmer.com/avio200

Analysis of SiO_2- and TiO_2-Containing Medications for Class 1 & 2A Elements with ICP-OES Following USP 232/233 Guidelines

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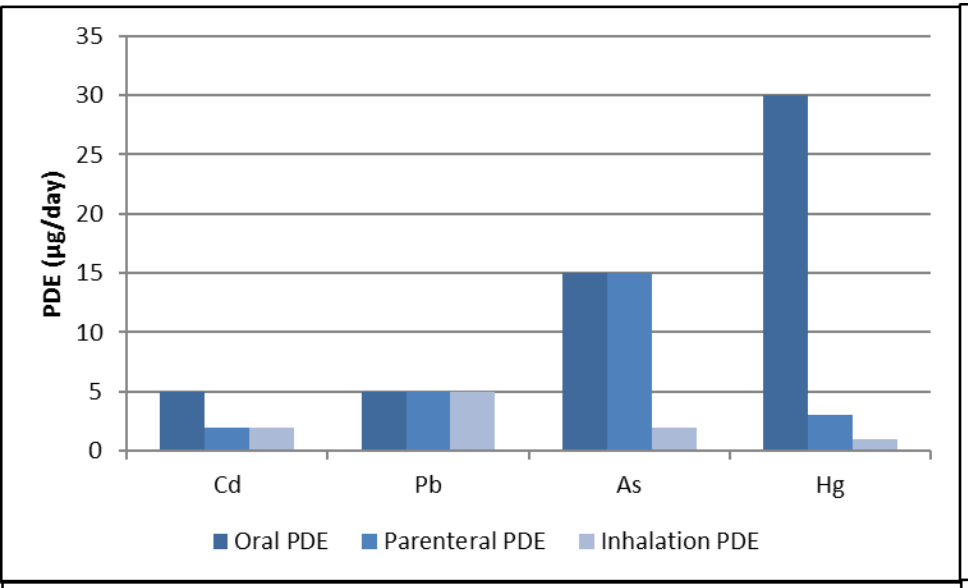
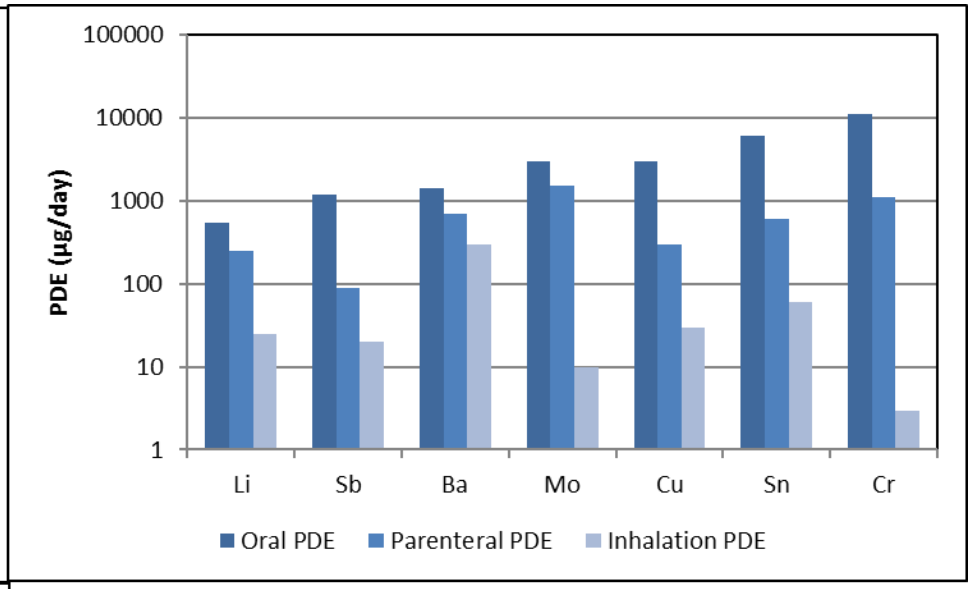
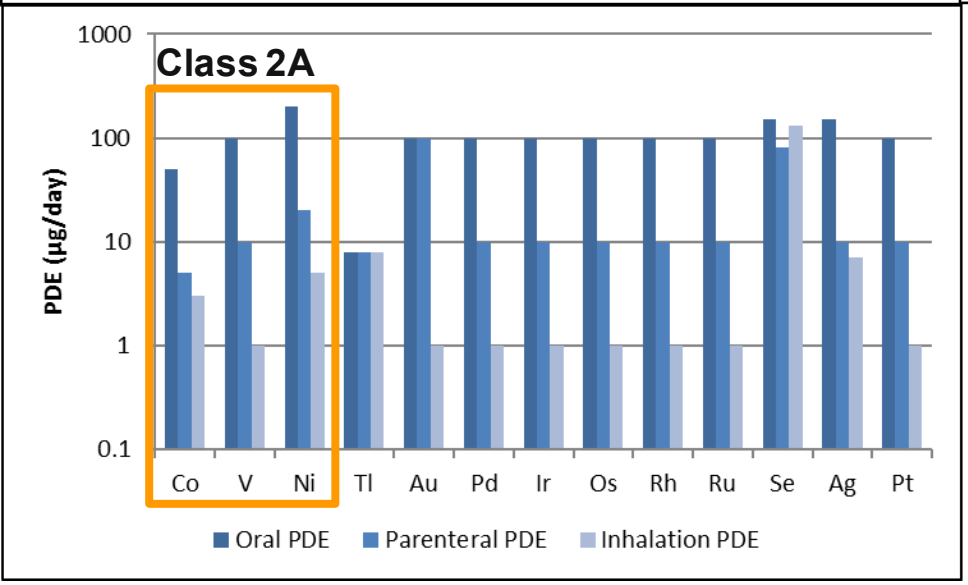
Introduction:
<USP 232> Defines Element & Impurity Limits







Class 1 Elements
- Most toxic

Class 2A Elements
- Most likely to be introduced during manufacturing process

Most common elements for testing

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Introduction:
<USP 233> Defines Sample Prep & Analysis Requirements

- **Sample Prep**
  - Closed-vessel digestion
- **Analysis**
  - **Accuracy**
    - Spikes at 50%, 100% & 150% of maximum PDEs
    - Recoveries must be 70%-150%
  - **Repeatability**
    - Measure 6 independent samples spiked at 100% of target limit
    - % RSDs over 6 samples must be < 20%
  - **Ruggedness**
    - Measure 6 solutions on different days, with different instrument, or with different analyst
    - %RSDs over 12 measurements must be < 25%
  - **System Suitability**
    - Measure high standard at beginning & end of each batch
    - Difference between results must be < 20%

Introduction: Samples

- Pharmaceutical tablets may contain a wide variety of excipients
  - Most are easy to digests
  - SiO_2 and TiO_2 are common and difficult to digest

- SiO_2 and TiO_2 are common excipients in a variety of over-the-counter medications
  - Acid reducers
  - Sleep aids
  - Motion sickness medication

Goal

- Develop sample preparation & analytical methodology for the analysis of Class 1 and 2A elements in SiO_2- and TiO_2-containing tablets with the Avio 200

- Class 1 & 2A elements
  - As, Cd, Co, Hg, Ni, Pb, V
  - Most common to analyze
- SiO_2 & TiO_2 medications
  - Challenging sample preparation
- Avio 200
  - Ideal for smaller number of elements
  - Avio 500 could also be used

Samples

All samples purchased from local stores

Medication Type	Excipient	Active Ingredient	Daily Dose	Mass Per Tablet (g)
Acid Reducer	TiO_2	Ranitidine, 75 mg	2 tablets	0.13
		Ranitidine, 150 mg	2 tablets	0.32
		Famotidine, 20 mg	2 tablets	0.21
Sleep Aid	SiO_2	Diphenylhydramine, 25 mg	2 tablets	0.43
		Diphenylhydramine, 25 mg	2 tablets	0.42
Motion Sickness	SiO_2	Meclizine, 25 mg	2 tablets	0.20

3 brands of acid reducers
2 brands of sleep aids
1 brand of motion sickness

Sample Preparation: Closed Vessel Microwave Digestion

Titan MPS

Sample Amounts & Acids per Digestion Vessel

Sample	HNO_3 70% (mL)	HCl 35% (mL)	HF 49% (mL)	Water (mL)
Tablet	1.5	0.5	0.5	7.5

- HNO_3
  - Keeps elements in solution
- HCl
  - Specifically for Hg
- HF
  - Dissolve SiO_2 and TiO_2
- Water
  - Keep acid concentrations to a minimum
  - 3% HNO_3 + 1% HCl in final solutions

Sample Preparation: Closed Vessel Microwave Digestion

Titan MPS

Titan Digestion Program

Step	Temperature (°C)	Pressure (Bar)	Ramp (Min)	Hold (Min)	Power (%)
1	160	35	5	1	90
2	190	35	5	5	100
3*	50	35	1	15	0

- Digestion Time = 16 minutes
- Cooling = 16 minutes

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Sample Preparation: Closed Vessel Microwave Digestion

- Complex HF
  - Allows use of standard sample introduction system
    - Can be skipped if use HF-resistant sample intro system
  - Add 3 mL of saturated boric acid solution to each vessel
  - Digest with following program

Titan MPS

Titan Digestion Program

Step	Temperature (°C)	Pressure (Bar)	Ramp (Min)	Hold (Min)	Power (%)
1	190	35	5	10	90
2*	50	35	1	15	0

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Calibration

- Calibration standards based on the J-Value
  - Defined in USP <233>
- Calibrate with 0.5J and 1.5 J standards
  - External calibration curves
  - Specified in USP <233>
- Calibration standards made in 3% HNO_3 + 1% HCl

Element	0.5J (mg/L)	1J (mg/L)	1.5J (mg/L)
Cd	0.025	0.05	0.075
Pb	0.025	0.05	0.075
As	0.075	0.15	0.225
Hg	0.15	0.3	0.45
Co	0.25	0.5	0.75
V	0.50	1	1.5
Ni	1	2	3

Instrumental Conditions: Avio 200

Parameter	Value
Nebulizer	MEINHARD® Type K, glass
Spray Chamber	Baffled glass cyclonic
Sample Uptake Rate	1.0 mL/min
RF Power	1500 W
Injector	2.0 mm id Alumina
Nebulizer Gas Flow	0.70 mL/min
Auxiliary Gas Flow	0.2 L/min
Plasma Gas Flow	8 L/min
Torch Position	-3
Plasma View Mode	Axial
Replicates	3

Standard Sample Intro Components & Conditions

Low Ar Use

Element	Wavelength (nm)
As	193.696
Cd	214.440
Co	238.892
Hg	194.168
Ni	231.604
Pb	220.353
V	309.310
Y (Int std)	371.029

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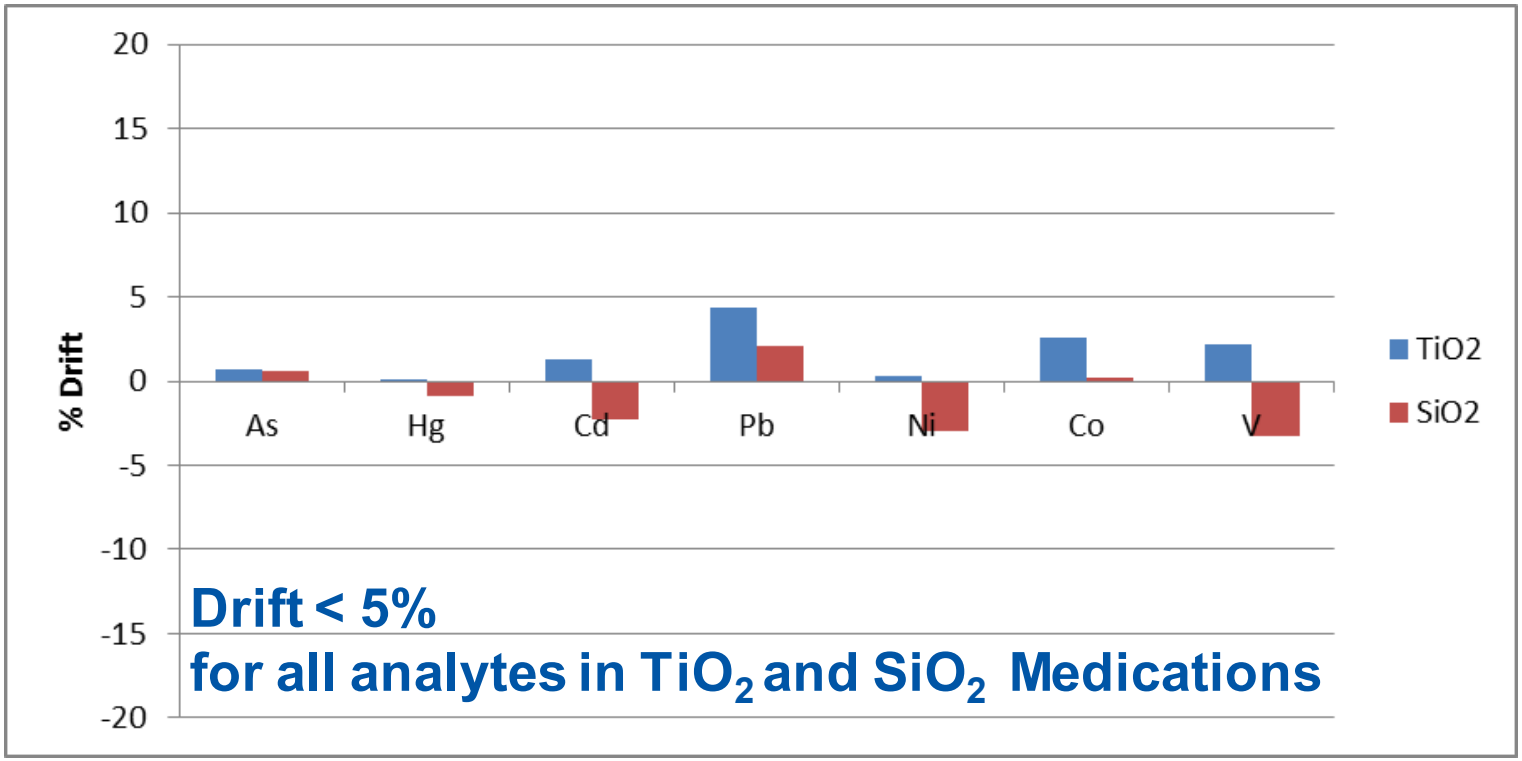
Results: Evaluation of Interferences

- 1.5 J single element standards of all analytes analyzed
- Overlay spectra to look for interferences on each analyte
- No interferences observed

Results: System Suitability

- USP <233> System Suitability Criteria (i.e. Drift Check)
  - Difference between 1.5J standard run at the beginning & end of a batch must be < 20%



System Suitability: Pass

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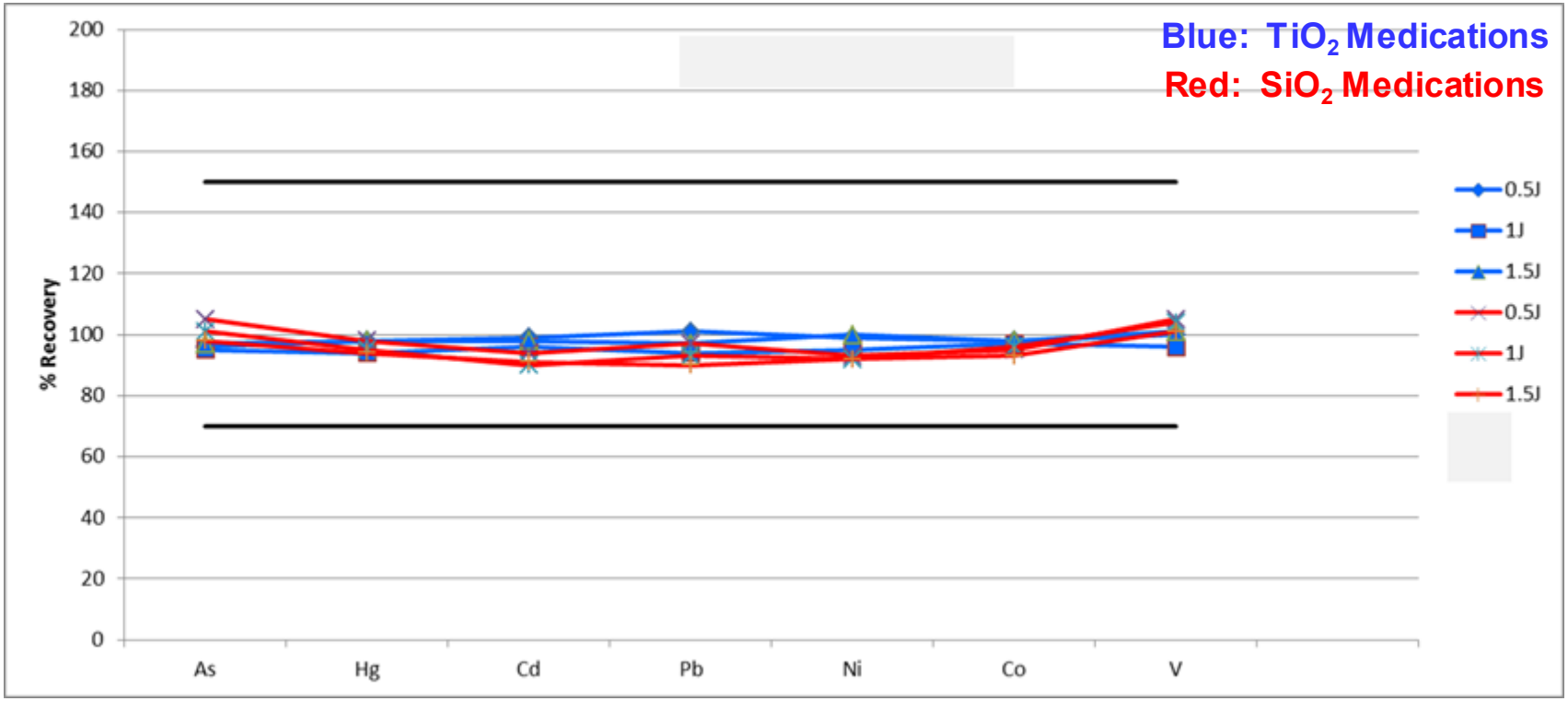
Results: Accuracy

- USP <233> Accuracy Criteria
  - Pre-digestion spike recoveries at 0.5J, J, &1.5J must be between 70-150%



Recoveries within 10%
for all spikes of all analytes in TiO_2 and SiO_2 Medications

Accuracy: Pass

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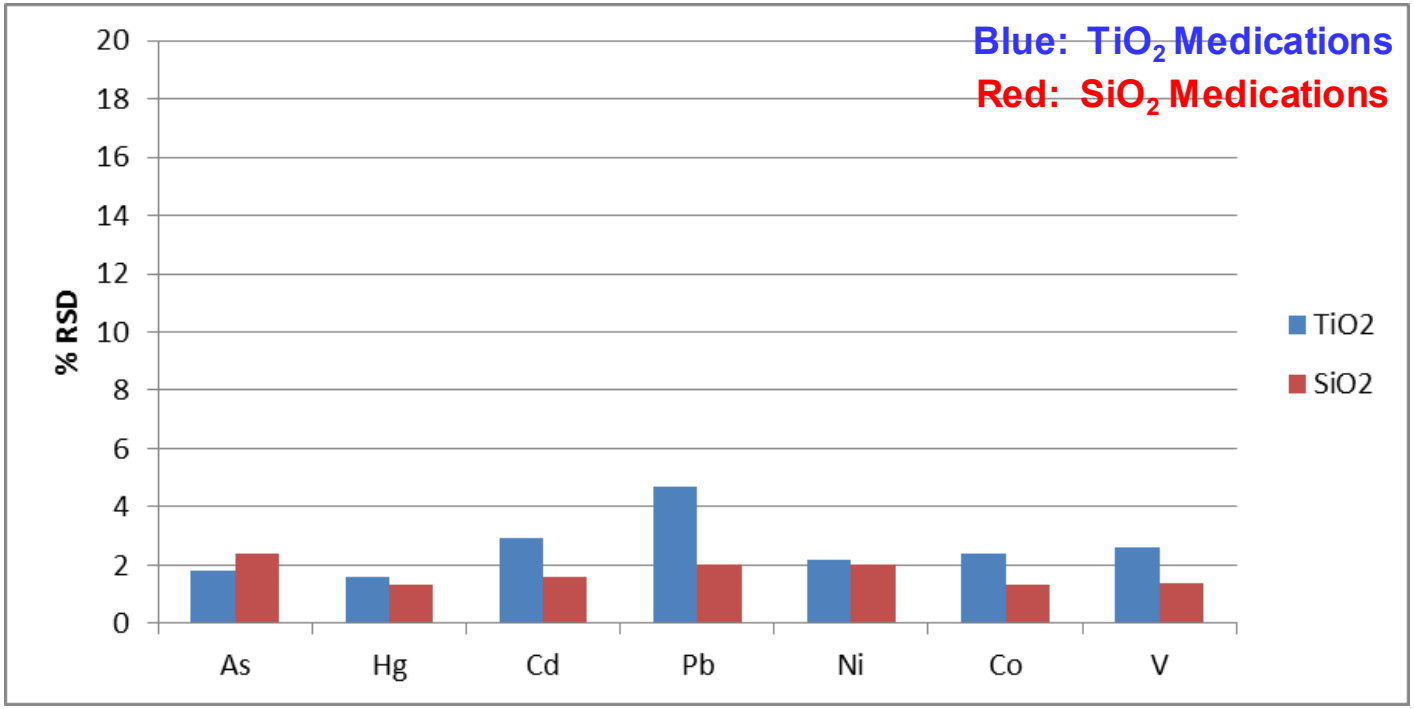
Results: Repeatability

- USP <233> Repeatability Criteria
  - Same medication must be prepared 6 times with J pre-digestion spikes
  - %RSD of the measurements for these 6 samples must be < 20%



RSDs < 5%
for all spikes of all analytes in TiO_2 and SiO_2 Medications

Repeatability: Pass

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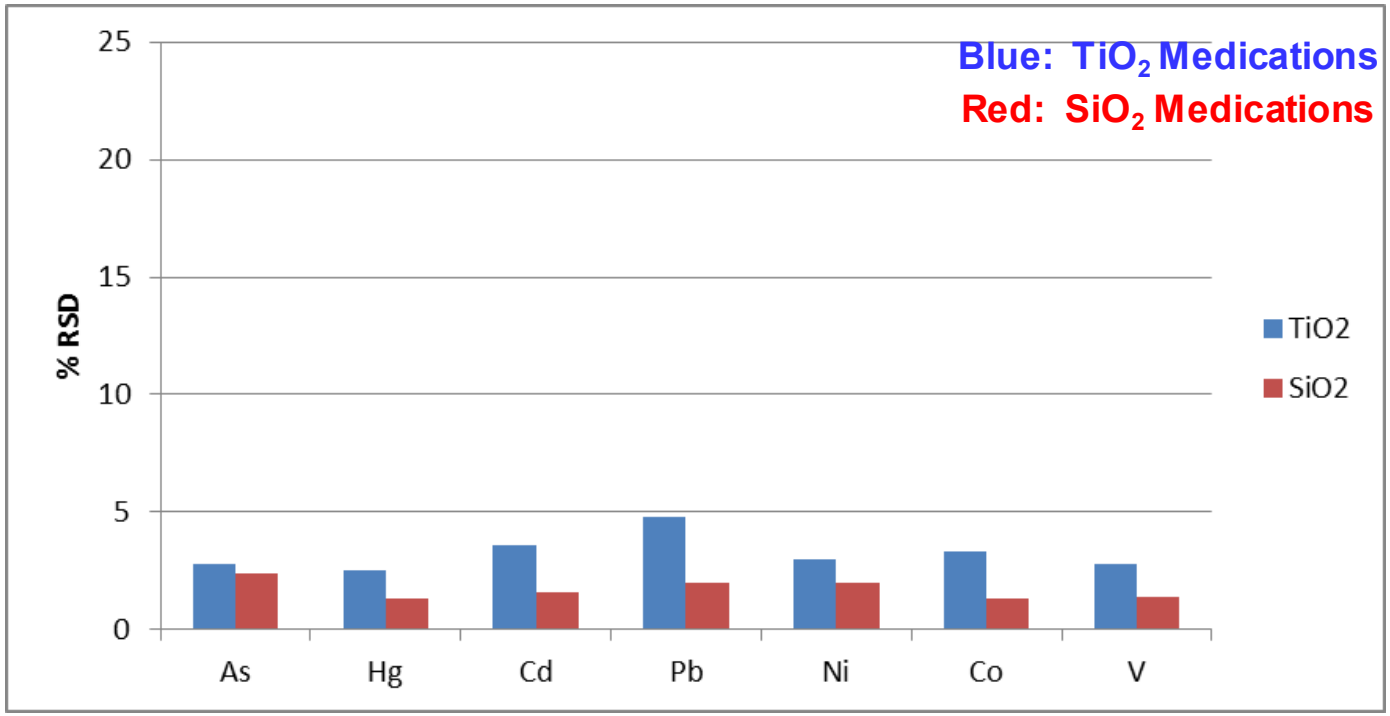
Results: Ruggedness

- USP <233> Ruggedness Criteria
  - Measure 6 samples used in Repeatability study on 2 different days
  - %RSD of the 12 measurements must be < 25%



RSDs < 5%
for all spikes of all analytes in TiO_2 and SiO_2 Medications

Ruggedness: Pass

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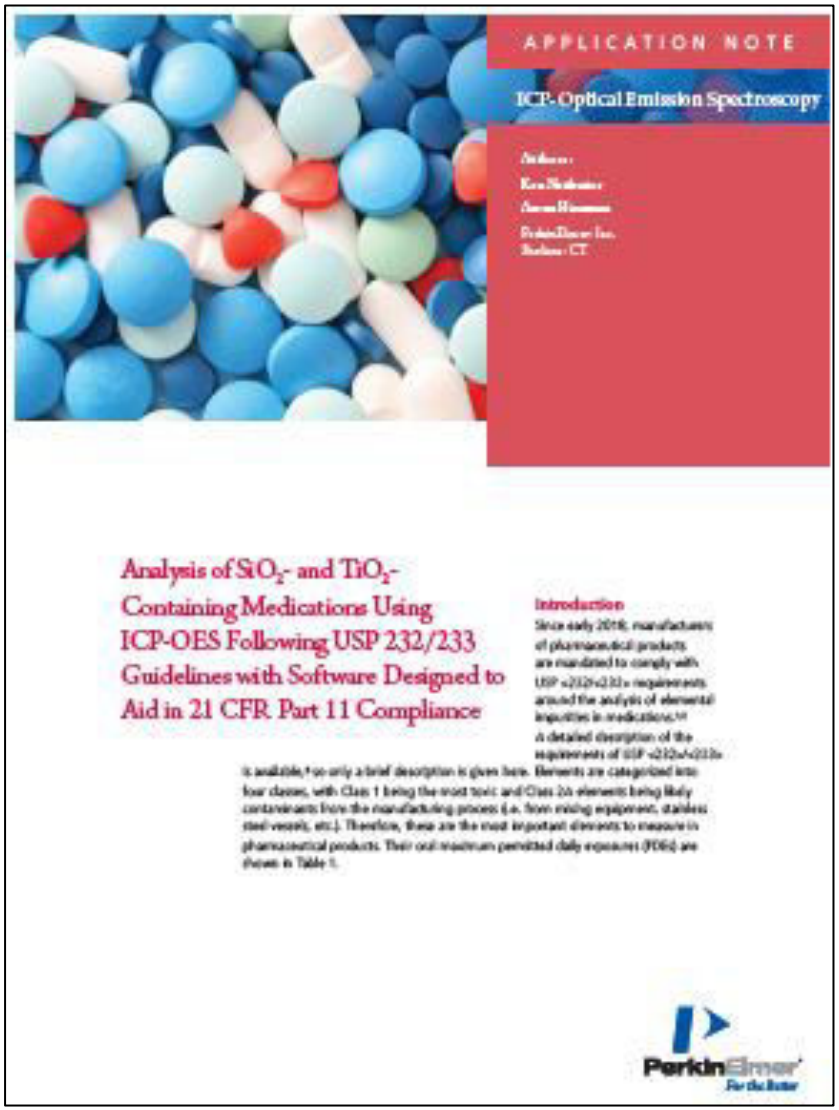
Results: Sample Analysis

- Concentrations of all elements in all samples < 0.3J
- 0.3J is considered an actionable level

Summary

- Avio 200 meets USP <233> criteria for Class 1 and 2A elements in medications containing TiO_2 or SiO_2 as excipients
  - Class 1 & 2A elements are the most commonly analyzed – perfect for Avio 200
  - In low throughput labs, the Avio 200 can also be used for Class 2B and 3 analytes
- Closed-vessel microwave digestion provides complete digestion with minimal acid
- Results easily surpass USP <233> criteria for accuracy, repeatability, ruggedness, and system suitability



Thank you for your attention!

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