# Chemical and Petrochemical Applications of Microwave Plasma – Atomic Emission Spectroscopy (MP-AES)

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**2012 Gulf Coast Conference**
**Galveston, TX**
**October 17, 2012**

# Common Challenges Facing Laboratories Doing Elemental Analysis Today

- Increased need for multi-element determination over a wide dynamic range
- Desire to reduce the overall cost of analysis due to rising costs (instrument supplies and consumables – power, labor, etc)
- Difficulty in sourcing some gases – especially in remote areas and emerging geographies
- Availability of suitably trained personnel to develop methods, perform sample measurement and interpret results
- Some laboratories under pressure to improve safety by removing flammable gases

# *NEW* Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

**New technique for elemental determination using atomic emission**

- Microwave excited plasma source
- Nitrogen based plasma - runs on air (using a $N_2$ generator)

## Improved performance compared with flame AA

- Higher sample throughput with fast sequential measurement
  - More than 2x faster than conventional flame AA
- Superior detection limits and improved dynamic range

## Easy to use

- New generation software featuring automated optimization and software applets that load a preset method
- One piece torch with easy torch removal and replacement – no alignment

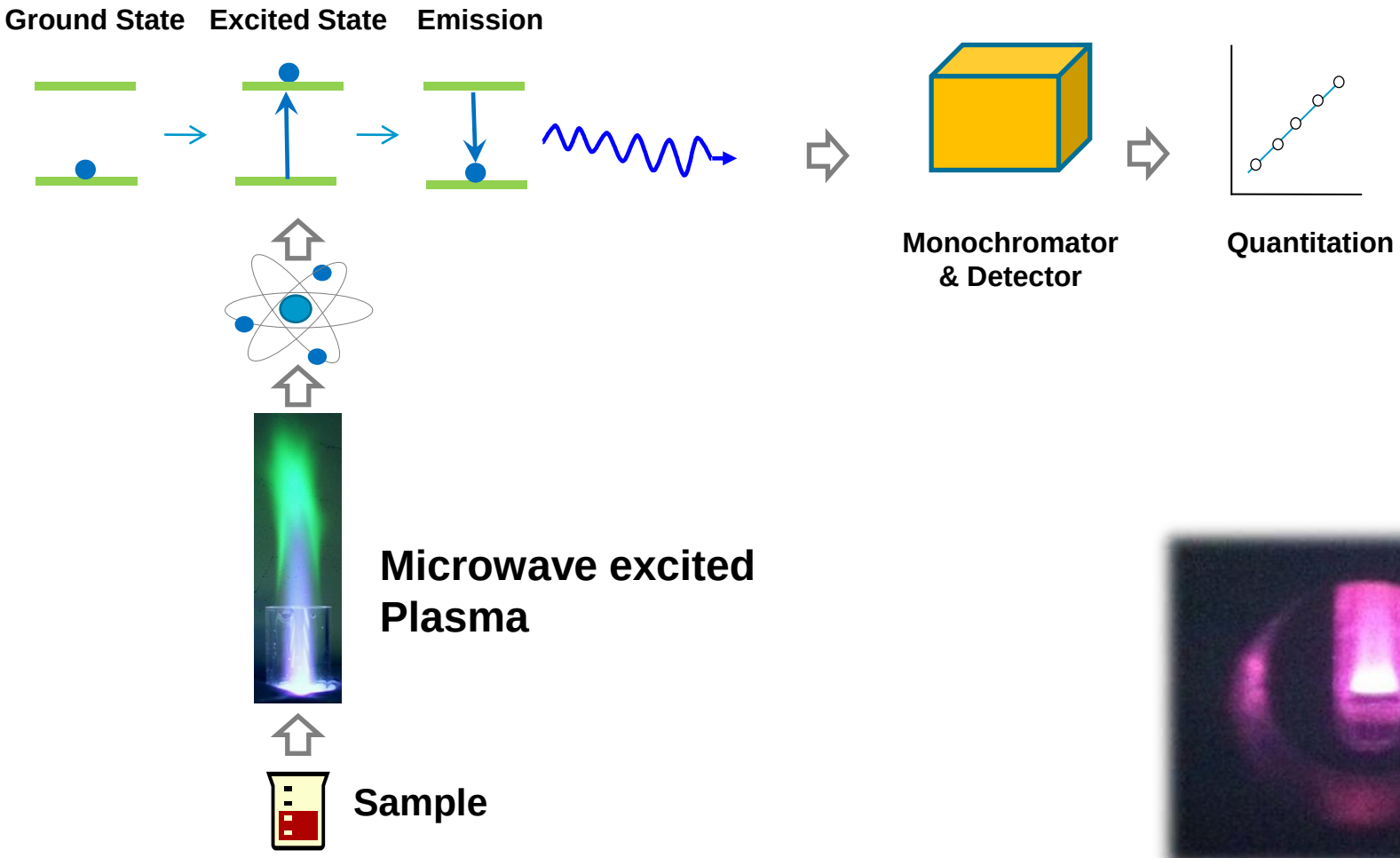
## Reduced operating costs

- Runs on air – eliminates need for Acetylene, Nitrous Oxide, Argon, etc.
- Eliminates need for source / hollow cathode lamps
- Simple installation – no chiller, 10 A supply

## Improved Safety

- Eliminates need for flammable gases and cylinder handling
- Safe, reliable unattended multi-element overnight operation

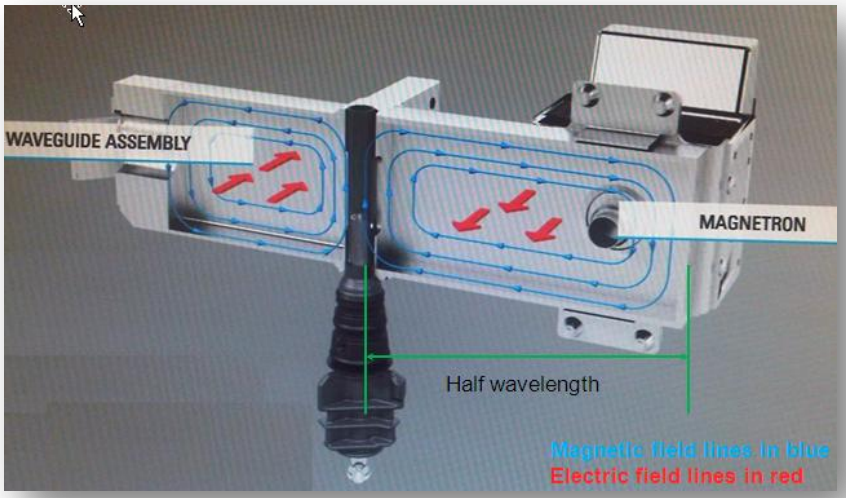
# Microwave Plasma Emission Overview

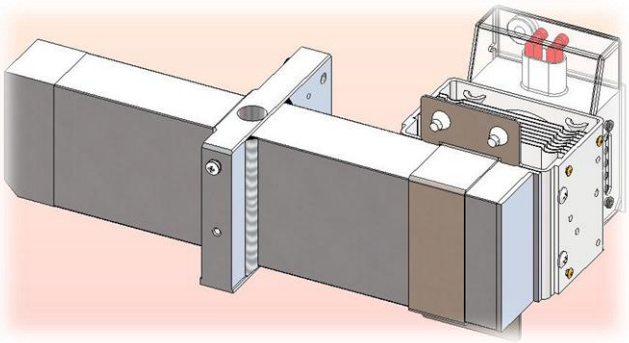


# How Does MP-AES Work?

## Agilent's patented microwave waveguide technology

- **Using nitrogen as the plasma gas (a diatomic gas) gives a robust plasma with a conventional torch. Nitrogen can be supplied either via bottled gas or nitrogen generator**
- **Magnetic excitation gives a toroidal plasma and an effective central zone for sample injection**
- **The microwave magnetically excited nitrogen plasma**
  - **Provides a robust, high temperature source in conventional torches (approx. 5000 K)**
  - **A cooler central channel suitable for sample atomization**
  - **Creates high intensity atomization emission lines**



# Performance Comparison – Typical Detection Limits

*DL's in ppb, clean water samples*

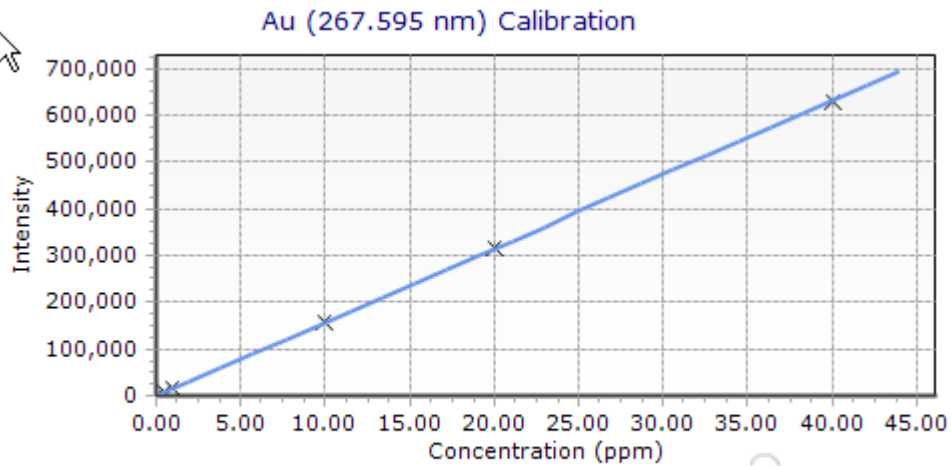
| Element | Flame AA | MP-AES |
|---|---|---|
| K | 0.8 | 0.65 |
| Ca | 0.4 | 0.05 |
| Mg | 0.3 | 0.12 |
| Na | 0.3 | 0.12 |
| Au | 5 | 1.8 |
| Pt | 76 | 4.5 |
| Pd | 15 | 3.8 |
| Ag | 1.7 | 0.5 |
| Rh | 4 | 0.5 |

| Element | Flame AA | MP-AES |
|---|---|---|
| As* | 60 | 45 |
| Cd | 1.5 | 1.4 |
| Cr | 5 | 0.5 |
| Mn | 1.0 | 0.25 |
| Pb | 14 | 4.4 |
| Sb | 37 | 12 |
| Se* | 500 | 70 |
| V | 20 | 0.2 |

**** 30 second integration time used for As and Se***

***3 sigma DLs using a 10 second integration time***

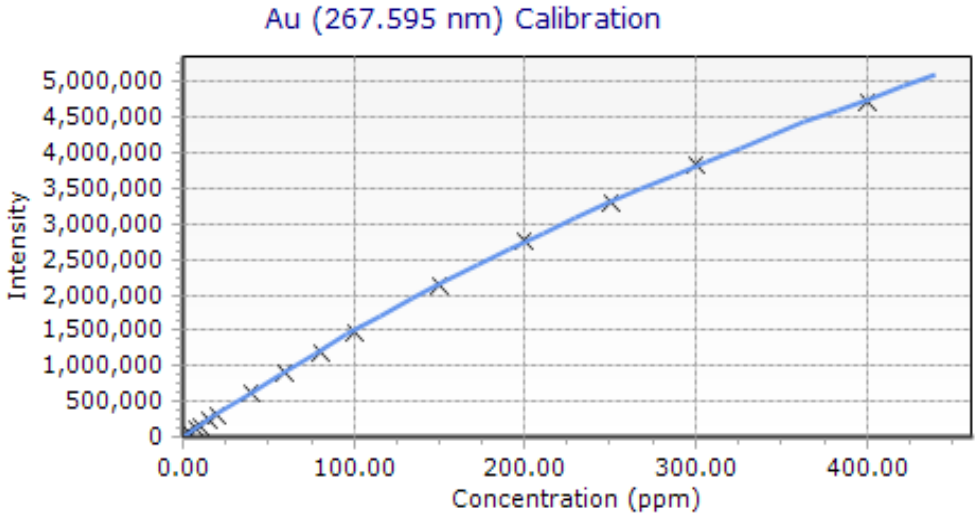
# Au – Extended Calibration Range




Intensity = 15775.550 * Concentration - 0.205
Correlation coefficient: 1.00000

**MP - Normal AA range**

**MP - Extended Range**




Intensity = (16408.841 * Concentration + 0.057) / (1 + 0.001 * Concentration)
Correlation coefficient: 0.99998

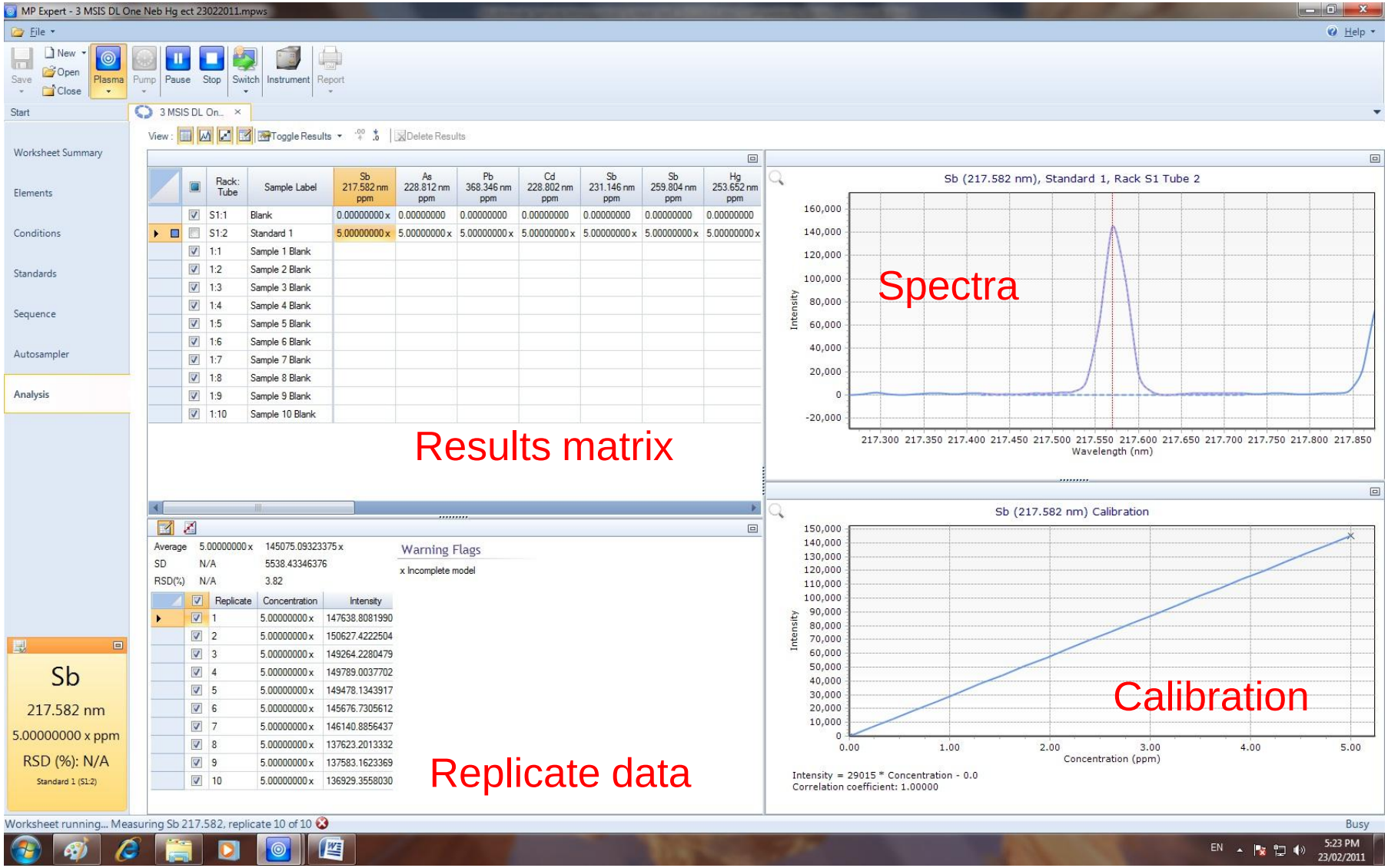
# Simple Torch Installation – No Alignment

# New Generation MP Expert Software

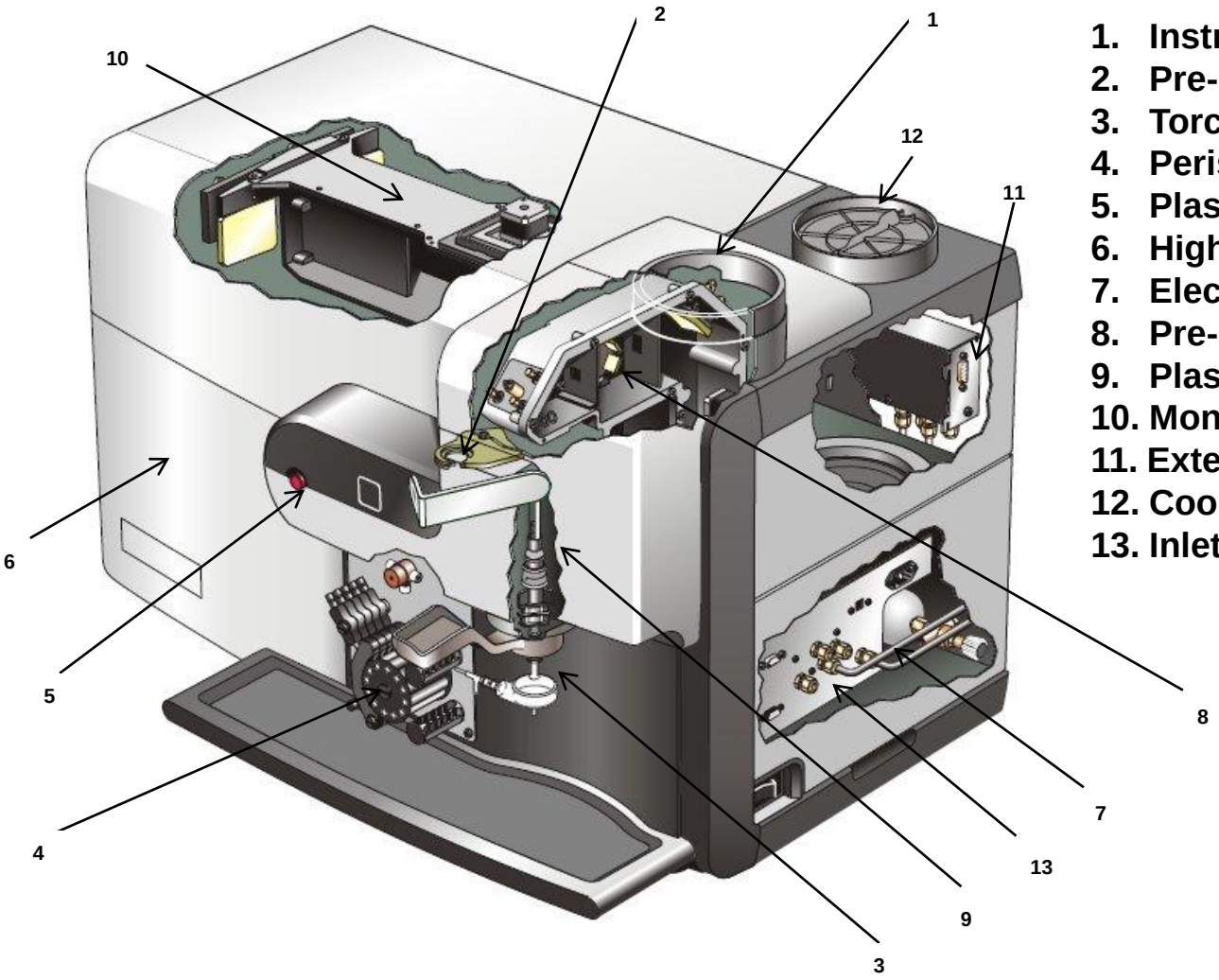
- Windows 7, worksheet based software
- Fresh, clean look
- Provides capability for applet style operation using preset methods, or access to full capabilities
- Innovative and simple to use background correction
- Automated optimization tools


# New Generation MP Expert Software

## Retains familiar “worksheet” based approach

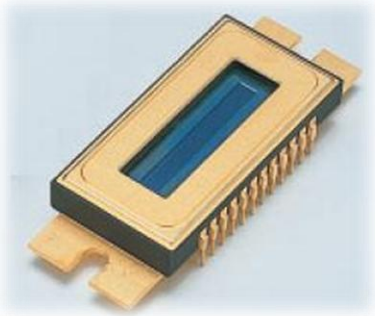


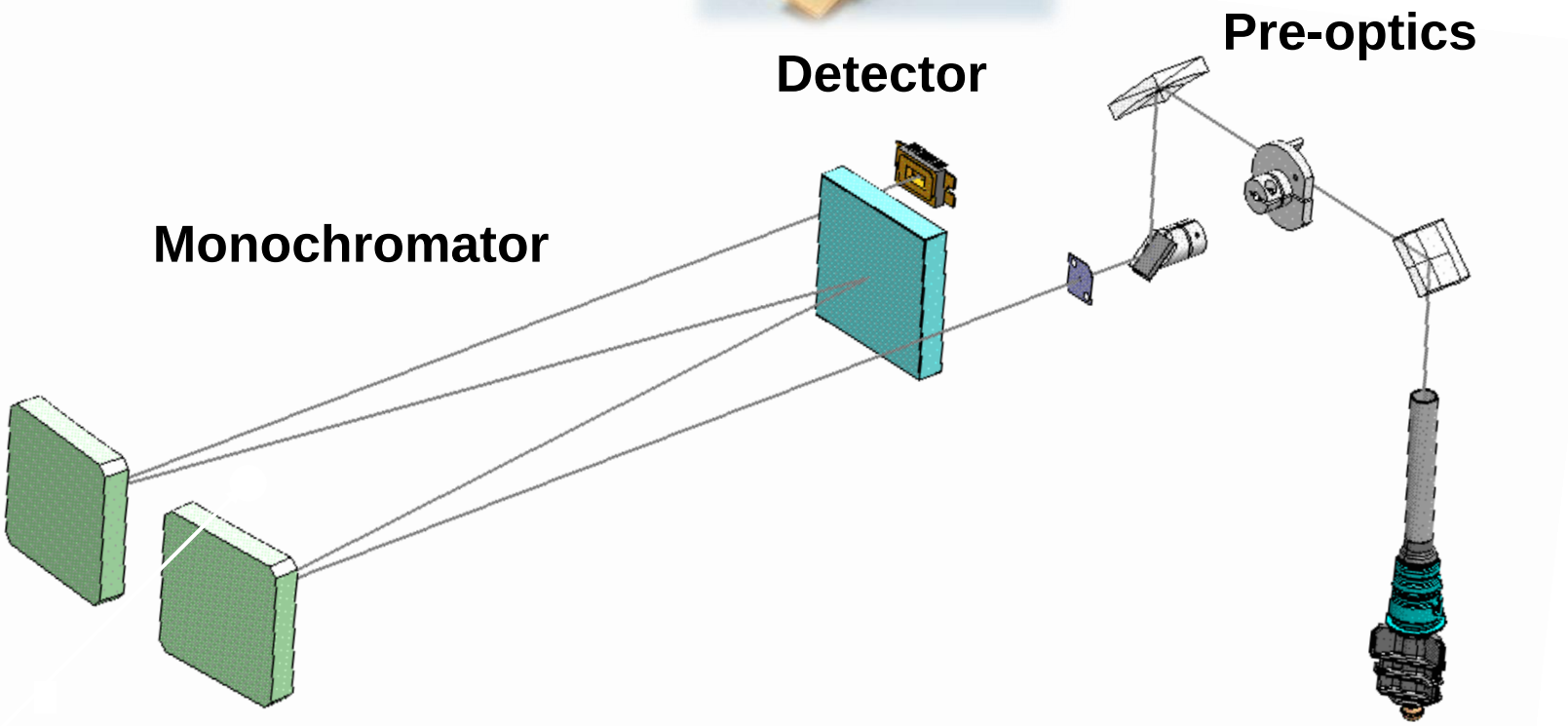
# Schematic Diagram




1. Instrument exhaust
2. Pre-optics window
3. Torch loader
4. Peristaltic pump
5. Plasma enable button
6. High voltage power supply
7. Electronics (control PWB)
8. Pre-optics
9. Plasma *(Magnetron)*
10. Monochromator with CCD detector
11. External gas control module
12. Cooling air inlet
13. Inlet gas connections

# Optical Diagram





# Accessory Options for the 4100 MP-AES

- Automate and simplify analysis with the SPS3 autosampler (required for unattended overnight operation)

- For organic applications, use the EGCM to bleed air into the plasma minimizing C build-up and reducing background
  - also requires the OneNeb inert nebulizer (included with the Organics kit)

- For low ppb level detection of As, Se or Hg, use the Multimode Sample Introduction System (MSIS)
  - also requires the 5 channel peristaltic pump option

# Technique Comparison: MP-AES and Flame AA

| Feature | MP-AES | Flame AA |
|---|---|---|
| Detection Limits | Better | Good |
| Linear Dynamic Range | Better | Good |
| Flammable Gas | Not Required | Acetylene |
| Oxidizing Gas | Not Required | Nitrous oxide |
| Fuel gas $CO_2$ | Not Required | 1 – 6 tonnes p.a. |
| Light sources | Not required | HC and D2 lamps |
| Drift correction | Not required | Double beam |
| Overnight unattended | Yes | No |
| Running costs | Lowest | High |
| High solids | Good | Good |

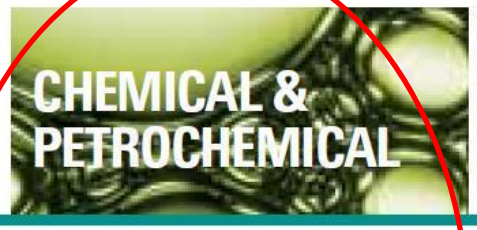
# Newmont's Carlin Lab AA Consumable Costs vs MP-AES*

| Consumable | Annual Cost | # AA Units | Mean Annual Cost per AA | Agilent MP-AES |
|---|---|---|---|---|
| Actylene | $ 63,615.36 | 9 | $ 7,068.37 | $0.00 |
| Au HCL | $ 37,440.00 | 9 | $ 4,160.00 | $0.00 |
| Ag HCL | $ 4,240.00 | 9 | $ 471.11 | $0.00 |
| Ni HCL | $ 1,672.00 | 9 | $ 185.78 | $0.00 |
| Cu/Ni HCL | $ 3,180.00 | 9 | $ 353.33 | $0.00 |
| Cu HCL | $ 4,180.00 | 9 | $ 464.44 | $0.00 |
| Fe HCL | $ 1,712.00 | 9 | $ 190.22 | $0.00 |
| As HCL | $ 2,464.00 | 9 | $ 273.78 | $0.00 |
| D2 Lamps | $ 8,436.68 | 9 | $ 937.41 | $0.00 |
| **TOTAL** | **$ 126,940.04** | **9** | **$ 14,104.45** | **$0.00** |

* Acknowledgement – John Borland, Newmont Mining Corporation

# Applications MP-AES Can Do – Examples


- Geochem samples in aqua regia digests
- Trace elements in geological samples
- Trace level gold in cyanide leach
- Analysis of high purity gold
- Platinum group elements in ore grade material
- Various elements in plating solutions




- Additives in lubricating oils
- Wear metal contaminants in used oils
- Analysis of coolant
- Analysis of petroleum and diesel fuel
- Major elements in polymers

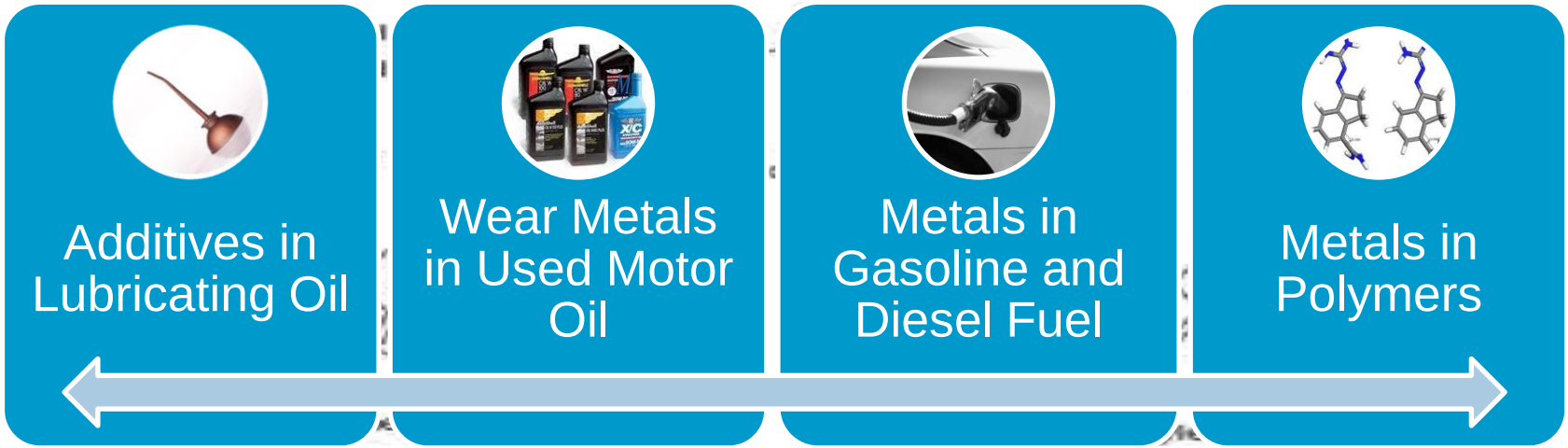

- Major elements in foods, beverages and agricultural samples
- Cations in soils
- Nutrients in soils
- Metals in soil extracts
- Metals in agricultural soil samples


- Hg, Pb, Cd and Cr in electronics and plastics (for WEEE/RoHs compliance)
- Heavy metals in soils
- As, Sb and Se in sediments and waste
- Analysis of waste waters, sediments and soils

# Chemical and Petrochemical Applications

Today we'll be looking at -

1. Determination of Cr, Ni, Pb and V in ethanol fuel
2. Determination of Ca, Mg, Na, K and Si in diesel and biodiesel
3. Direct determination of impurities in gasoline
4. Determination of wear metals and additives in oil



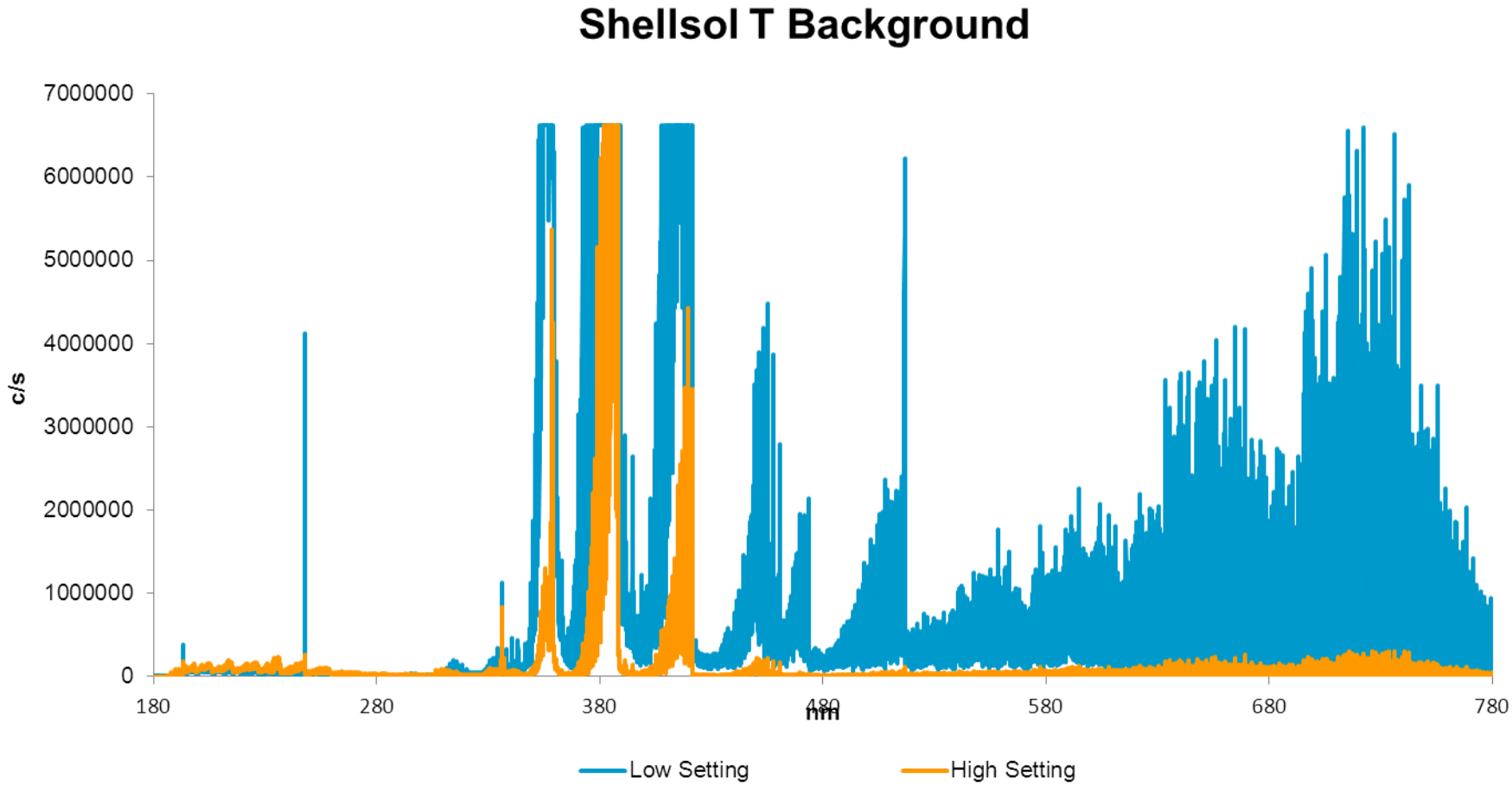
# Chemical and Petrochemical Applications – The Challenge

| | |
|---|---|
| High vapour pressure from solvents | • Plasma instability<br>• May extinguish the plasma |
| Carbon build up on injector | • Poor precision and drift<br>• Down time - injector may require regular cleaning |
| Nebulizer blockage | • Poor precision<br>• Down time - nebulizer needs cleaning |

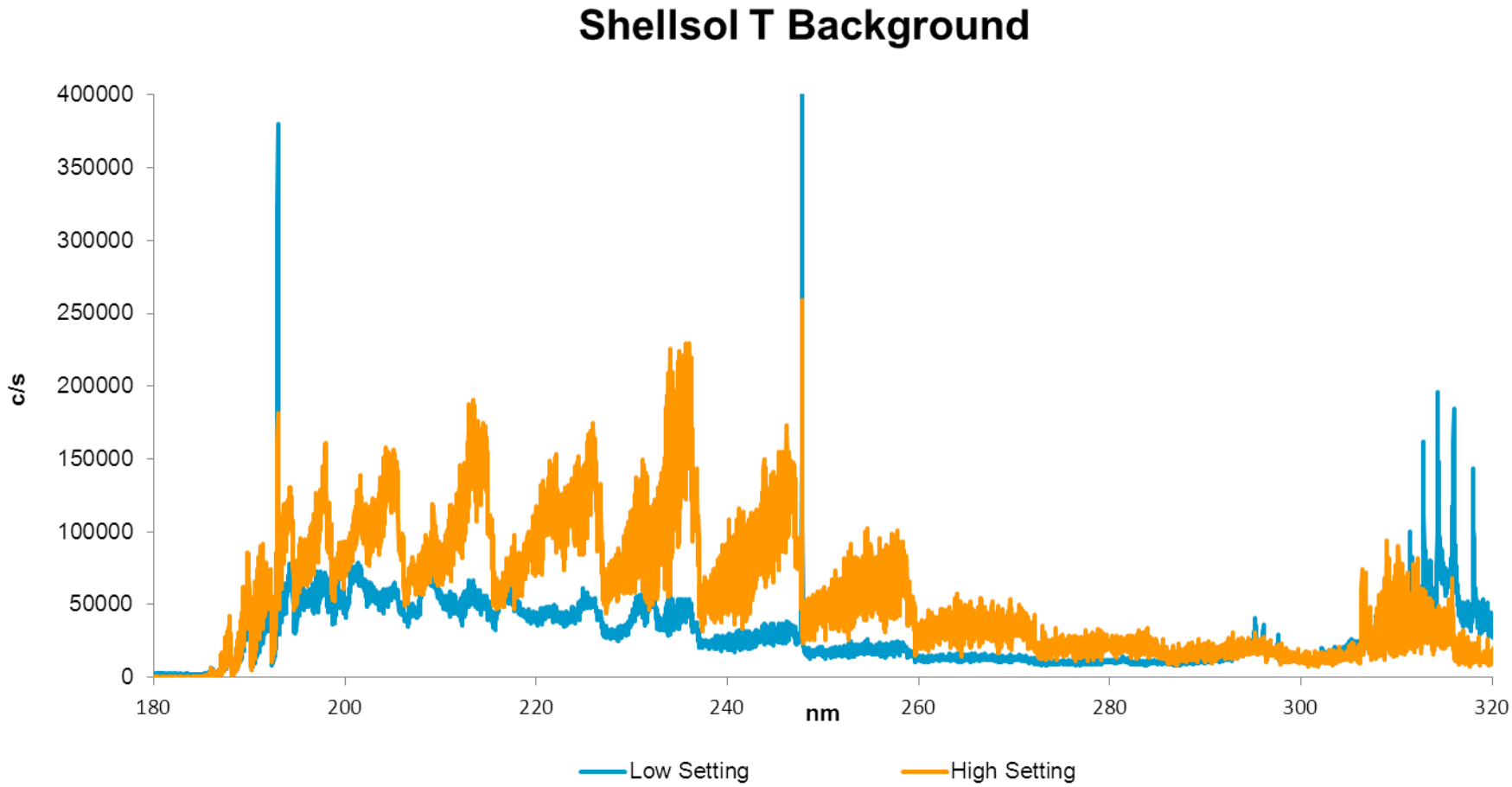
# Organic Samples and Solvents
## - External Gas Control Module (EGCM)

1. Prevents carbon build up on the injector when running organics
2. Reduces the background emissions from the plasma
3. A controlled flow of air is bled into the Auxiliary gas flow through the torch
4. Automatic - PC control of air flow

# Solvent Background - Minimized with EGCM

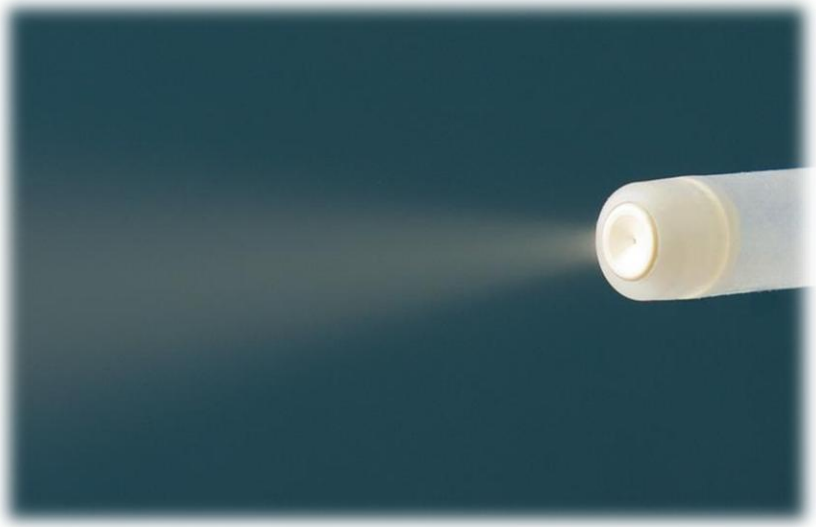


# Solvent Background - Minimized with EGCM



# For Challenging Applications
## – *OneNeb Nebulizer*

- Robust PFA and PEEK construction
  - Inert - resistant to strong acids such as HF
  - Resistant to breakage
  - Molded plastic design provides improved nebulizer to nebulizer reproducibility
- Constant diameter narrow bore tubing through to nebulizer tip
  - Ideal for high solids/particulates
  - Improved tolerance to high TDS samples
- Narrow aerosol size distribution provides improved precision
- Handles a wide flow range from 0.1 to 2 mL/min.
  - No sensitivity loss at low flow rates



# Principle of Operation – Inert OneNeb Nebulizer

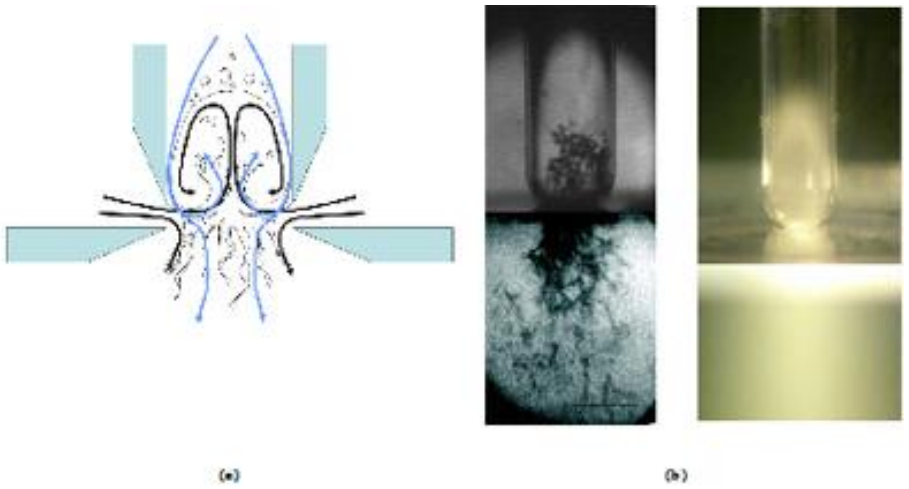
Tip geometry dimensioned to allow carrier gas to mix with the sample

Turbulent mixing of liquid and gas occurs

- Produces aerosol with a narrow size distribution range

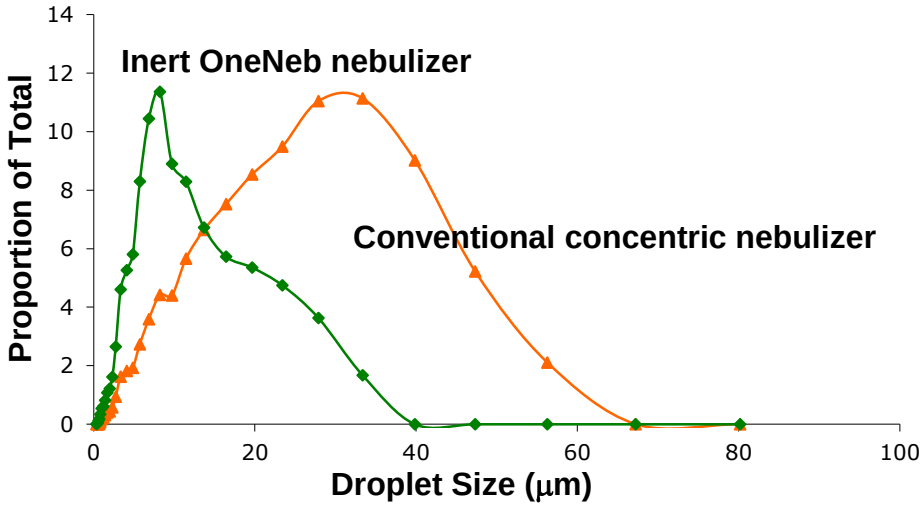
Droplets mixed into gas flow

No area of low pressure



Unique Flow Blurring action increases nebulization efficiency

- Greater efficiency than conventional concentric nebulizer
- Improved sensitivity



# Determination of Cr, Ni, Pb and V in Ethanol Fuel

# Introduction – Cr, Ni, Pb and V in Ethanol Fuel

Metals in ethanol fuel may reduce engine performance and deteriorate fuel quality. Ethanol can also contain toxic elements derived from the soil where the sugar cane used to produce the ethanol was grown, or introduced during production, storage or transport. After fuel combustion, these elements can significantly increase air pollution.

A simple 'dilute-and-shoot' procedure for determination of Cr, Ni, Pb and V in ethanol fuel by microwave plasma atomic emission spectrometry (MP-AES) was proposed. Samples were easily prepared and neither special nor expensive gases were needed for performing analyses. All limits of detection, from 0.3 to 40 µg/L, were compatible with requirements pertaining to fuel impact on the environment and engine performance.

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# Measurement Challenge

## Challenge

Simply and effectively determining Cr, Ni, Pb and V in ethanol fuel.

## Solution

The Agilent 4100 MP-AES spectrometer allows direct analysis of ethanol fuel samples. The external gas control module (EGCM) prevents carbon deposition on the torch and pre-optics, reducing background signal and enhancing accuracy.

# Experimental

## Instrumentation

- Instrument:  Agilent 4100 MP-AES spectrometer
- Sample introduction system:  Solvent-resistant tubing, double-pass cyclonic spray chamber, and inert OneNeb nebulizer.
- Accessory:  External gas control module (EGCM) to inject air into the nitrogen plasma.

**4100 MP-AES**

# Experimental

## Instrument operating conditions

| Instrument parameter | Operating condition |
|---|---|
| Nebulizer | Inert OneNeb |
| Spray chamber | Cyclonic double-pass |
| Read time (s) | 5 |
| Number of replicates | 3 |
| Stabilization time (s) | 15 |
| Background correction | Auto |

# Experimental

## Reagents and standard solutions

- Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone, Sorisole, Italy) was used to prepare all solutions.

- Stock single element solutions containing 1000 mg/L of Cr, Ni, Pb or V (Tec-Lab, Hexis, São Paulo, SP, Brazil) were used to prepare standard reference solutions and to carry out spike experiments.

- Analytical grade ethanol (J. T. Baker, Hexis, São Paulo, SP, Brazil) was used to matrix match the standard reference solutions used to build the analytical calibration curves.

# Experimental

## Sample and sample preparation

- Ethanol fuel samples (hydrated ethanol) were obtained in local gas stations in São Carlos, SP, Brazil.
- Samples were diluted 10-fold in 1% $HNO_3$ (v/v).
- Standard reference solutions used in the external calibration method were prepared by diluting adequate volumes of inorganic standard solutions of Cr, Ni, Pb or V in 1% $HNO_3$ (v/v).
- Ethanol was also added to each standard reference solution to a final concentration of 10% ethanol (v/v).

# Results

## Figures of merit for Cr, Ni, Pb and V determinations in ethanol fuel by MP-AES

| Element | LOD* (µg/L) | LOQ* (µg/L) | LOD in the sample† (µg/kg) |
|---|---|---|---|
| Cr | 0.7 | 2.2 | 9 |
| Ni | 16 | 52 | 200 |
| Pb | 40 | 130 | 490 |
| V | 0.3 | 0.9 | 4 |

* Instrumental limits of detection and quantification.
† Limit of detection considering sample dilution (1:9 v/v ethanol fuel in $HNO_3$ 1% v/v).

# Results

## Spike experiments for Cr, Ni, Pb and V determination in ethanol fuel samples

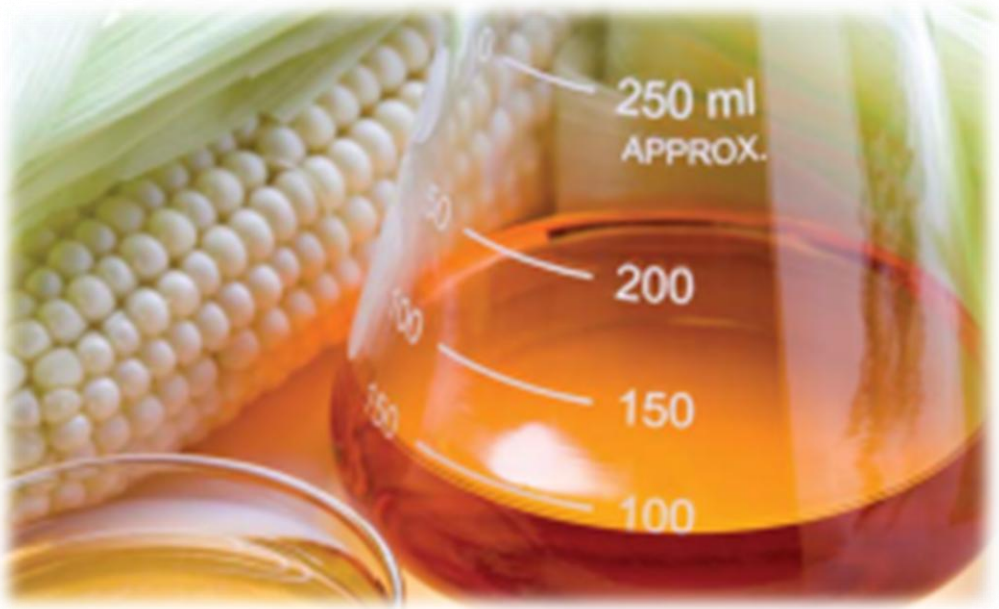
| Element | Added (µg/L) | Found (µg/L) | Recovery (%) |
|---|---|---|---|
| **Cr** | 20 | 21.2 ± 1.2 | 106 |
| | 100 | 95.1 ± 1.2 | 95 |
| | 500 | 460 ± 30 | 92 |
| **Ni** | 100 | 95.3 ± 0.8 | 95 |
| **Pb** | 400 | 430 ± 10 | 108 |
| | 1000 | 990 ± 10 | 99 |
| **V** | 20 | 19.8 ± 1.6 | 99 |
| | 100 | 98.4 ± 1.4 | 98 |
| | 500 | 460 ± 20 | 92 |

# Conclusions

- Direct analysis of ethanol fuel samples using the Agilent 4100 MP-AES is a simple and effective method that can easily be implemented in routine analysis.
- Four samples were analyzed and none were contaminated. No sample preparation is required and a simple “dilute-and-shoot” procedure, with solutions in 1% $HNO_3$ (v/v), is adequate for accurate and precise determinations of Cr, Ni, Pb and V in ethanol.
- The EGCM prevented carbon deposition on the torch and pre-optical components, contributing to reduced background signals and improved accuracy.

# Determination of Ca, Mg, Na, K and Si in Diesel and Biodiesel

# Direct Determination of Impurities in Gasoline



# Limits on Target Elements in Diesel Fuel - EN14538

| Property | ASTM Method | Limits | Units |
|---|---|---|---|
| Calcium & Magnesium, combined | EN 14538 | 5 max | ppm (ug/g) |
| **Flash Point (closed cup)** | **D 93** | **93 min.** | **Degrees C** |
| Alcohol Control (One of the following must be met) | | | |
| 1. Methanol Content | EN14110 | 0.2 Max | % volume |
| 2. Flash Point | D93 | 130 Min | Degrees C |
| **Water & Sediment** | **D 2709** | **0.05 max.** | **% vol.** |
| Kinematic Viscosity, 40 C | D 445 | 1.9 - 6.0 | $mm^2/sec.$ |
| Sulfated Ash | D 874 | 0.02 max. | % mass |
| **Sulfur**<br>**S 15 Grade**<br>**S 500 Grade** | <br>**D 5453**<br>**D 5453** | <br>**0.0015 max. (15)**<br>**0.05 max. (500)** | <br>**% mass (ppm)**<br>**% mass (ppm)** |
| Copper Strip Corrosion | D 130 | No. 3 max. | |
| Cetane | D 613 | 47 min. | |
| **Cloud Point** | **D 2500** | **Report** | **Degrees C** |
| Carbon Residue 100% sample | D 4530* | 0.05 max. | % mass |
| **Acid Number** | **D 664** | **0.50 max.** | **mg KOH/g** |
| **Free Glycerin** | **D 6584** | **0.020 max.** | **% mass** |
| **Total Glycerin** | **D 6584** | **0.240 max.** | **% mass** |
| Phosphorus Content | D 4951 | 0.001 max. | % mass |
| Distillation, T90 AET | D 1160 | 360 max. | Degrees C |
| Sodium/Potassium, combined | EN 14538 | 5 max | ppm |
| **Oxidation Stability** | **EN 14112** | **3 min** | **hours** |
| **Workmanship** | **Free of undissolved water, sediment, & suspended matter** | | |

**BOLD = BQ-9000 Critical Specification Testing Once Production Process Under Control**

* The carbon residue shall be run on the 100% sample.

# Sample Preparation – Method EN14538

A commercial diesel sample was analyzed

- 1:10 dilution with Shellsol

Standards made from Conostan S21+K

- 0.5 ppm, 1 ppm, 5 ppm, 10 ppm

All samples and standards matrix matched with blank oil

# Instrument Parameters

| Parameter | Setting |
|---|---|
| Nebulizer | Inert OneNeb |
| Spray chamber | Double-pass glass cyclonic |
| Sample tubing | Orange/green solvent resistant |
| Waste tubing | Blue/blue solvent resistant |
| Read Time | 3 s |
| Replicates | 3 |
| Stabilization time | 15 s |
| Fast Pump (80 rpm) | On |
| Background correction | Auto |
| Pump speed | 5 rpm |

# Method Detection Limits

3σ, 3s read time, 10 blanks

| Element | Wavelength (nm) | MDL (ppb) |
|---|---|---|
| Mg | 285.213 | 2.7 |
| Ca | 422.673 | 8.2 |
| Na | 588.995 | 18.7 |
| K | 766.491 | 2.7 |

# Spike Recoveries - Diesel Fuel

Diesel fuel sample spiked with 0.55 ppm S21+K

| Element | Sample (ppm) | Spiked Sample (ppm) | Recovery (%) |
|---|---|---|---|
| Mg 285.213 nm | < MDL | 0.53 | 97 |
| Ca 422.673 nm | < MDL | 0.51 | 93 |
| Na 588.995 nm | < MDL | 0.51 | 93 |
| K 766.491 nm | < MDL | 0.51 | 93 |

# Introduction - Si in Diesel and Biodiesel

The presence of metals and metalloids such as silicon compounds in petrochemical products can influence the performance of engines, and contribute to shortening the lifetime of the machinery. In addition, some elements act as catalyst poison, contributing to increases in the amount of toxic gases and particulate matter emitted by vehicles. Recent legislation in Brazil has established the maximum concentration of Si plus Al in diesel as 80 mg/kg. This study describes the determination of Si in diesel and biodiesel samples using the Agilent 4100 MP-AES.

Different sample preparation procedures were evaluated and the instrument robustness was demonstrated by analyzing samples diluted in 90% ethanol. Adequate recoveries were achieved even by applying a simple non-matrix-matched external calibration method with aqueous standard solutions.

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# Measurement Challenge

## Challenge

To safely and cost effectively perform biodiesel analysis at sufficient sensitivity to meet increasingly stringent International Standards

## Solution

The use of the Agilent 4100 MP-AES simplifies biodiesel analysis. The microwave plasma is extremely tolerant to solvent loading, without the need to change conditions.

Automated gas controls, in conjunction with the EGCM, take the uncertainty out the setup and let you concentrate on the analysis.

# Experimental

## Instrumentation

- Instrument:  4100 MP-AES spectrometer
- Accessory:  External gas control module (EGCM) for injecting air into the plasma and preventing carbon deposition on the torch and optical components.  Also contributes to plasma stability and background emission reduction in organic sample analyses.
- A closed-vessel microwave oven equipped with 45 mL PFA vessels for the digestion of diesel and biodiesel samples.

**4100 MP-AES**

# Experimental

## Operating conditions

| Parameter | Value |
|---|---|
| Nebulizer | Inert OneNeb |
| Spray chamber | Cyclonic double-pass |
| Read time | 10 s |
| Number of replicates | 3 |
| Stabilization time | 15 s |
| Background correction | Auto |

# Experimental

## Reagents and standard solutions

- Nitric acid previously purified by a sub-boiling distillation system, and hydrogen peroxide (30%) were used to digest the samples.
- Polyoxylene(10)octylphenyl ether, n-propanol and light mineral oil, without additional purification, were used for the micro-emulsion preparation.
- A 1000 mg/L Si stock solution was diluted to prepare aqueous and micro-emulsion standard reference solutions and to carry out spiking studies in digested samples and micro-emulsions.
- Analytical grade ethanol was used for direct sample dilution.
- A Si 1000 mg/L stock solution in organic medium was used in spike studies of ethanol-diluted diesel and biodiesel samples.
- External calibration with aqueous standard reference solutions in 1% $HNO_3$ (v/v) was performed for Si determination in both the digested samples and those diluted in 90% ethanol (v/v).

# Experimental

## Sample preparation

- Biodiesel samples were provided by the Center of Characterization and Development of Materials (CCDM, Federal University of São Carlos, São Carlos, SP, Brazil).
- Diesel fuel samples containing 5% v/v of biodiesel (B5), in accordance to the Brazilian legislation, were obtained from local gas stations of São Carlos, SP, Brazil.
- Three sample preparation procedures were evaluated: microwave-assisted digestion, micro-emulsion preparation in n-propanol, and dilution in ethanol.
  - Sample digestions were performed by using 50% $HNO_3$ (v/v - 7 mol/L) and 3.0 mL of $H_2O_2$ (30%).
  - Micro-emulsions were prepared by adding 0.5 mL of Triton X-100 and 0.5 mL of a 20% $HNO_3$ (v/v) aqueous solution to 1.0 mL of diesel or biodiesel. The volume was then made up to 10 mL with n-propanol and the mixture was homogenized for 2 min with a vortex mixer. During preparation of the micro-emulsion standard reference solutions, the sample was replaced by 0.2 mL of mineral oil, which simulates the sample matrix viscosity.
  - The direct dilution of samples in ethanol was carried out by adding 9 mL of ethanol to 1 mL of sample.

# Results

## Figures of merit

| | $HNO_3$ 1% v/v | | | Micro-emulsion | | |
|---|---|---|---|---|---|---|
| | **LOD (µg/L)** | **LDR* (Decades)** | **RSD† (%)** | **LOD (µg/L)** | **LDR* (Decades)** | **RSD† (%)** |
| Si (251.611 nm) | 20 | 2.3 | 1.6 | 5 | 2.6 | 1.6 |
| Si (288.158 nm) | 240 | 0.9 | 1.3 | 5 | 2.5 | 0.4 |

***** Linear dynamic range starting at the limit of detection.
† Repeatability presented as the relative standard deviation for a 2 mg/L Si solution (n = 10).

# Results

## Spike experiments after sample digestion, dilution in 90% v/v ethanol or micro-emulsion preparation (mg/L)

| Sample | Si emission line (nm) | Digestion* | | Ethanol† | | Micro-emulsion* | |
|---|---|---|---|---|---|---|---|
| | | Added | Recovered | Added | Recovered | Added | Recovered |
| Biodiesel | 251.611 | 3.0 | 3.05 0.07 | 0.5 | 0.45 0.03 | 1.0 | 0.89 0.05 |
| | | | | 1.0 | 0.99 0.09 | | |
| | 288.158 | 3.0 | 3.05 0.01 | 0.5 | 0.40 0.04 | 1.0 | 0.89 0.06 |
| | | | | 1.0 | 1.02 0.17 | | |
| Diesel | 251.611 | 3.0 | 3.09 0.10 | 0.5 | 0.47 0.01 | 1.0 | 0.96 0.03 |
| | | | | 1.0 | 0.91 0.01 | | |
| | 288.158 | 3.0 | 3.07 0.15 | 0.5 | 0.46 0.01 | 1.0 | 0.96 0.04 |
| | | | | 1.0 | 0.95 0.01 | | |

* Spike solution in aqueous medium.
† Spike solution in organic medium.

# Conclusions

- In this work, accurate Si determinations were successfully carried out simply by diluting the samples in ethanol, and using external calibration with aqueous solutions. Considering its simplicity and sample throughput, this method is recommended for the determination of Si in diesel and biodiesel samples.
- The sample preparation procedures evaluated are environmentally friendly, because less toxic solvents are used.
- No carbon deposit or reduction of performance was observed while introducing high carbon loads to the Agilent 4100 MP-AES (without the use of a cooled spray chamber).
- Two important advantages of this instrument are:
  - low running costs, and
  - laboratory safety, as no flammable gases are required.
- Considering cost, performance and multi-element capabilities, the 4100 MP-AES is a suitable and efficient alternative to flame AA for this application, and presents better performance for critical elements such as the one investigated here.

# Direct Measurement of Impurities in Gasoline

Same limits as ASTM D6751 and EN14538

- Ca, Mg combined 5 ppm
- Na, K combined 5 ppm

High volatility of the gasoline is a challenge

- Cooled spray chamber -10 $^{o}$C
- Standard Additions calibration
- Direct measurement of samples

# Instrument Parameters

| Parameter | Setting |
|---|---|
| Nebulizer | Inert OneNeb |
| Spray chamber | IsoMist cooled spray chamber (-10 $^{o}$C) |
| Sample tubing | Orange/green solvent resistant |
| Waste tubing | Blue/blue solvent resistant |
| Read Time | 3 s |
| Replicates | 3 |
| Stabilization time | 30 s |
| Fast Pump (80 rpm) | On |
| Background correction | Off-peak |
| Pump speed | 5 rpm |

# Sample Preparation

- Gasoline fuel standards were prepared by spiking a sample with an oil-based metal calibration standard, S21+K (Conostan), giving final concentrations of 0.89 ppm, 1.92 ppm and 3.94 ppm.

- Standard additions calibration allows the gasoline samples to be directly analyzed, without further sample preparation.

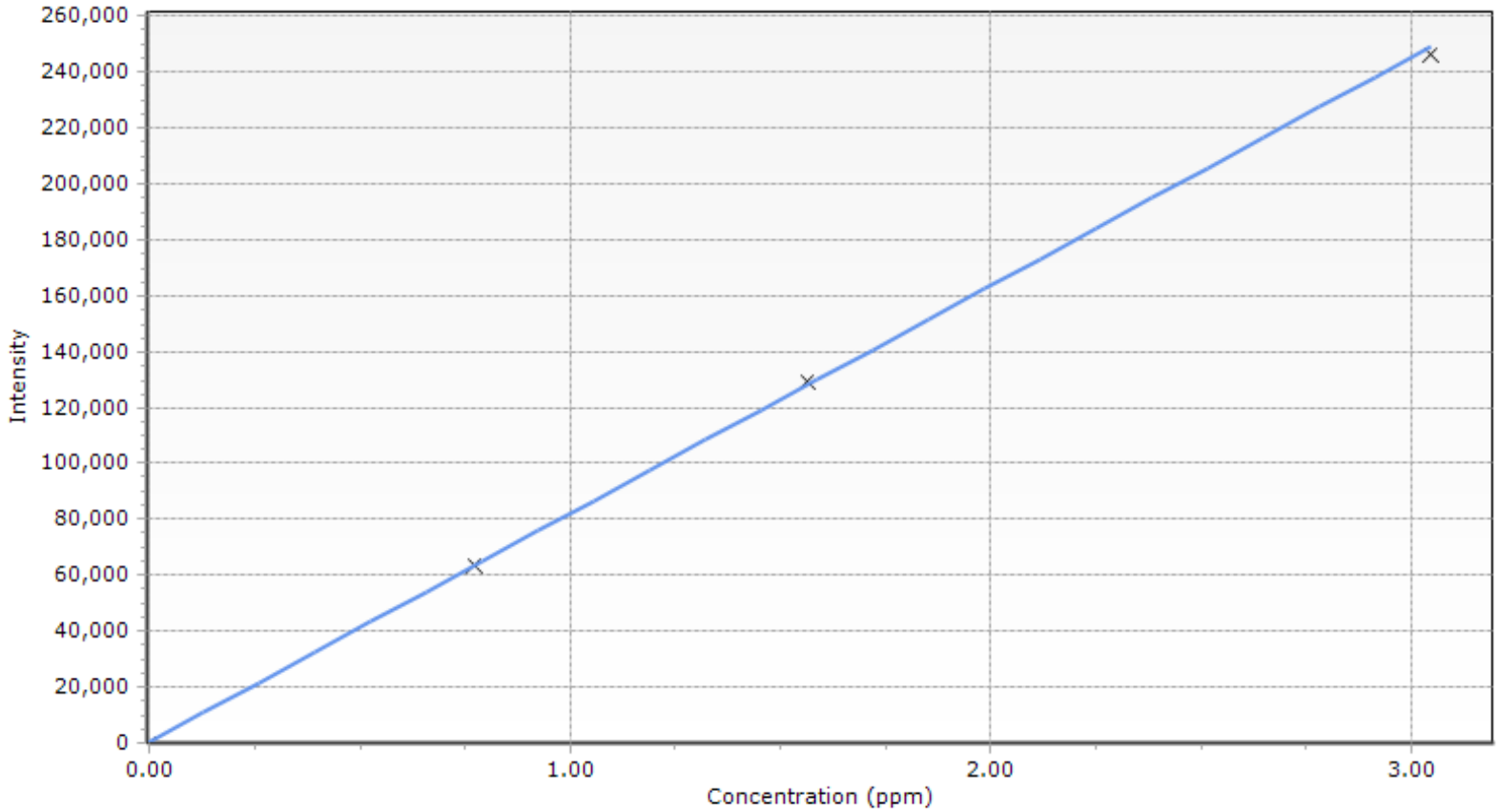
- For the spike recovery test, gasoline samples were spiked with S21+K to give spike concentrations of 1.1 ppm.

# Calibrations and Detection Limits

| Element | Wavelength (nm) | Correlation Coeff | MDL (ppb) |
|---|---|---|---|
| Mg | 285.213 | 0.99993 | 2.7 |
| Ca | 422.673 | 0.99934 | 4.3 |
| Na | 588.995 | 0.99939 | 5.3 |
| K | 766.491 | 0.99975 | 29.4 |

# Excellent Standard Additions Linearity - Gasoline

Mg 285.213 nm




Intensity = 81779.569 * Concentration + 239.829
Correlation coefficient: 0.99993

# Spike Recoveries - Gasoline

Gasoline fuel sample spiked with 1.1 ppm S21+K

| Element | Sample (ppm) | Spike (ppm) | Recovery % |
|---|---|---|---|
| Mg 285.213 nm | < MDL | 1.11 | 100 |
| Ca 422.673 nm | < MDL | 1.06 | 95 |
| Na 588.995 nm | < MDL | 1.11 | 100 |
| K 766.491 nm | 0.05 | 1.12 | 96 |

# Determination of Wear Metals and Additives in Oil

# Instrument Parameters

| Parameter | Setting |
|---|---|
| Nebulizer | Inert OneNeb |
| Spray chamber | Double-pass glass cyclonic |
| Sample tubing | Orange/green solvent resistant |
| Waste tubing | Blue/blue solvent resistant |
| Read Time | 3 s |
| Replicates | 3 |
| Stabilization time | 15 s |
| Rinse time | 45 s |
| Fast Pump (80 rpm) | On |
| Background correction | Auto |
| Pump speed | 5 rpm |

# Standard and Sample Preparation

Wear metals and contaminants

- 1:10 dilution with Shellsol

Additives

- 1:100 dilution with Shellsol

Standards

- Prepared from 500 ppm S21 (Conostan)

All matrix matched with blank oil for constant viscosity

# Measured Results for SRM 1085b Wear Metals

| Element & wavelength (nm) | Measured (mg/kg) | Certified (mg/kg) | Recovery (%) |
|---|---|---|---|
| Fe 259.940 | 314.7 ± 0.3 | 301.2 ± 5.0 | 104 |
| Mn 259.372 | 289.9 ± 0.2 | 300.7 ± 2.0 | 96 |
| Cd 226.502 | 290.9 ± 2.9 | 302.9 ± 5.1 | 96 |
| Cr 276.653 | 305.2 ± 0.1 | 302.9 ± 3.9 | 101 |
| Si 251.611 | 295.7 ± 1.9 | 300.2 ± 5.0 | 99 |
| Ni 305.081 | 291.6 ± 0.1 | 295.9 ± 7.4 | 99 |
| Cu 327.395 | 300.9 ± 0.1 | 295.6 ± 8.5 | 102 |
| Ag 328.068 | 308 ± 0.2 | 304.6 ± 8.9 | 101 |
| Pb 283.305 | 296.1 ± 0.1 | 297.7 ± 6.8 | 99 |
| V 310.229 | 287.6 ± 0.1 | 297.8 ± 4.6 | 97 |
| Ti 323.452 | 293.9 ± 0.1 | 301.1 ± 2.9 | 98 |
| Sn 303.411 | 295.3 ± 0.3 | 299.4 ± 4.8 | 99 |
| Mo 319.398 | 296.9 ± 0.1 | 300.6 ± 3.2 | 99 |
| Al 396.152 | 291.7 ± 0.2 | 300.4 ± 9.3 | 97 |
| Na 589.592 | 297.4 ± 0.1 | 305.2 ± 7.0 | 97 |

Great recoveries for all key elements

# Measured Recoveries on 10 ppm Spike of Gear Oil

| Element | Wavelength (nm) | Unspiked gear oil (ppm) | Spiked gear oil (ppm) | Spike recovery (%) |
|---|---|---|---|---|
| Ag | 328.068 nm | 0.27 | 11.01 | 105 |
| Al | 396.152 nm | 0.32 | 10.31 | 98 |
| Cd | 228.802 nm | 0.14 | 9.85 | 95 |
| Cr | 276.653 nm | 0.25 | 9.92 | 95 |
| Cu | 327.395 nm | 2.68 | 13.14 | 103 |
| Fe | 259.940 nm | 10.41 | 20.09 | 95 |
| Mn | 259.372 nm | 0.80 | 11.54 | 105 |
| Mo | 319.398 nm | 9.02 | 19.34 | 101 |
| Na | 589.592 nm | 0.46 | 10.70 | 100 |
| Ni | 305.081 nm | 0.07 | 10.13 | 99 |
| Pb | 283.305 nm | 0.25 | 11.36 | 109 |
| Si | 251.611 nm | 2.23 | 11.60 | 92 |
| Sn | 303.411 nm | 0.16 | 10.62 | 103 |
| Ti | 323.452 nm | 0.01 | 10.87 | 106 |
| V | 310.229 nm | 0.15 | 10.71 | 104 |

Great recoveries for all key elements

# Measured Results for Additive Elements

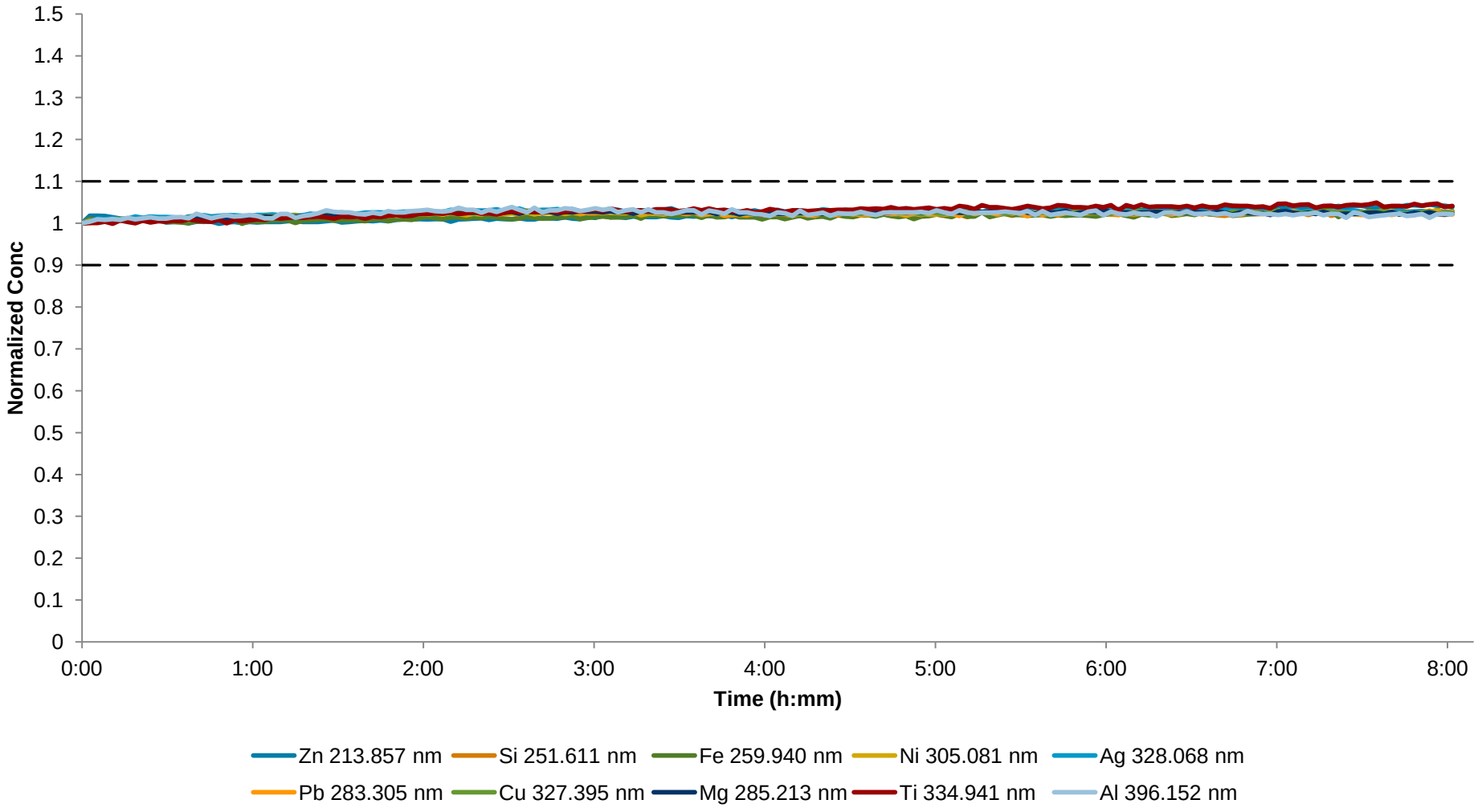
## Measured Results vs Certified Values

| Element | Measured (mg/kg) | Certified (mg/kg) | Recovery % |
|---|---|---|---|
| P 213.618 | 301.5 ± 0.1 | 299.9 ± 7.2 | 101 |
| Zn 481.053 | 314.9 ± 0.3 | 296.8 ± 6.8 | 106 |
| Mg 285.213 | 300.6 ± 0.2 | 297.3 ± 4.1 | 101 |
| Ca 422.673 | 279.6 ± 0.1 | 298 | 94 |
| Ba 614.171 | 281.2 ± 0.1 | 300.1 ± 2.4 | 94 |

## Measured Recoveries on 10 ppm Spike of Gear Oil

| Element | Mixed Gear (ppm) | Spike (ppm) | Recovery % |
|---|---|---|---|
| P 213.618 | 17.16 | 26.71 | 95 |
| Zn 481.053 | 6.99 | 17.17 | 101 |
| Mg 285.213 | 1.53 | 11.32 | 97 |
| Ca 422.673 | 8.89 | 19.69 | 107 |
| Ba 614.171 | 0.00 | 9.16 | 91 |

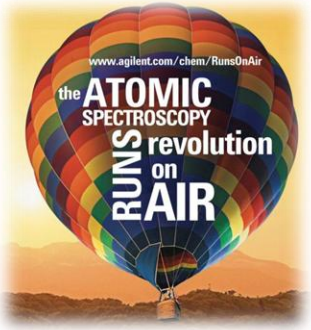
# Organics – Long Term Stability




10 ppm S21. All lines show precision <1% RSD.

# 4100 MP-AES Solves the Challenges

| | |
|---|---|
| High vapour pressure from solvents | • OneNeb nebulizer<br>• Reduced sample flow (double pass SC, smaller pump tubing and lower rpm) |
| Carbon build up on injector | • EGCM |
| Nebulizer blockage | • OneNeb nebulizer |




# Agilent 4100 MP-AES

***Runs on air – the most significant advance in atomic spectroscopy***

- **Lowest running cost** of any atomic spectroscopy technique due to capability to run on air – ideal for remote and at site operation
- **Improved safety** – capability to run on air means no flammable gases and no manual handling of cylinders
- **Easy-to-use** software with MP applets and plug and play torch which simplify operation and maximize uptime
- **Superior performance to flame AA**, with capability to run unattended overnight

# *Thank you!*

## *Questions?*

**Agilent MP-AES**

**Agilent AA**

**Agilent ICP-OES**

**Agilent ICP-MS**

## The Market Leaders in Atomic Spectroscopy