Elemental Analysis for Refining and Petrochemicals

Seamless Laboratory and Process Analysis for Total Sulfur and Nitrogen

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Presenters:

Karl Kuklenz
Product Manager
Process Analytics

Koen Vink
Product Manager
Atomic Analysis

Karl Kuklenz

Product Manager Process Analytics

Karl has been in the refining industry for 13 years, most of it in the field of process chemical treatment. In that time, he has held roles in research and product management for companies like General Electric and SUEZ. His principal area of expertise is in oil and water separations. Karl has authored publications in renowned organizations such as IAPG and NACE and is the inventor of two patents. He holds a master's degree in chemistry from Sam Houston State University and lives in Houston, TX.

Interests:

Koen Vink

Product Manager Atomic Analysis

Koen received a Bachelor of Science, Analytical Chemistry degree from the University of Rotterdam and joined PAC in 2012 where he made significant contributions to the launch of a number of successful new products in the GC and Elemental portfolio that are used in the petroleum industry today.

In 2019, Koen transitioned to his current product leadership role where he has taken ownership over all PAC's lab Atomic analysis solutions that scientists and analysts rely on every day.

Interests:

Importance of Elemental Analysis

Changing feedstock quality

Crude oil inputs are becoming heavier and more sour. The amount of nitrogen and sulfur in the crude is increasing, requiring more focus on processing and control.

Stricter regulation

Manufactured fuel products are increasingly regulated for their sulfur content.

Petrochemical market dynamics

The shift to petrochemical and crude oil-to-chemicals (COTC) projects is expected to expand through 2050. Petrochemical grade feedstocks and products have tight tolerances for sulfur and nitrogen.

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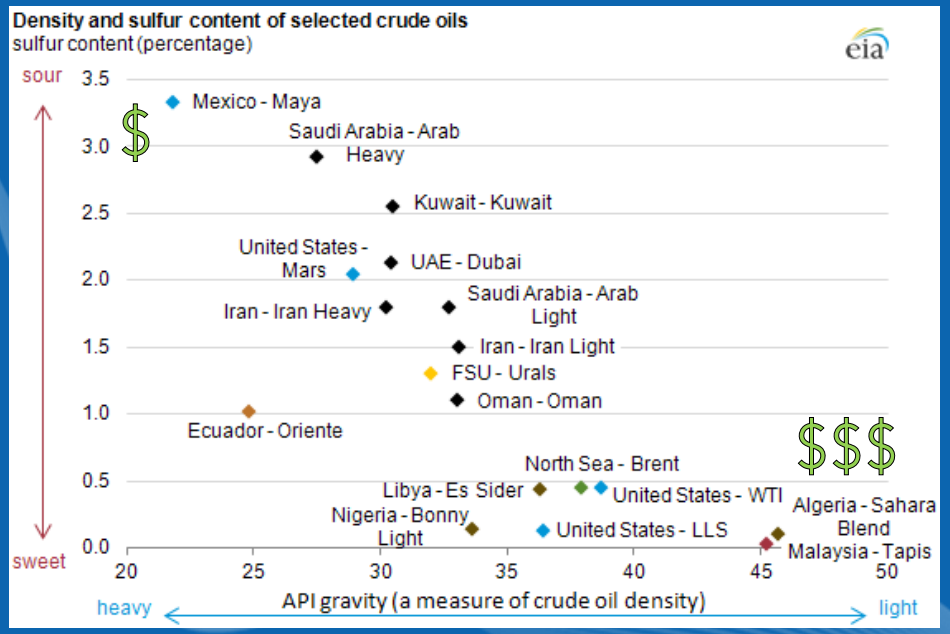
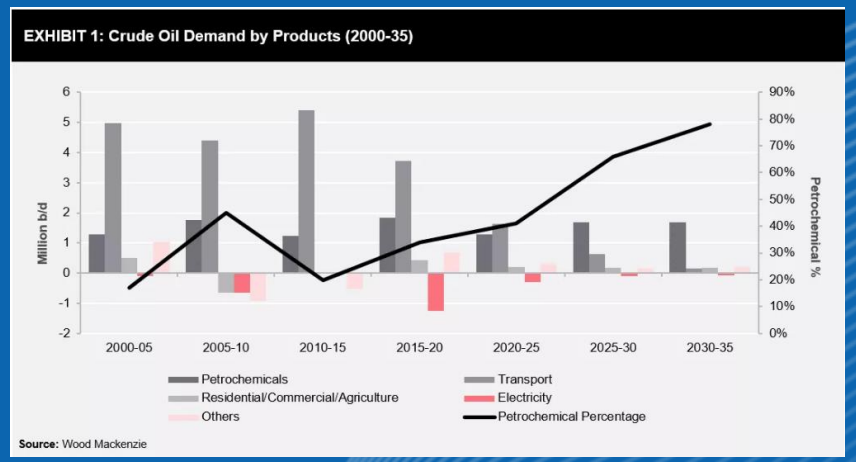
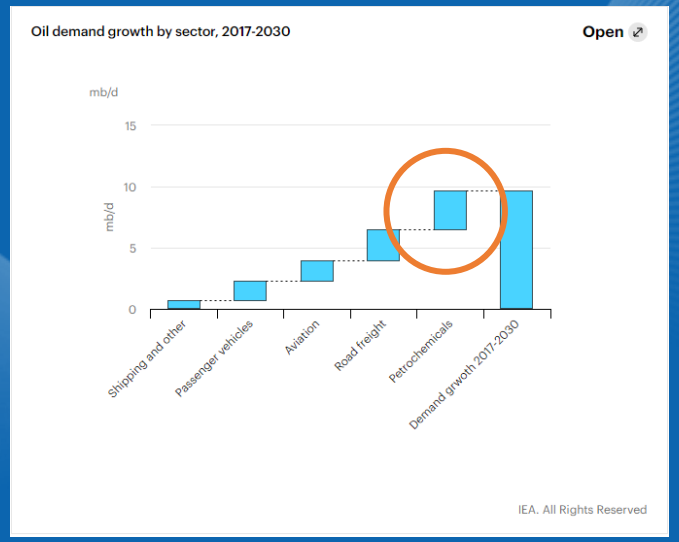
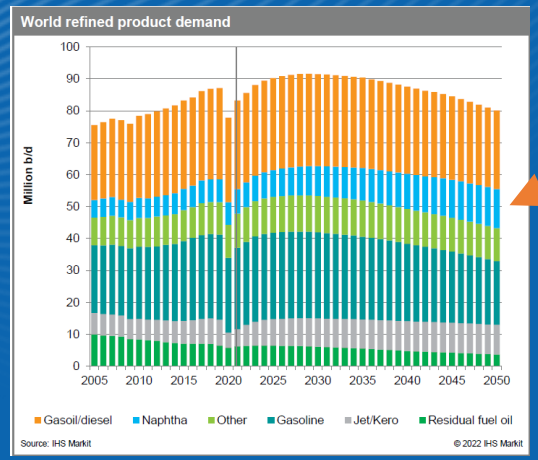
Crude Quality



Petrochemical Race







Process Control

Hydroprocessing

Protection of refinery infrastructure
Fuel limit regulations

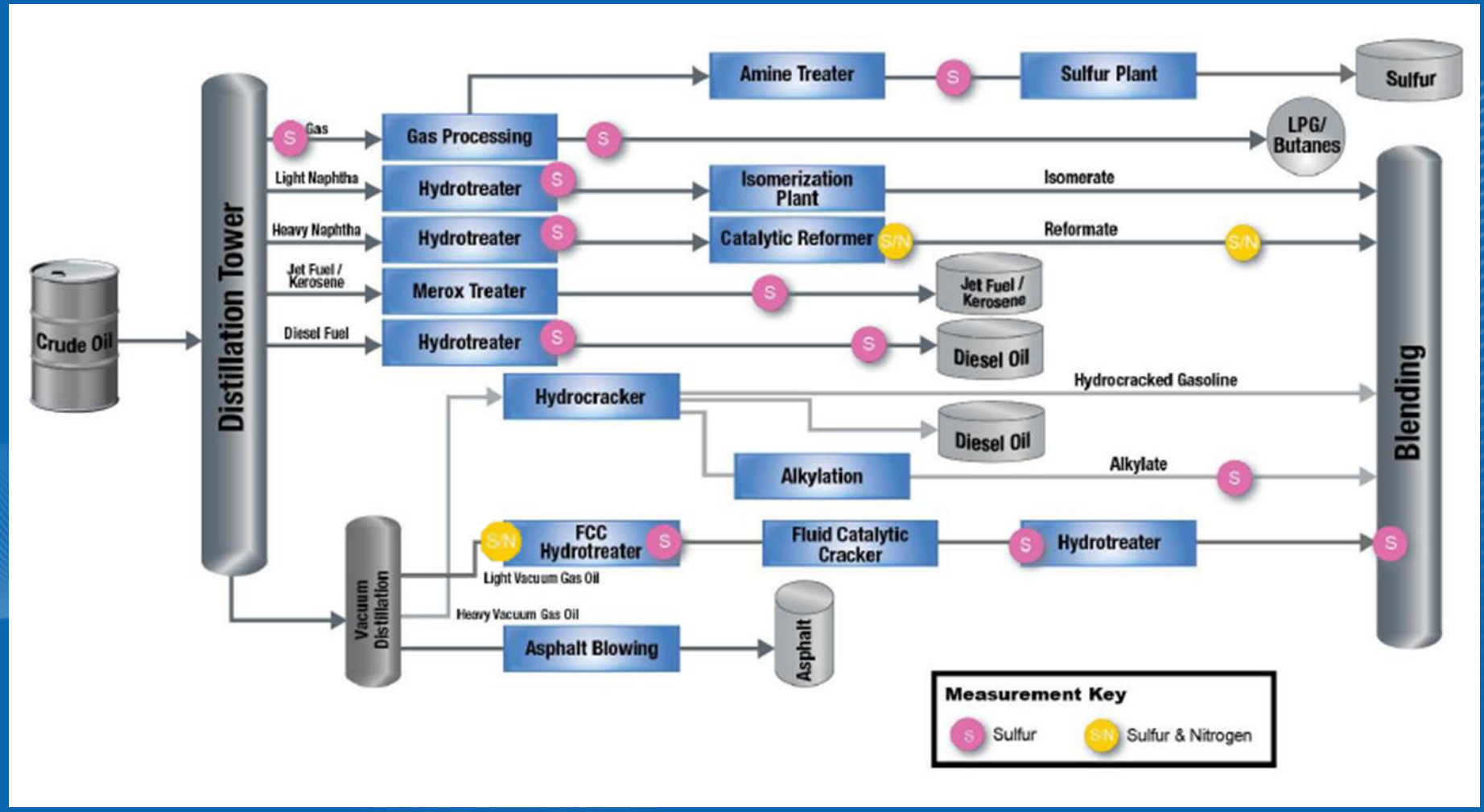
Catalytic Cracking

Typical FCC for gasoline operations
Modified FCC for olefins

Cost optimization and reduction in give-away

Removal of sulfur and nitrogen is costly, measuring in real-time with a process analyzer allows refiners to get close to spec while optimizing cost

Elemental Analysis in the Refinery



Product Certification

Quality Assurance of final products

Fuels: gasoline, diesel, jet

Process intermediates: BTX, LPG, naphtha

Polymers and polymer feedstocks:
ethylene, propylene, butane, PE, PP, and butadiene

Base chemicals: paraffins, cyclohexane, aromatics, organic acids and dye

Solvents: alcohols, aldehydes and hydrocarbons

Test Methods & Specifications

	Gas & LPG	Gasoline	Diesel	Jet Fuel	Aromatics	Alcohols / E85 / M85
ASTM D4629		N	N			N
ASTM D5762		N	N	N		N
ASTM D5453		S	S	S		S
ASTM D6667	S					
ASTM D7183					S	
ASTM D7184					N	
ASTM D7551	S					
EN ISO 20846		S	S			
EN 17178	S					
EN 15486						S
IP 490		S	S			
IP 554						S
DIN 51444		N	N	N		
UOP 936	N					
UOP 971					N	

Environmental

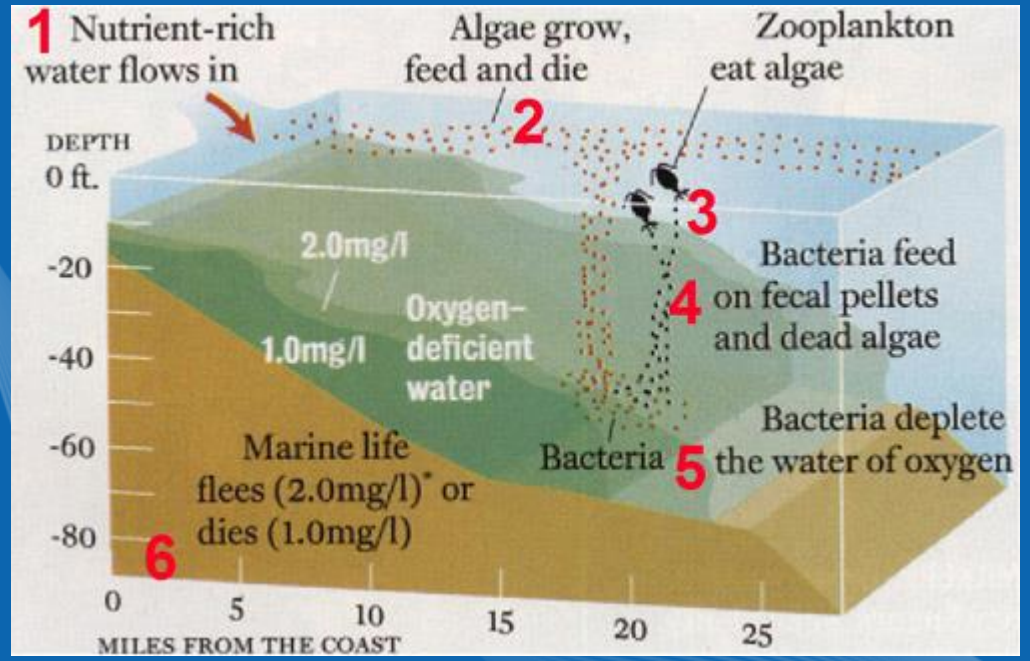
Environmental Control

Monitoring of sulfur and nitrogen in refinery products and waste streams

Emissions of sulfur, SO2 and NOX from refinery stacks, transportation, power generation and home heating oils

Higher levels nitrogen and sulfur refinery waste-water streams increases the uptake of oxygen and has a negative impact on marine life

Nitrogen's Effect on Water Quality



From gulfhypoxia.net

Elemental Analysis Technology

ANTEK Elemental Lab and Process Analyzers

- Combustion analyzers for the simultaneous analysis of Total Sulfur and/or Total Nitrogen
- Based on
  - UV Fluorescence principle for Sulfur
  - Chemiluminescence principle for Nitrogen
- In compliance with/correlates to global standard methods
- Correlates with oxidative micro-coulometry methods
- Available for Process and Lab measurement with excellent correlation
- Provides a solution for Solids, Liquids and Gas analysis in one single instrument.

Measuring Principle - Sulfur

- High Temperature Oxidation of Sulfur Compounds:

$$R - S + O_2 \xrightarrow{1050°C} SO_2 + CO_2 + H_2O + R$$

- SO_2 molecules are converted to excited SO_2^* by the absorption of energy of a UV lamp and emitting light (Fluorescence) while falling back to a stable state

$$SO_2 + h\upsilon_1 \rightarrow SO_2^*$$

$$SO_2^* \rightarrow SO_2 + h\upsilon_2$$

- A photomultiplier tube measures the emitted light signal
- The response signal is integrated to calculate the area. The concentration is calculated using the linear regression function obtained with standards of a known concentration (area vs concentration)

Measuring Principle - Nitrogen

- High Temperature Oxidation of Nitrogen Compounds:

$$R - N + O_2 \xrightarrow{1050°C} NO + CO_2 + H_2O + R$$

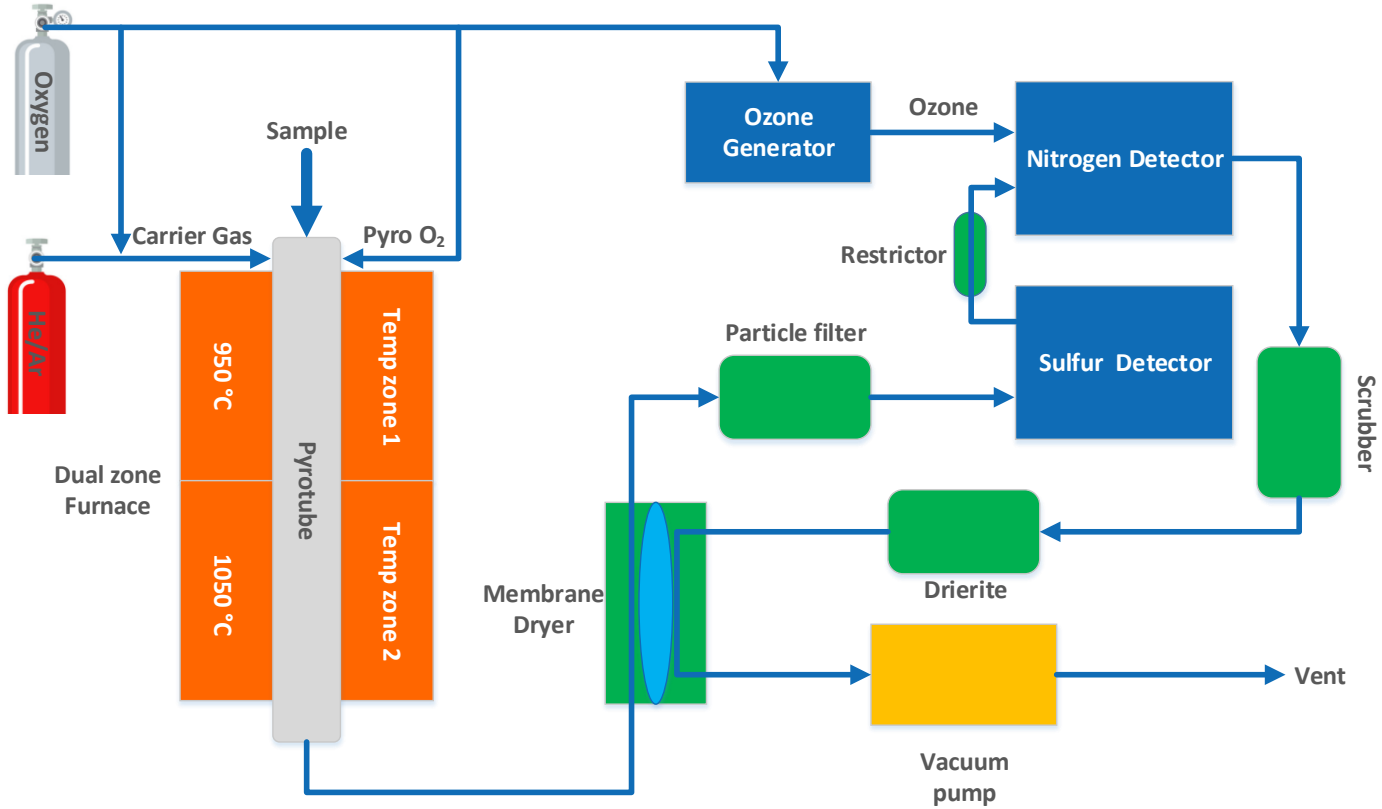
- NO molecules are converted to excited NO_2^* by the addition of Ozone and emitting light (Chemiluminescence) while falling back to a stable state

$$NO + O_3 \rightarrow {NO_2}^* + O_2$$

$${NO_2}^* \rightarrow NO_2 + h\upsilon$$

- A photomultiplier tube measures the emitted light signal
- The response signal is integrated to calculate the area. The concentration is calculated using the linear regression function obtained with standards of a known concentration (area vs concentration)

Simplified System Diagram



ElemeNtS Features

SPEED | EASE OF USE | PRECISION | LOW COST OF OWNERSHIP | ROBUST | HIGH UPTIME

Autosampling

Compatible with high capacity **Liquid**

Autosampler 749 or manual injection in **BID**

Ease of Use

10” user interface for direct instrument control

Available as S-only, N-only, or N+S configuration

Accura Compatible

For gaseous and LPG sample introduction

Front Maintenance Door

Allows easy access to consumable parts

User Interface

Instrument Control

- Overview of Instrument Status
- Direct Sample Queue Management
- Result Preview on the Instrument
- Easy Diagnostics Features
- Full instrument control through IRIS Software (client-server compatible)

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ElemeNtS – Laboratory Elemental Analysis

- Integrated **network switch** for easy connectivity
- **Single design pyrotube** per configuration for all application types
- A build-in **oil-free vacuum pump** for automated leak test
- **Easy switching** between different sample types
- Sensitive and robust **integrated photomultiplier tubes**
- **Peltier-cooled** sample boat introduction
- Easy **Gas/LPG sampler** connectivity

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NSure Features

ONLINE | EASE OF USE | PRECISION | LOW COST OF OWNERSHIP | ROBUST | HIGH UPTIME

Robust 1100°C Furnace

Operate for years at a time until service is needed

Ease of Use

Large touch screen compatible with gloved fingers and no touch pen required

Available as S-only, N-only, or N+S configuration

IECEx, ATEX, NEC certified

Deployable anywhere in the world

Freestanding or Wall-mountable

NSure – Process Elemental Analysis

- Measure **Total Sulfur, Total Nitrogen**, or both in a single analyzer, continuously online
- **Best in-class precision** measurement of gas, liquid, LPG as well as heavy gas or oil samples
- Sensitivity from **20ppb to % levels**
- Correlates to **standard test methods** like: ASTM D5453, D6667, D4629, D5176 and ISO 20846
- Analog 4-20 mA outputs, Digital I/O for alarms and status, RS485 MODBUS & Ethernet MODBUS TCP/IP
- **Easy to maintain**

Applications

Sample Overview

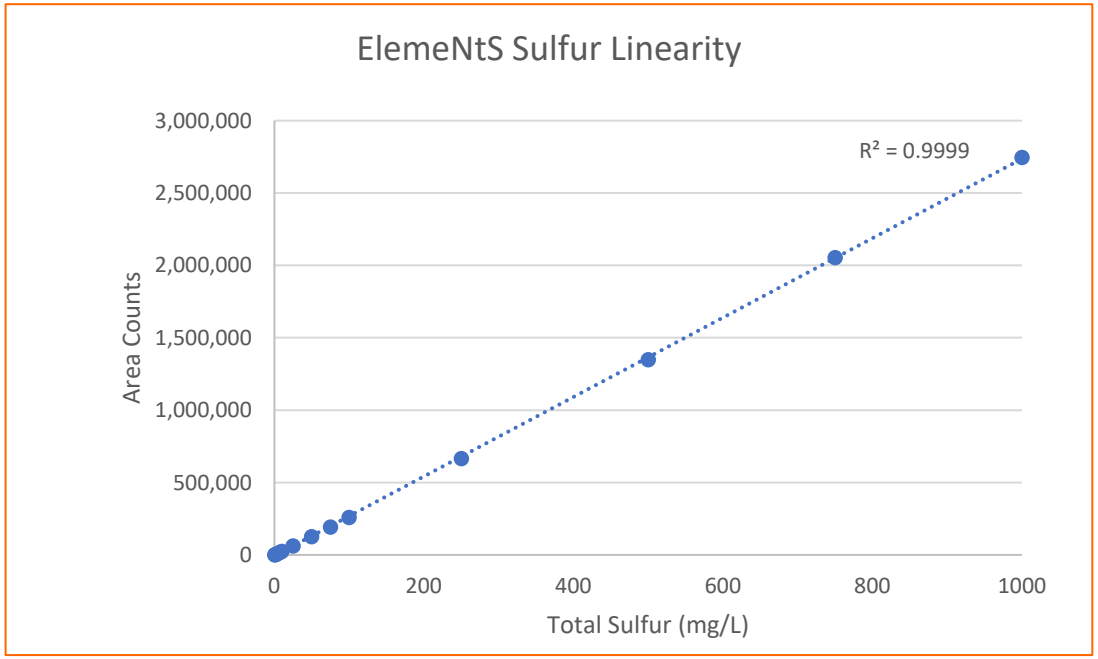
Compound	Boiling Point (°C)	Carbon # range
LPG & Gasses	< 40	C1 – C5
Gasolines	0 – 200	C4 – C12
Aromatics	80 – 150	C6 – C12
Naphtha's	0 – 220	C4 – C12
Jet Fuel	100 – 315	C8 – C18
(Bio) Diesels	170 – 430	C10 – C28
Fuel Oils	350 – 650	C20 – C70

Sulfur & Nitrogen Species can be found in all sample streams

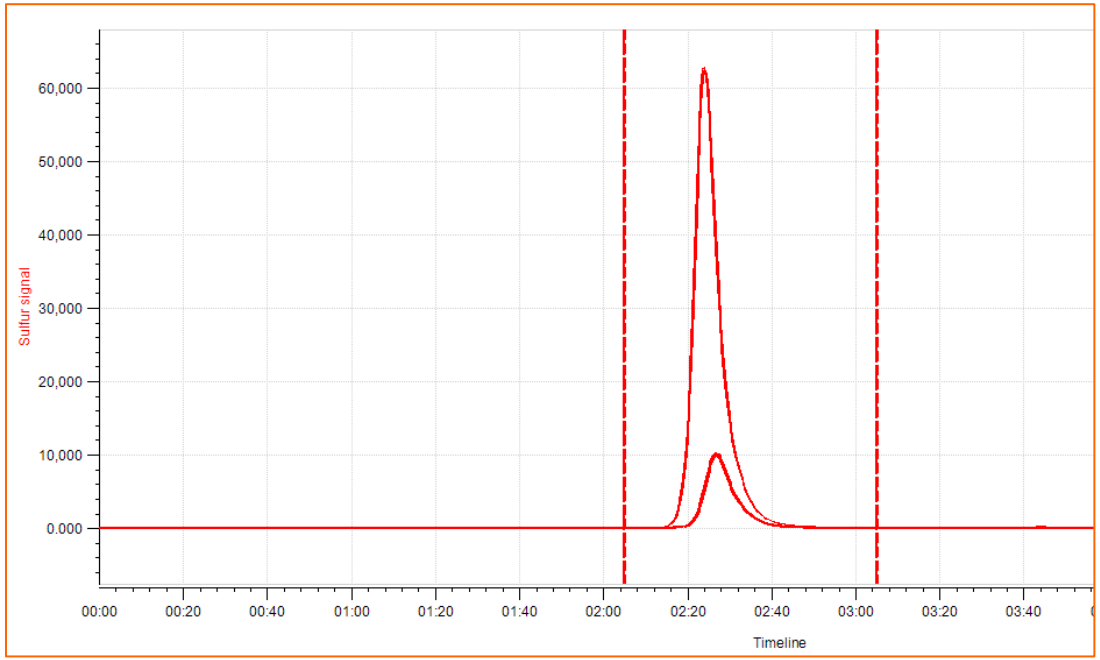
Sulfur Analysis

ElemeNtS and **NSure** are the instruments of choice when it comes to accurate sulfur analysis from Trace till %-level

- Unrivaled **Linear** detector response
- Excellent **Precision** and **Accuracy** validated using certified reference materials
- **Reliable** analysis at Trace level



Typical Sulfur Calibration 0.1 – 1000 mg/L



Overlay SRM 732 and SRM 737 signal (n=5)

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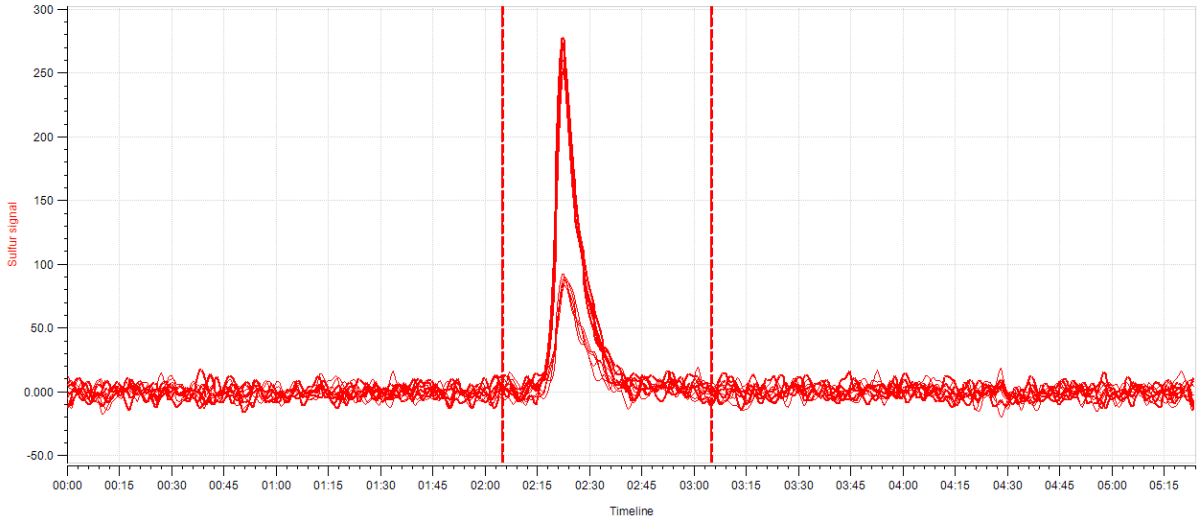
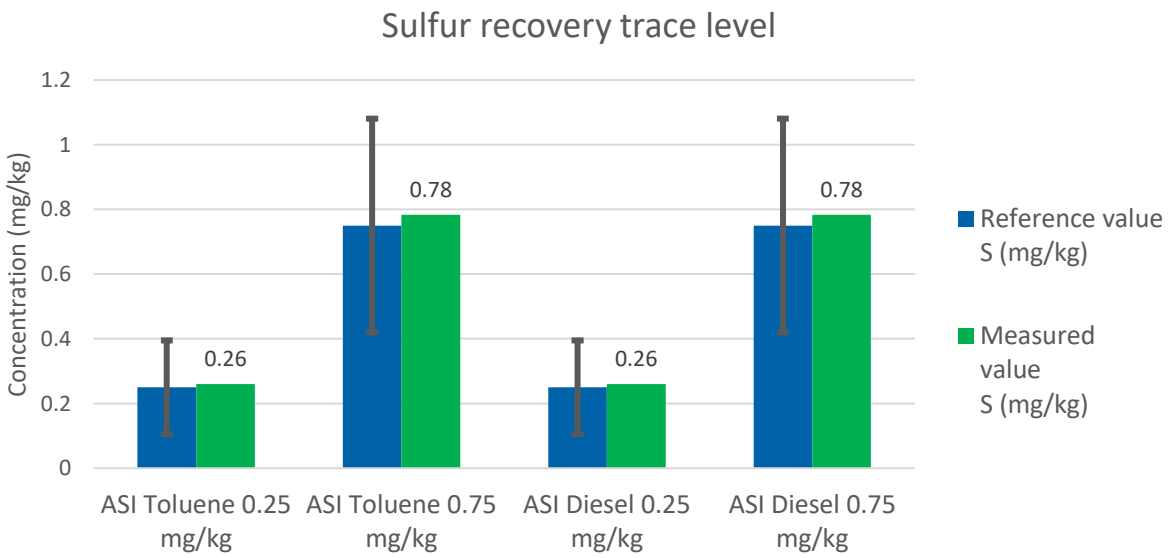
Sulfur Analysis – Trace Level





ASI SRM	Toluene 0.25	Diesel 0.75
Matrix	Toluene	Diesel
Sulfur mg/kg ASI	0.25 (± 0.14)	0.75 (± 0.33)
Sulfur mg/kg Measured	0.26	0.78
Observed Difference mg/kg	0.01	0.03
Within ASI uncertainty limits	Yes	Yes

Comparison of ASI reference samples

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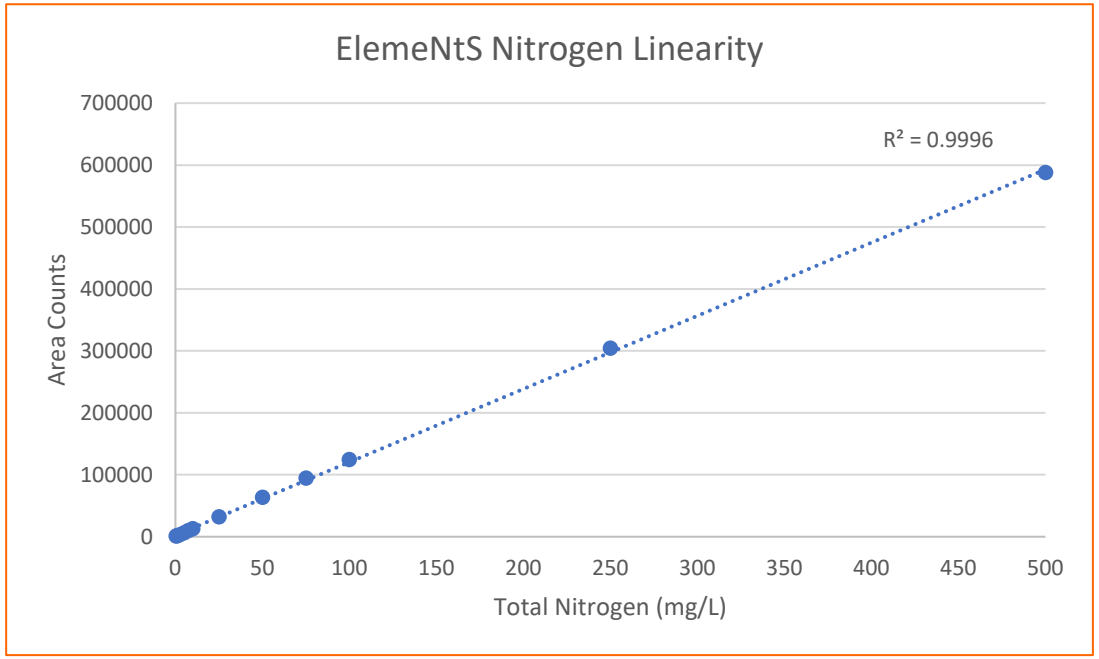
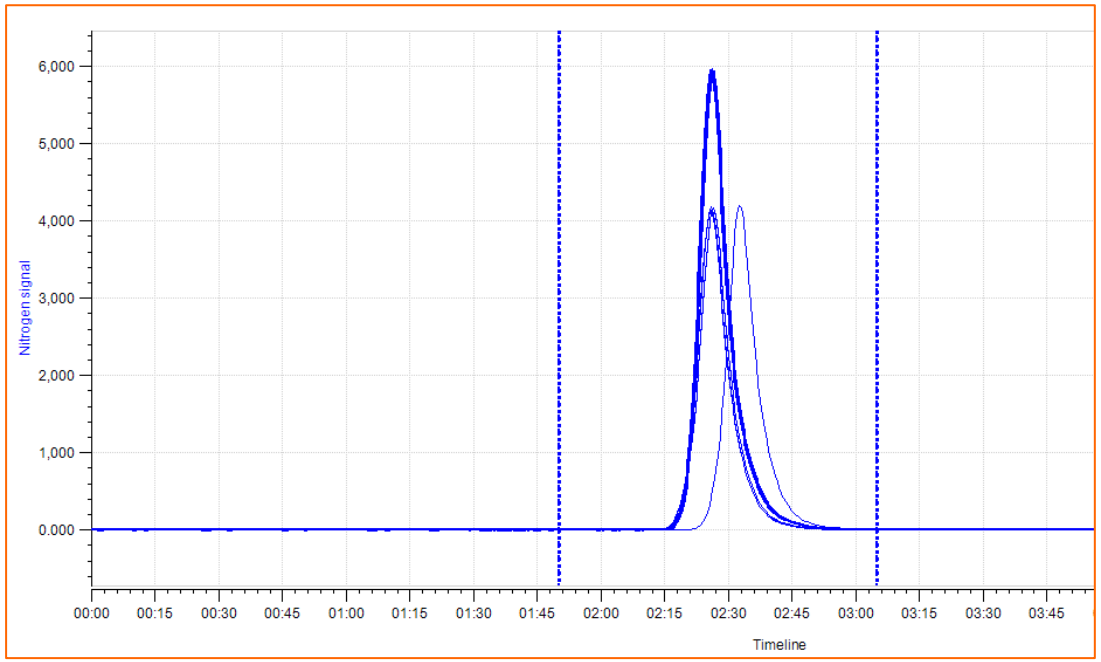
Nitrogen Analysis

ElemeNtS and **NSure** outperform the method requirements for the analysis of Total Nitrogen

- Excellent **Linear** detector response up to 3 decades
- Excellent **Precision** and **Accuracy** validated using certified reference materials
- Great **Sensitivity** in the ppb range



Typical Nitrogen Calibration 0.5 – 500 mg/L



Overlay SRM 735 and SRM 737 signal (n=5)

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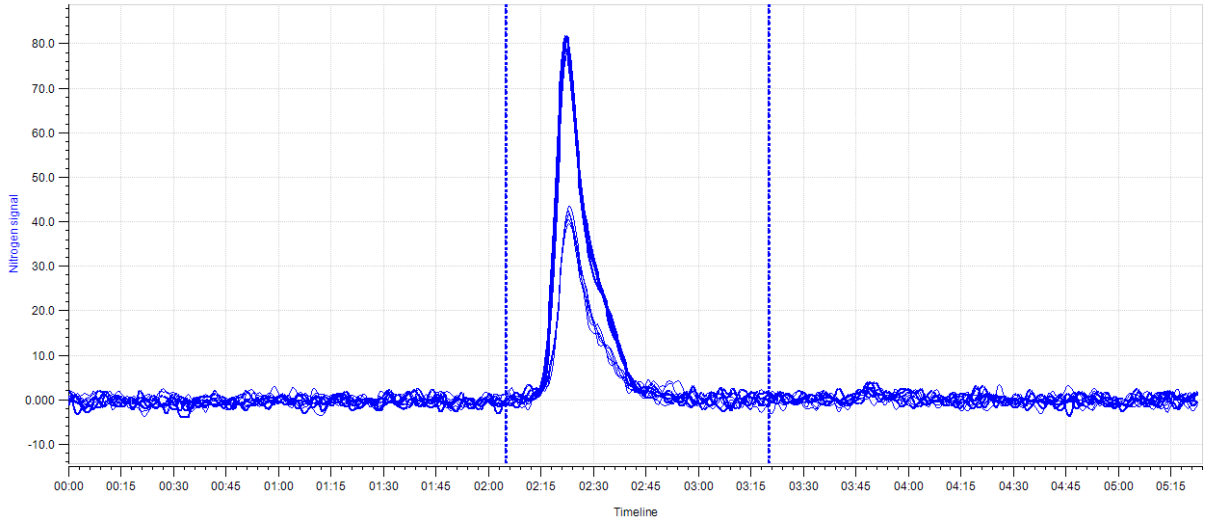
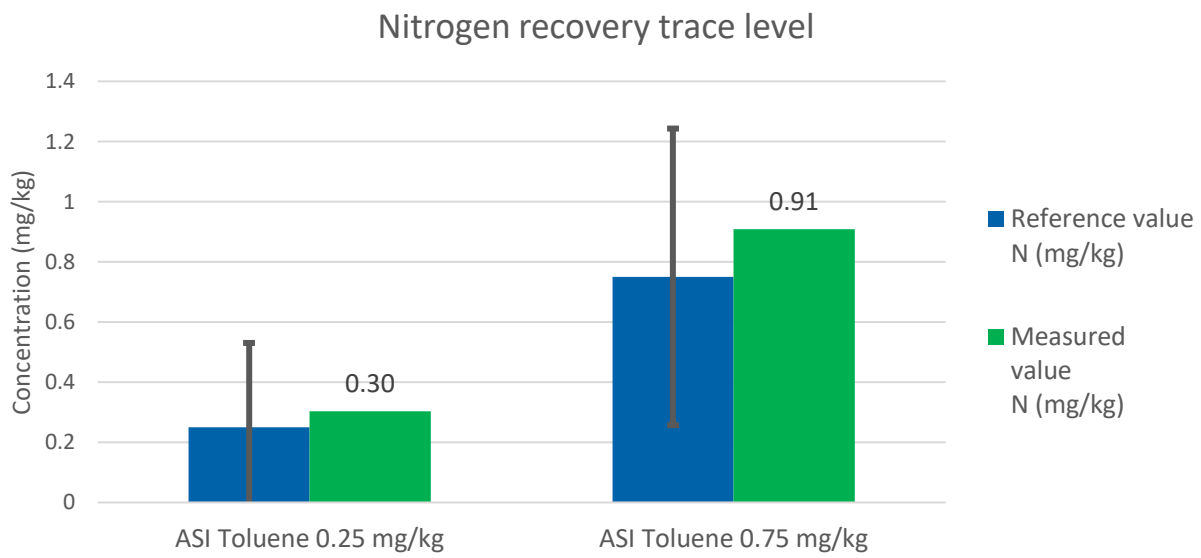
Nitrogen Analysis – Trace Level





ASI SRM	Toluene 0.25	Toluene 0.75
Matrix	Toluene	Toluene
Sulfur mg/kg ASI	0.25 (± 0.28)	0.75 (± 0.49)
Sulfur mg/kg Measured	0.30	0.91
Observed Difference mg/kg	0.05	0.16
Within ASTM uncertainty limits	Yes	Yes

Comparison of ASI reference samples

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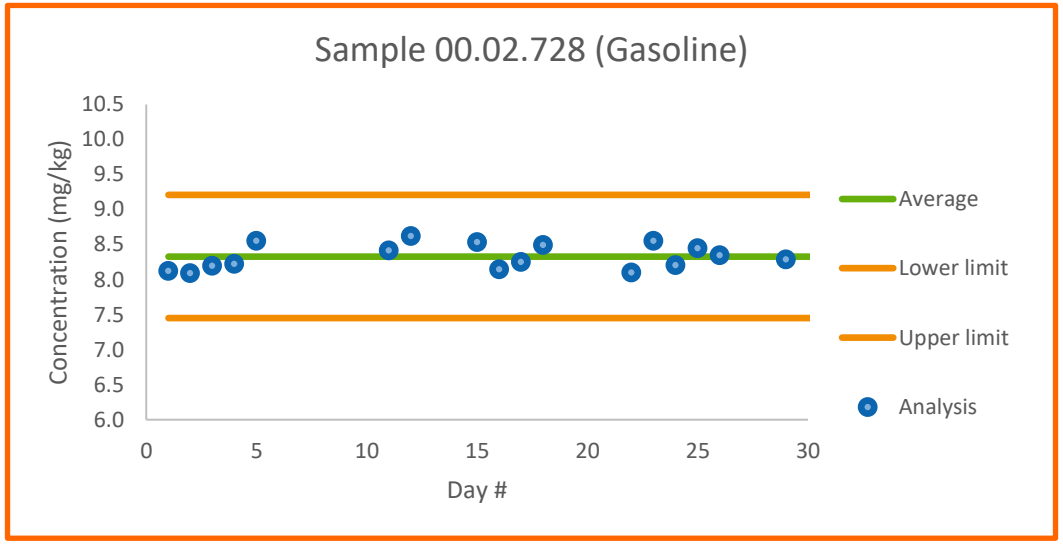
Summary

Value Proposition

- The **ANTEK** portfolio ensures an **excellent correlation** between your laboratory and process analysis
- The only solution for **ppb** level control of sulfur and/or nitrogen **in both laboratory and process**
- Long term **Stability** reduces calibration frequency (meeting TIER III requirements)
- The available "**Nitrogen Interference kit**" ensures accurate analysis of **diesel, doped with cetane improver,** on the ElemeNtS
- Ability to run a range of low ppb up to percent level with a **Single Analyzer**
- **No Interference** from oxygen containing components.



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Value Proposition

ANTEK guarantees:

- **Factory Tuned**, Calibrated & Validated systems including documented method
- **Start-Up Kit included** for fast commissioning of **ElemeNtS**
  - Septa, Syringes, Vials, Gas Filters, HC Calibration set, Test Samples etc.
- **12-Month Standard Warranty**
  - Additional warranty possible
  - On-line remote Support
  - Optional Factory Acceptance Test for **ElemeNtS**
  - Standard FAT for **NSure**

ANTEK® by PAC

Thank you!

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