# Advanced Petrochemical Applications With ICP-OES

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**Application Engineer**

# Elemental Analysis of Petrochem-Based Solutions

Refineries and Petrochemicals

Sulfur content of gasoline

Acceptance testing of imported fuels

Biodiesel analysis (ASTM D6751)

Wear metals in oil

Oil additive analysis (process control and trend)

Metals in Catalyst & Catalyst Oil

Metals in Process Solutions

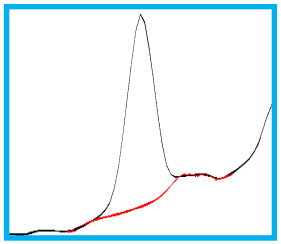
Metals in Drilling Fluids

Other: Metals in Brines

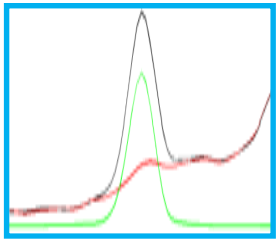
Etc…!

# ICP-OES Design and Performance for Petrochem

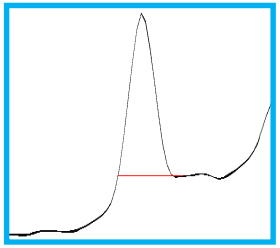
## *Unmatched Background Correction Techniques*



- ***Automatic (Polynomial Fitted Technique)***

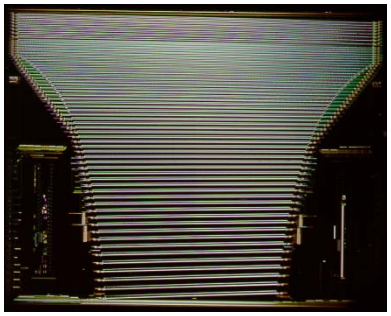


- ***FACT (Fast Automated Curve-Fitting Technique)***



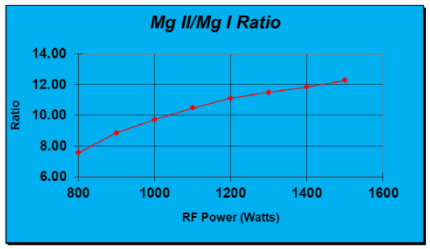
- ***Offpeak BC–Left & Right Together***

## *Continuous Wavelength Coverage*



- ***33,000 wavelengths ready at all times***
- ***Freedom from interferences***
- ***MultiCal***

## *Robust RF & Plasma*




- ***Robust, fast, frequency-matching 40MHz RF generator***

# Application Considerations

The challenge:

- High vapour pressure from solvents
  - Plasma instability
  - Extinguished plasma
- Carbon build up in injector
  - Poor precision and drift
  - Down time - injector requires regular cleaning
- Nebulizer blockage
  - Poor precision
  - Down time - nebulizer needs cleaning

# Application Considerations

The solution:

- Plasma stability
  - High Efficiency RF Generator
  - Reduce solvent loading
    - Double-pass spray chamber
    - Plasma torch with 1.4mm ID injector
    - Smaller id. peristaltic pump tubing
  - Reduce pump speed
  - Higher plasma power and plasma gas flows

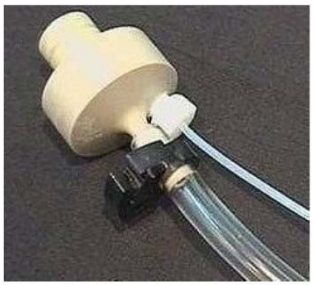
# Spray Chambers

- Double-pass glass cyclonic spray chamber
  - Double pass design
  - Reduces solvent load
  - Increased sensitivity
  - Fast washout
  - Suitable for low vapour organic solvents
    - e.g. Kerosene, ShellSol

# Nebulizers

- Sample particulates may block standard concentric nebulizers
  - Dependent on sample composition e.g. wear metal particulates
  - Poor precision
  - Down time - nebulizer needs cleaning
- Quartz nebulizer
  - Conikal, Seaspray and Slurry
  - Faster washout
- V-groove nebulizer
  - Made of PEEK polymer
  - Minimizes particulate blockage
- OneNeb Nebulizer

**Quartz nebulizer**



**V-groove nebulizer**

**OneNeb nebulizer**

# Compatibility of Pump Tubing

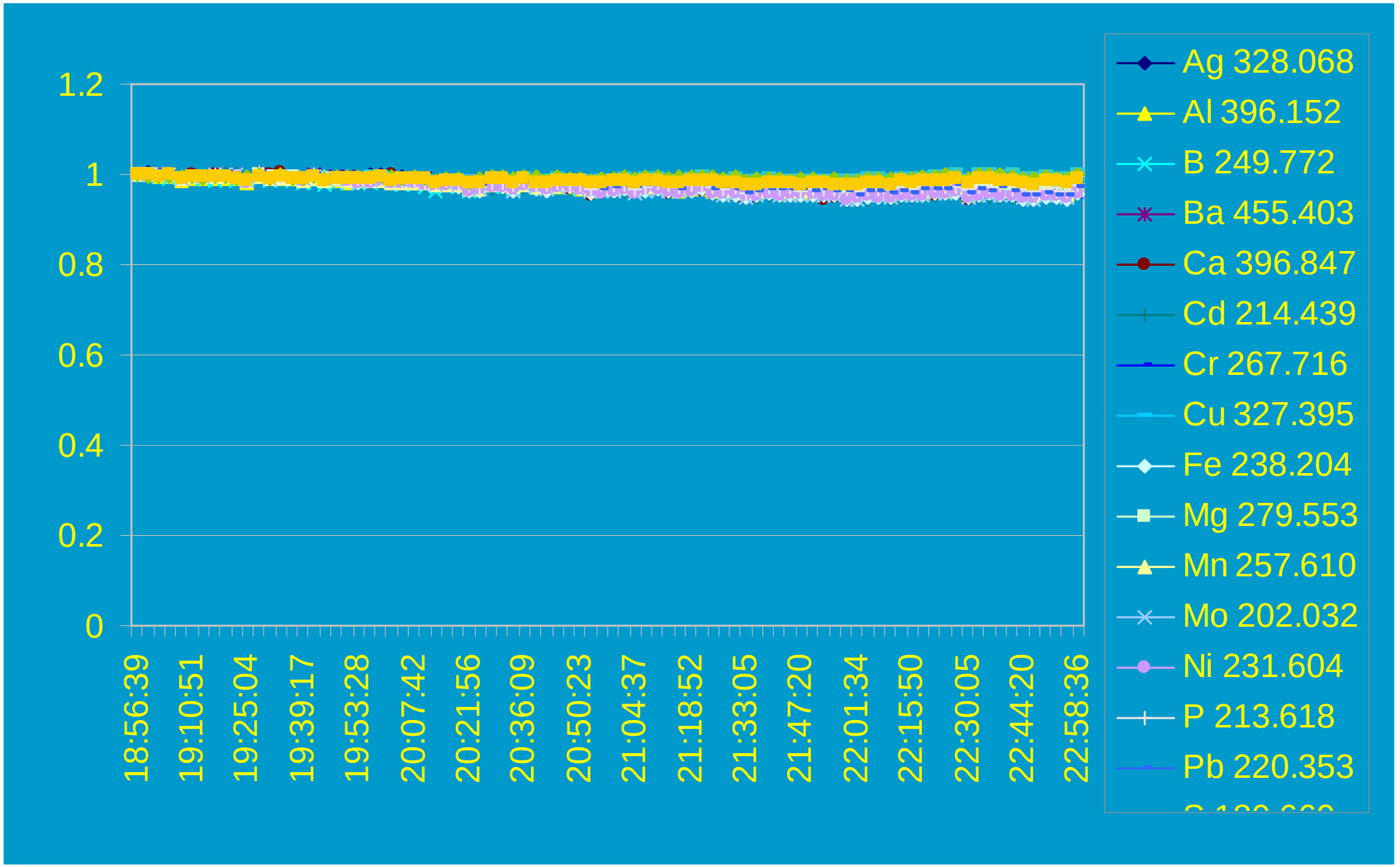
| Solvent | Pump Tubing | | |
|---|---|---|---|
| | PVC | Viton | PVC Solva |
| Kerosene | ✗ | ✓ | ✓ |
| Gasoline | ✗ | ✓ | ✗ |
| Fuel | ✗ | ✓ | ✗ |
| Coolant | ✓ | ✓ | N/A |

✗ = unsatisfactory, ✓ = satisfactory, N/A = no data available

# Typical Instrument Conditions

| | |
|---|---|
| Plasma power | 1.3 - 1.5kW |
| Plasma gas flow | 15 – 18 L/min |
| Auxiliary gas flow | 0.75 – 2.25 L/min (axial – radial) |
| Nebulizer gas flow (axial) | Optimize (0.5 – 0.8 L/min) |
| Nebulizer gas flow (radial) | Set bullet to top of torch (0.5 – 0.8 L/min) |
| AGM-1 setting | 2 - 6 |
| Stabilization delay | Optimize via timescan |
| Pump speed | 5 – 10 rpm |
| Uptake Rate | < 1 mL/min |
| Fast Pump | Yes or No? |

# Elemental Analysis of Diesel Fuel by ICP-OES

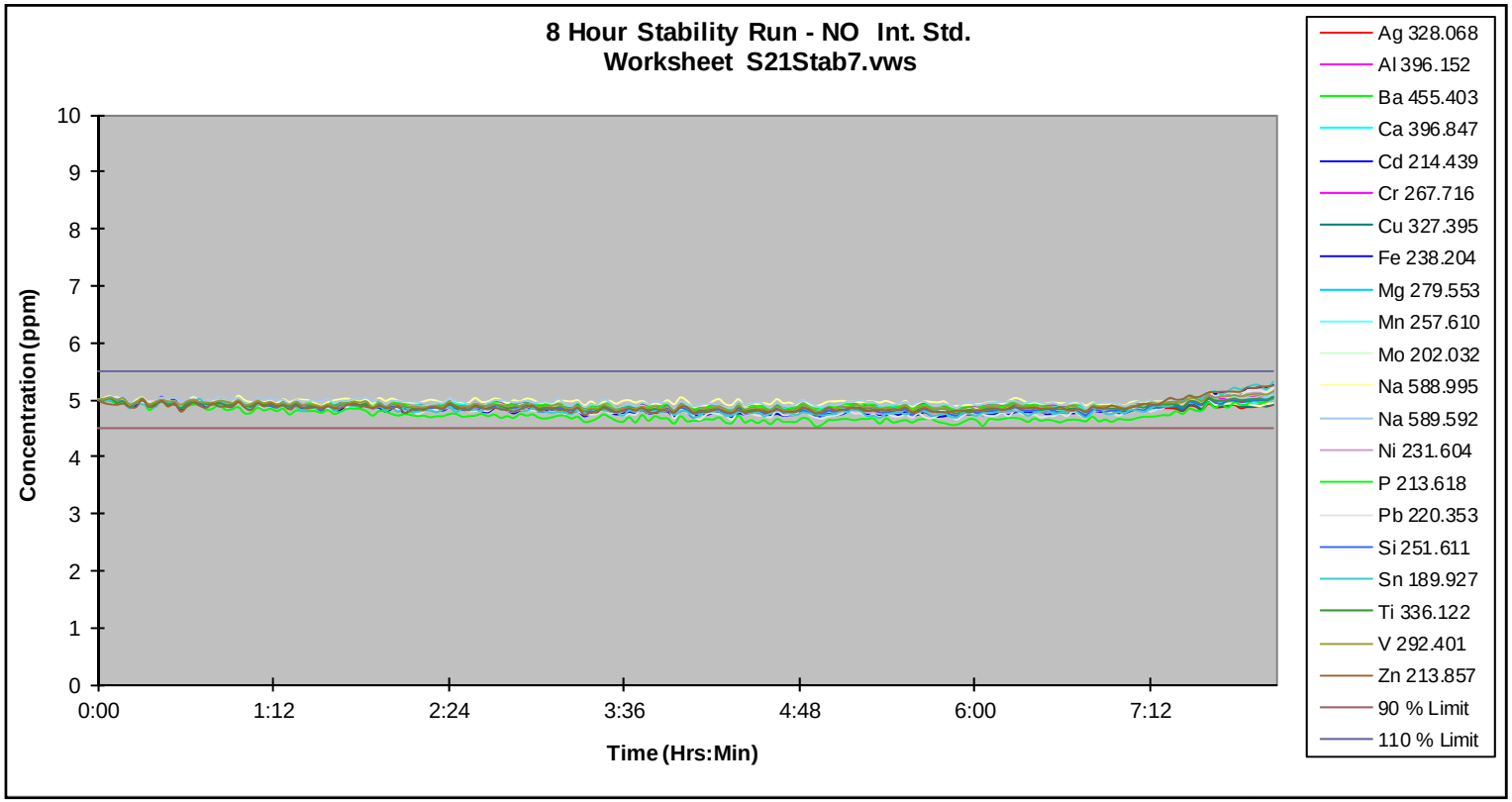


# Elemental Analysis of Diesel Fuel by ICP-OES

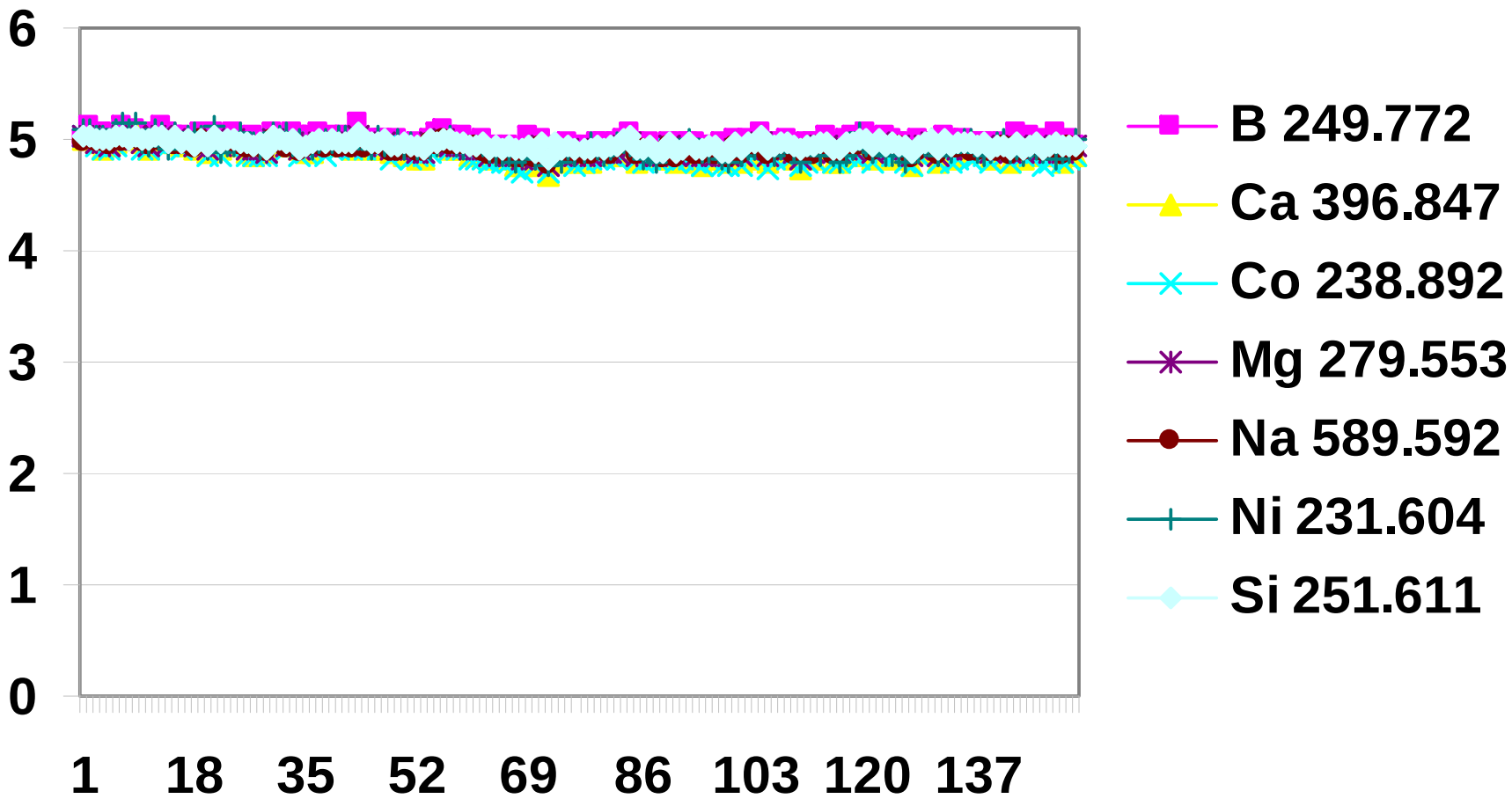
| Element/Wavelength (nm) | DL (ppb) |
|---|---|
| Ag 328.068 | 5 |
| Al 396.152 | 20 |
| B 249.772 | 9 |
| Ba 455.403 | 0.8 |
| Ca 396.847 | 0.5 |
| Cd 214.439 | 4 |
| Cr 267.716 | 7 |
| Cu 327.395 | 7 |
| Fe 238.204 | 5 |
| Mg 279.553 | 1 |

| Element/Wavelength (nm) | DL (ppb) |
|---|---|
| Mn 257.610 | 1 |
| Mo 202.032 | 10 |
| Na 589.592 | 6 |
| Ni 231.604 | 18 |
| P 213.618 | 60 |
| Si 251.611 | 39 |
| Ti 336.122 | 2 |
| V 392.401 | 9.6 |
| Zn 213.857 | 4.7 |

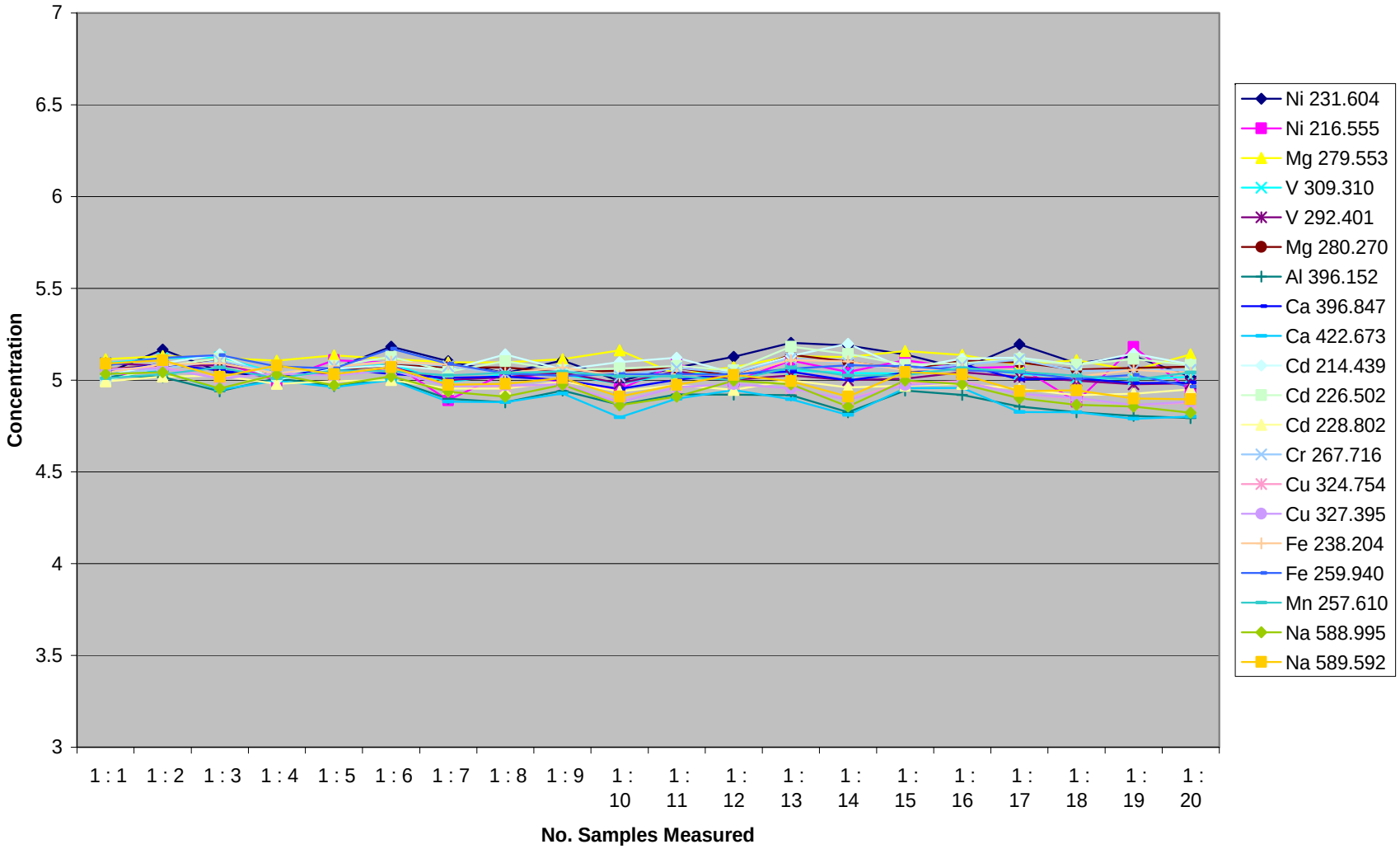
# Stability of Kerosene by ICP-OES



# Stability – Coolant Analysis



# Plasma Stability of Naphtha




**Short term stability over 30 mins. for Naphtha**

# Organic Applications

Other challenges:

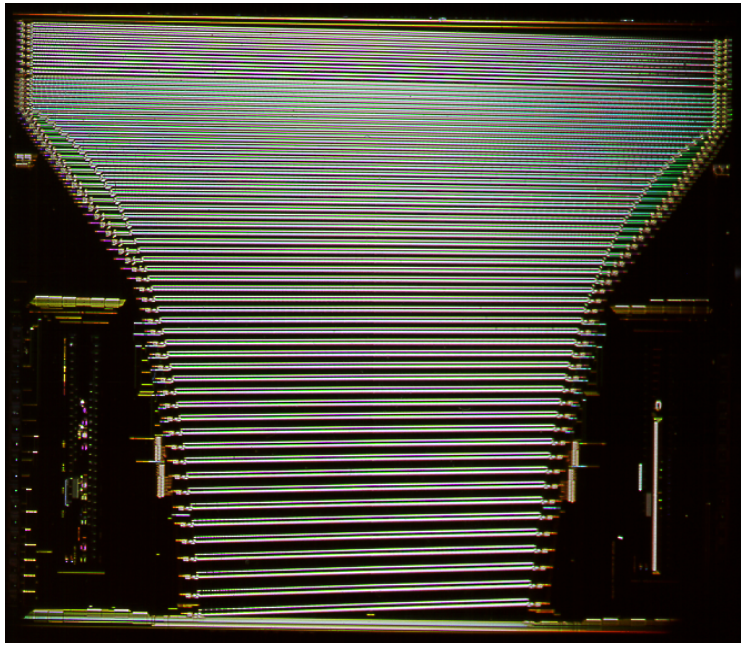
- Wear metals and additive analysis
  - Require large linear dynamic range
- Structured backgrounds
  - Molecular band observed at wavelengths > 330nm
- Speed of analysis
  - Throughput = time = money

# Speed of Analysis

## *World's Most Innovative Detector*

- Simultaneous ICP using custom designed and patented CCD detector
  - Full wavelength coverage 167 – 785 nm
    - Use alternate wavelengths to extended dynamic range and confirm results
  - True simultaneous measurement
  - Improved resolution
- Pixels arranged to exactly match 2 dimensional echelle image
- Duplex readout circuitry halves readout time
  - Processing electronics off-chip for high QE
  - 40 times faster due to 1 MHz processing speed
- Typical analysis times
  - **Can measure 1 sample in < 1 min.**

    **(all elements)**



# Performance Test – Linear Range

## *Radial, S21 Conostan Oil Standards in Kerosene*

| Element & Emission Line Wavelength | Maximum Concentration (mg/L) |
|---|---|
| Ag 328.068 | 250 + |
| Al 308.215 | 250 + |
| Al 396.192 | 100 |
| B 249.772 | 250 + |
| Ba 455.403 | 100 |
| Ba 493.408 | 250 + |
| Ca 317.933 | 2500 |
| Ca 396.847 | 100 |
| Cd 226.502 | 250 + |
| Cr 284.325 | 250 + |
| Cu 327.395 | 250 + |
| Fe 259.940 | 250 + |
| Fe 274.932 | 1000 |
| Mg 280.270 | 100 |
| Mn 257.610 | 250 + |
| Mo 202.032 | 250 + |
| Na 589.592 | 250 + |
| Ni 230.299 | 250 + |
| P 213.618 | 2500 |
| Pb 220.353 | 1500 |
| Si 251.608 | 250 + |
| Sn 283.998 | 250 + |
| Ti 336.122 | 250 + |
| V 311.837 | 250 + |
| Zn 206.200 | 2500 |
| Zn 213.857 | 250 |

# Biodiesel

# Analytical Requirement for Biodiesel

ASTM requires the analysis of Biodiesel

Must satisfy all the requirements of ASTM D 6751-07be1, including:

- Sulphur and phosphorus (D6751)
- Total calcium and magnesium (D6751- 07a)
- Total sodium and potassium (D6751- 07a)
- Includes other properties such as:
  - Flash point
  - Water and sediment
  - Free glycerin

# Analytical Results
## *– ASTM Specified Elements in Biodiesel*

| Element | P | S | Na | K | Ca | Mg |
|---|---|---|---|---|---|---|
| **Wavelength (nm)** | 213.618 | 181.972 | 589.592 | 766.491 | 393.366 | 279.553 |
| **B-100a ppm** | < IDL | 1.695 | 0.162 | 0.507 | 0.013 | 0.011 |
| **B-100b ppm** | < IDL | 1.710 | 0.130 | 0.469 | 0.012 | 0.012 |
| **B-100+1.0 ppm (%R)** | 105 | 103 | 104 | 107 | 105 | 104 |
| **B-100+2.5 ppm (%R)** | 102 | 106 | 102 | 104 | 103 | 101 |
| **IDL (ppb)** | 19.9 | 76.5 | 4.1 | 21.8 | 0.1 | 0.1 |
| **Bkgd Correction** | Fitted | Fitted | FACT | FACT | Fitted | Fitted |

# Analytical Results
## *– Other Elements in Biodiesel*

| Element | Al | Ba | Cd | Cr | Fe | Mn | Mo | Ni |
|---|---|---|---|---|---|---|---|---|
| Wavelength (nm) | 308.215 | 233.527 | 226.502 | 267.716 | 259.940 | 259.372 | 202.032 | 216.555 |
| B-100a ppm | < IDL | < IDL | < IDL | < IDL | 0.032 | < IDL | < IDL | < IDL |
| B-100b ppm | < IDL | < IDL | < IDL | < IDL | 0.037 | < IDL | < IDL | < IDL |
| B-100+1.0 ppm (%R) | 102 | 105 | 103 | 103 | 104 | 103 | 103 | 104 |
| B-100+2.5 ppm (%R) | 103 | 103 | 101 | 102 | 103 | 102 | 103 | 102 |
| IDL (ppb) | 5.4 | 1.0 | 0.6 | 1.6 | 1.0 | 0.3 | 5.7 | 6.9 |
| Bkgd Correction | Fitted | Fitted | Fitted | Fitted | Fitted | Fitted | Fitted | Fitted |

| Element | Pb | Sc | Si | Sn | Ti | V | Zn |
|---|---|---|---|---|---|---|---|
| Wavelength (nm) | 220.353 | 361.383 | 288.158 | 283.998 | 334.941 | 309.310 | 213.857 |
| B-100a ppm | < IDL | < IDL | 0.141 | < IDL | < IDL | < IDL | 0.024 |
| B-100b ppm | < IDL | < IDL | 0.139 | < IDL | < IDL | < IDL | 0.024 |
| B-100+1.0 ppm (%R) | 102 | 104 | 104 | 102 | 104 | 105 | 104 |
| B-100+2.5 ppm (%R) | 101 | 103 | 103 | 104 | 102 | 104 | 102 |
| IDL (ppb) | 25.2 | 0.1 | 4.7 | 11.7 | 0.1 | 0.6 | 1.1 |
| Bkgd Correction | Fitted | Fitted | Fitted | Fitted | Fitted | Fitted | Fitted |

# Naphtha

# Why Determine Trace Elements in Naphtha?

• Growing need to determine trace metals in hydrocarbon samples

• The presence of trace metals can:

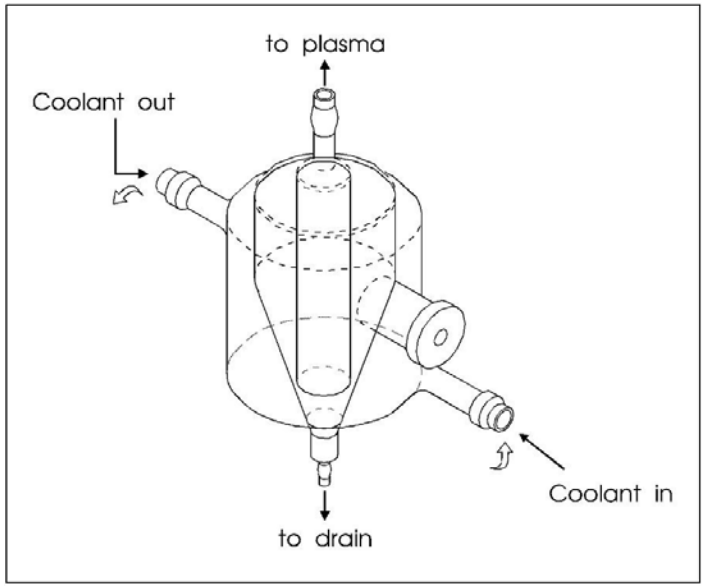
- Severely hamper the catalytic reforming process
- Poison the catalysts used e.g. S and N compounds can deactivate catalysts

**Catalysts used in catalytic cracking or reforming**

**Photo courtesy Phillips Petroleum Company**

# Improved Sample Introduction Systems

- Cooled spray chamber
  - Externally jacketed design
  - Ethylene glycol mixture circulated to cool sample to -12 $^{o}$C
  - Reduces solvent load
  - Made of quartz
  - Excellent for highly volatile organic solvents e.g. naphtha




# Sample and Standard Preparation

## Standard Preparation

- Multi-element organometallic standard (e.g. Conostan S-21)
- Select dilution ratio to achieve required concentration
- Add extra neutral base oil to ensure consistent viscosity
- Diluted with Isopropanol (iso propyl alcohol)

# Detection Limit Performance (ppm)

| Element | Instrument DL |
|---|---|
| Al 167.019 nm | 0.41 |
| Al 396.152 nm | 0.06 |
| Ni 231.604 nm | 0.23 |
| Ni 216.555 nm | 0.61 |
| Mg 279.553 nm | 0.05 |
| Mg 280.270 nm | 0.2 |
| V 309.310 nm | 0.04 |
| V 292.401 nm | 0.07 |
| Ca 393.366 nm | 0.05 |
| Ca 306.847 nm | 0.05 |
| Ca 422.673 nm | 0.04 |
| Cr 267.716 nm | 0.05 |

# Detection Limit Performance (ppm)

| Element | Instrument DL |
|---|---|
| Cd 214.439 nm | 0.09 |
| Cd 226.502 nm | 0.10 |
| Cd 228.802 nm | 0.08 |
| Cu 324.754 nm | 0.06 |
| Cu 327.395 nm | 0.06 |
| Fe 238.204 nm | 0.06 |
| Fe 259.940 nm | 0.06 |
| Mn 257.610 nm | 0.06 |
| Na 588.995 nm | 0.05 |
| Na 589.592 nm | 0.04 |

# Wear Metals Analysis

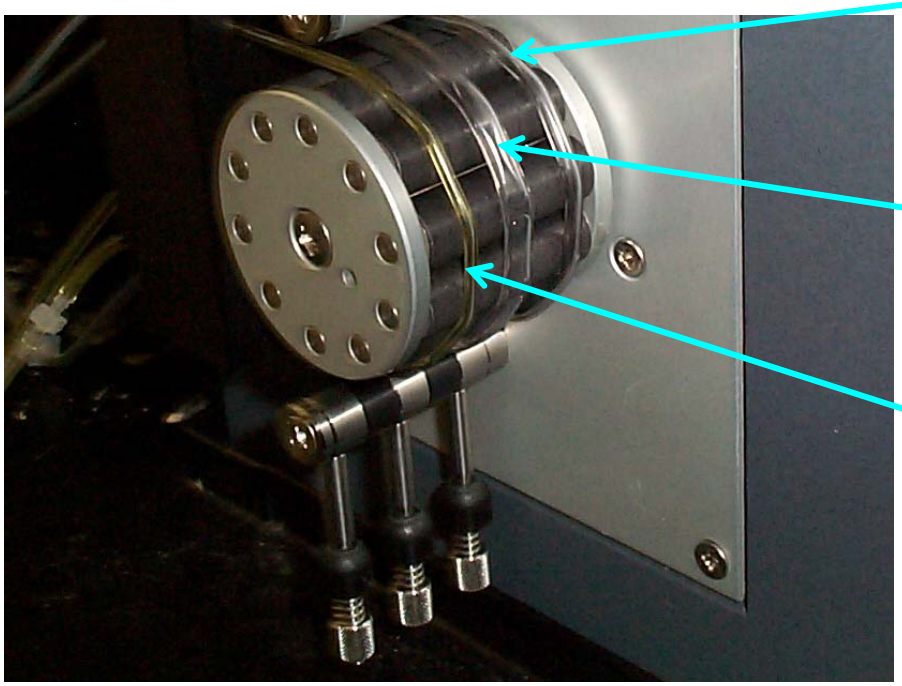
# Rapid Wear Metal Analyses

To improve sample throughput must look at:

- Sample introduction
- Instrument delays
- Rinse time
- Instrument setup and preventative maintenance time

# Rapid Flow Fast Nebulization

A triple channel peristaltic pump is required

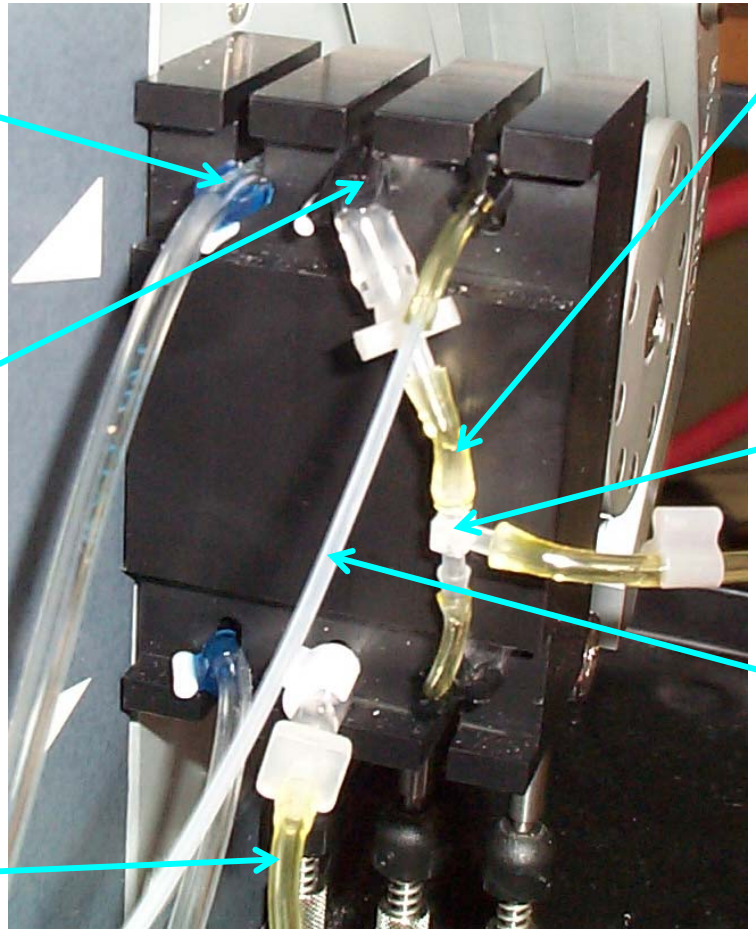


**Channel 1: Waste removal**

**Channel 2: Large ID tube for *FAST FLOW* sample introduction**

**Channel 3: Narrow ID tube for control of flow into nebulizer**

# Rapid Flow Fast Nebulization



# Sample Throughput

Throughput speed

2 orders of magnitude washout

Using Cetac ASX 500 autosampler

| Sample Introduction System | Rinse Time (s) | Sample Throughput (s) |
|---|---|---|
| Rapid flow fast nebulisation | 11 | 39 |
| Unmodified sample introduction | 30 | 85 |

# Elemental Analysis of 25% Brine by ICP-OES

## *Undiluted Analysis of 25% Brine*

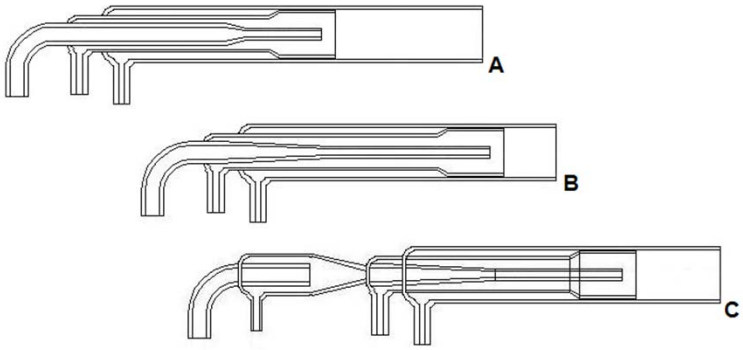
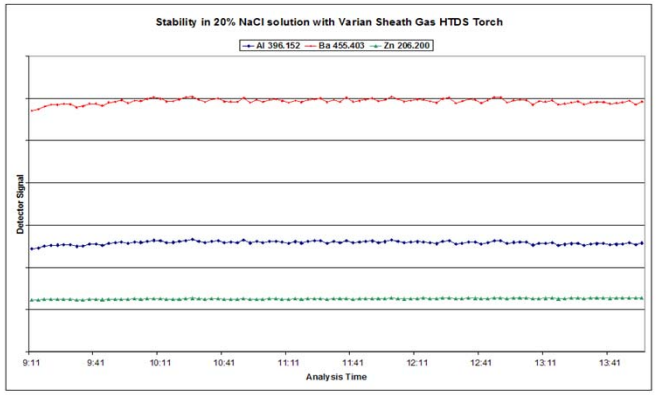



Figure 1 Standard torch (A), high TDS torch (B) ans sheat gas high solids torch (C)




| Element | Atomic or Ionic | Wavelength (nm) | $E_{exc}$ or $E_{ion}$ (eV) | STD (%) |
|---|---|---|---|---|
| Al | Atomic | 396.152 | 3.14 | 1.60 |
| Ba | Ionic | 455.403 | 7.93 | 1.05 |
| Zn | Ionic | 206.200 | 15.40 | 1.05 |

Figure 2 ICP-OES Stability achived with the sheath gas high solids torch.

| Element/Wavelength (nm) | Detection Limit (µg/L) |
|---|---|
| Ag 328.068 | 0.7 |
| Al 167.019 | 0.5 |
| As 188.980 | 5 |
| Ba 455.403 | 0.2 |
| Be 313.042 | 0.07 |
| Cd 214.439 | 0.4 |
| Co 238.892 | 1 |
| Cr 205.560 | 1 |
| Fe 238.204 | 1.7 |
| K 766.491 | 1.5 |
| Li 670.783 | 0.4 |
| Mg 279.553 | 0.1 |
| Mn 257.610 | 0.2 |
| Mo 202.032 | 2 |
| Ni 231.604 | 2.5 |
| Pb 220.353 | 6 |
| Sb 206.834 | 5 |
| Se 196.026 | 10 |
| Sr 407.771 | 0.1 |
| Ti 336.122 | 0.5 |
| Tl 190.794 | 9 |
| V 292.401 | 1 |
| Zn 213.857 | 0.5 |

**Table 1.** Measured Instrument Detection Limits for a sample containing >250 g/L TDS using the Sheath Gas Torch with the Agilent 720/730 Series ICP-OES. Replicate read time was 20 s.

# Application Papers

Available on the Agilent Technologies Web site (http://www.agilent.com)

- SI-A-1413 Determination of metals in oils by ICP-OES
- SI-A-1417 Determination of V, Ni and Fe in crude oils and bitumen with Sc as an internal standard
- SI-A-1420 Determination of wear metals in lubricating oil with Axial ICP
- SI-A-1422 Determination of Pb in Unleaded Gasoline with Axial ICP
- SI-A-1423 Determination of trace elements in a xylene solution of oil by ICP-AES with ultrasonic nebulization and membrane desolvation
- SI-A-1427 Multi-element analysis of fuel and lubricating oils by simultaneous ICP-OES
- SI-A-1431 Improving Throughput for Oils Analysis by ICP-OES

PLUS: SI-A-1202, SI-A-1415 and SI-A-1418

# THANK YOU

# QUESTIONS?