WEBINAR 2021

Reducing Hazardous Elements in Automotive Fuels and Monitor the Success with XRF

Kai Behrens and Frank Portala

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Reducing Hazardous Elements in Automotive Fuels and Monitor the Success with XRF

Kai Behrens, Head of XRF Product Management, Karlsruhe, Germany

Ph D of Analytical Chemistry, Hamburg

2001 Method Development Bruker AXS

Now Head of Product Management XRF

Karlsruhe, Germany

Frank Portala, Product Manager XRF, Karlsruhe, Germany

Chemical Engineer (Dipl. FH)

2012 Product Management Bruker AXS

Product Management XRF

Karlsruhe, Germany

Outline

Oil Price & Economy & Environment & Future

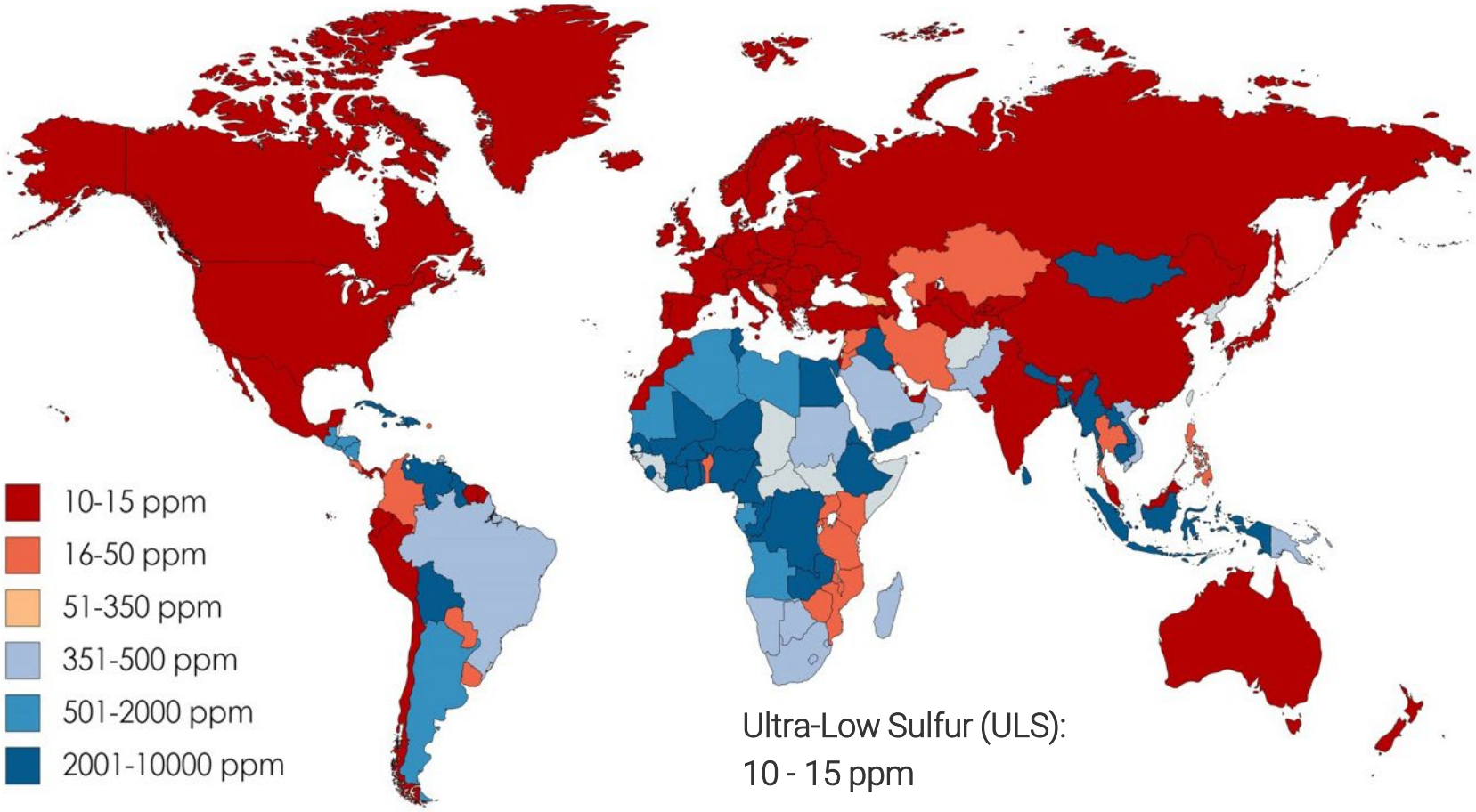
The economy has been driven over more than 100 years by the oil business
Dramatic changes are reasons for crisis, but prices are also good indicators for wealth and growth

- Oil was the motor of economic growth over the past 1oo years
  - It has fueled human development, economic growth, nations and regions
- Oil is the game changer for nations and their global role
- Extensive use of oil in combustion (energy, heating, traffic) caused
  - Environmental impact
  - One of the driver of climate change
- Reduction of hazadrous elements (S, Cl, HM) will have enormous positive impact
- Oils will stay important: For chemistry (Polymers, reagants) but maybe less in mobility

Sulfur Limits for On-Road Diesel, 2020

Euro VI Sulfur

- To prevent from extensive SO_x emissions
- Sulfur in automotive fuels are globally dramatically reduced from % in crude to ppm in fuels
- Future regulation for ship fuel, heating oils, etc.



Ultra-Low Sulfur (ULS):
10 - 15 ppm

Detailed information on limits and regulations:
www.stratasadvisors.com.

Oil Refinery Products

Crude Oil

20°	$C_1 - C_4$	Gas (for PE, PP)
70°	$C_5 - C_9$	Naphtha (Chemicals)
120°	$C_5 - C_{10}$	Gasoline
170°	$C_{10} - C_{16}$	Kerosene, Paraffin
270°	$C_{14} - C_{20}$	Diesel
	$C_{20} - C_{50}$	Lubricating Oil
600°	$C_{20} - C_{70}$	Fuel Oil (Marine, Heating)
	$> C_{70}$	Residue (Bitumen, Petcoke)




Petrochemical Applications
Refineries

Refineries:

- Monitoring **sulfur** content from **crude oil** feedstock and cracking products to final **Ultra-Low Sulfur (ULS)** levels in **automotive fuels**
- Monitoring important elements in refinery processes such as
  Ni, V, and Fe, Si, Cl,...

Downstream sector:

- **S** analysis along the downstream supply chain at **tank terminals**, storage tanks, **depots**, pipelines, petrol stations, custom control at harbors, and **service** and **inspection labs**

Sulfur and Ultra-Low Sulfur (ULS) in Petroleum Products

WDXRF norms:

- ASTM D2622 (3 ppm – 4.6%)
- ISO 20884 (5 – 500 ppm)

EDXRF norms:

- ASTM D7220 (3 – 942 ppm)
- ISO 13032 (8 – 50 ppm)
- ASTM D4294 (16 ppm – 5 %)
- ISO 20847 (30 – 500 ppm)
- ISO 8754 (300 ppm – 5 %)

How does current Petrochemical Element Analysis often looks like?

Atomic Absorption Spectrometry (AAS)

- Sample must be prepared/diluted
- Requires daily instrument calibration
- Requires gases for flame or graphite tubes
- Usually, single element analysis

Inductively Coupled Plasma Spectrometry (ICP-OES)

- Similar to AAS
- Requires expensive Argon gas for plasma
- Requires adjustment of plasma gas conditions

UV/VIS Spectroscopy (UV)

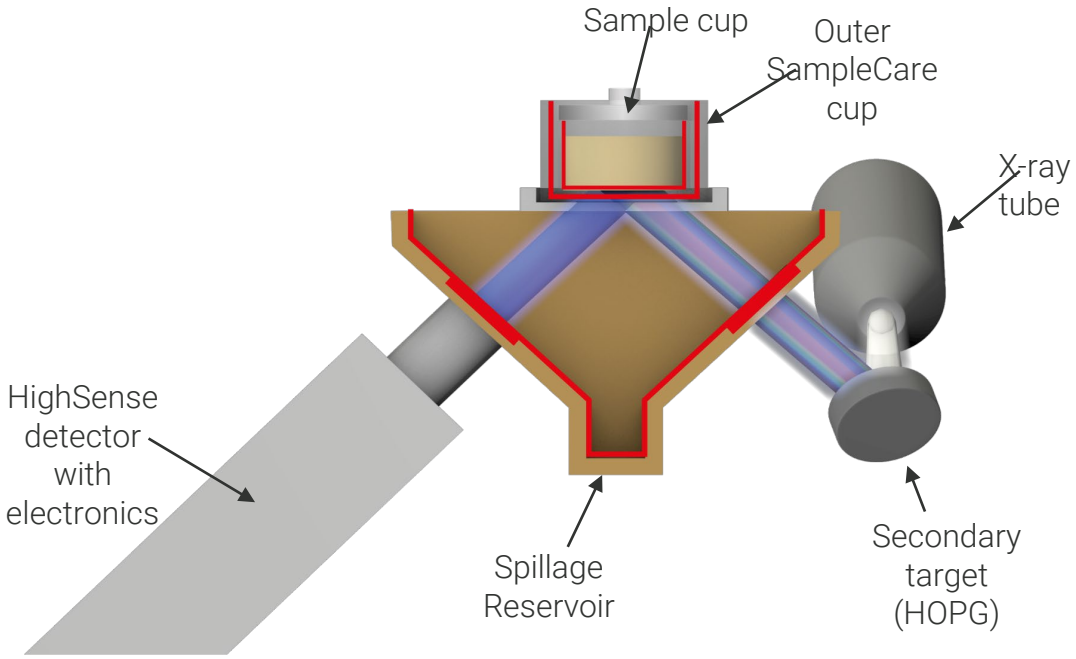
- Requires reagents for UV reaction

Sample Preparation in XRF
Easy and straight forward

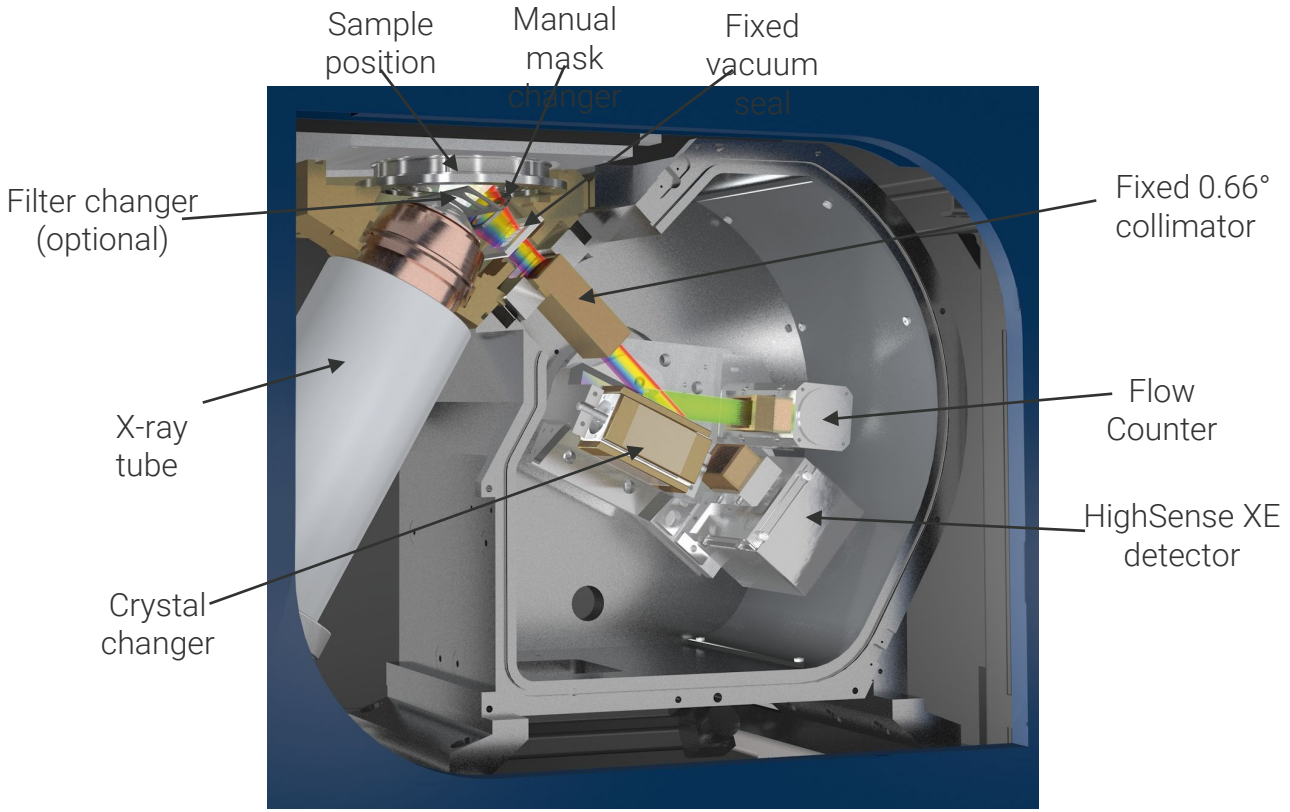
- First step: **Prepare the sample cup**
- Second step: **Fill the sample cup**
- Place the cup on the balance
- Fill with approx. 7 g of sample
- Third step: **Load the sample**
- Place the cup in the chamber of the instrument
- Done! **No dilution, no digestion!**
- **Low costs of ownership with standard liquid cups!**

Energy-Dispersive XRF (EDXRF) vs. Wavelength-Dispersive XRF (WDXRF)

EDXRF



WDXRF



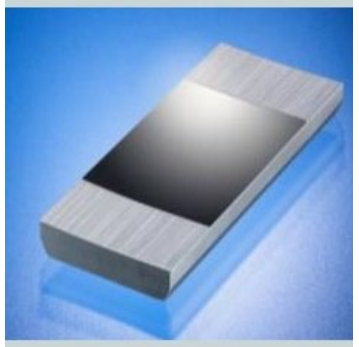
X-ray fluorescence analysis (XRF)
The Comparison of Wavelength and Energy Dispersive Spectrometers

EDX

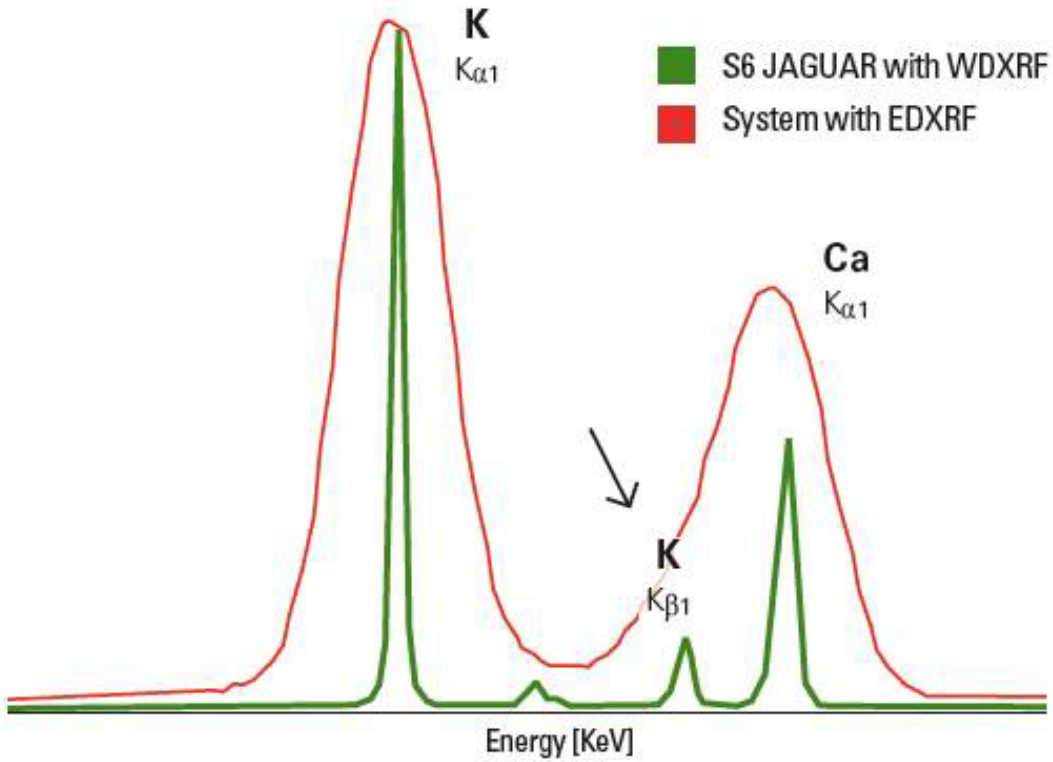
- Mechanical simplicity
- Cheaper
- Sensitivities: down to the ppm level
- Easy handling
- Smaller, “can be brought to the sample”

WDX

- High precision mechanics
- Higher capital
- Precision: <0.05%
- Higher resolution
- Sensitivities: down to the ppm level, but roughly one to two orders more sensitive
- Very fast analysis
- Highest sample throughput




S6 JAGUAR
HighSense™ Goniometer: High Resolution



- The S6 JAGUAR with WDXRF HighSense Goniometer excels
- ED based systems in resolution and analytical precision
  - Better peak to background signal ratio
  - Higher intensity (signal in left picture is scaled)
  - Better separation of mneighboring signals

S6 JAGUAR- Benchtop WDXRF
High Performance Benchtop WDXRF

Configurable from single element analyzer for S to multi-purpose unit for the periodic table

All-new technology and software:

- Long lifetime X-ray tube
- Compact goniometer with high precision gears and closely coupled X-ray beam path
- Optimized analyzer crystals for the entire element range and special applications
- HighSense detection with 2 Mcps countrate
- HighSense XE detector for medium and heavy elements
- SPECTRA.Elements analytical SW
- SMART-QUANT WD with new FP algorythms

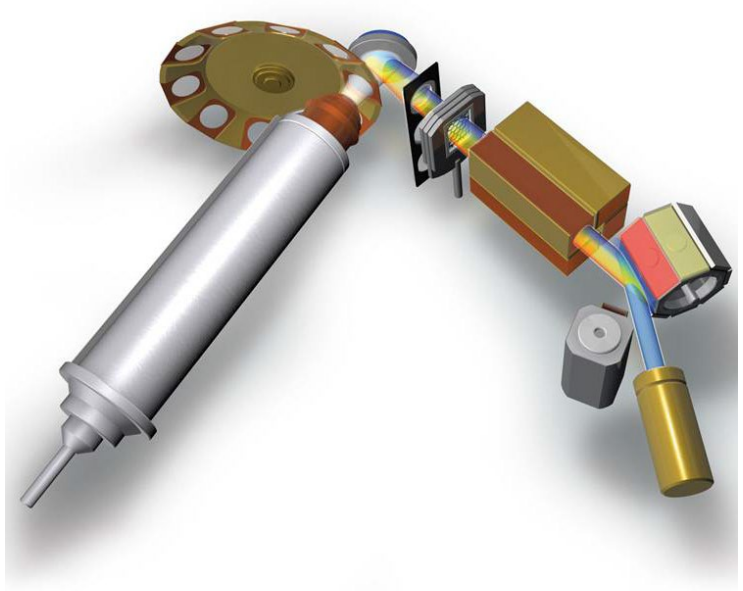
S6 JAGUAR Benchtop WDXRF

400 W excitation

Multi Purpose Sequential WDXRF Spectrometer S8 TIGER for the central lab

Analytical flexibility and high performance for sub-ppm traces

- 4 kW excitation
  20 – 60 kV
- 5 – 170 mA
- 10 beam filters
- 4 collimators
- 8 crystals
- 2 detectors



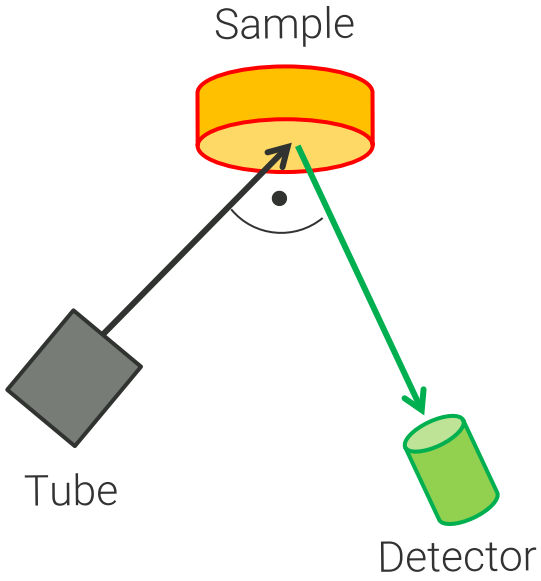
S8 TIGER WDXRF Beam path

Floorstanding WDXRF S8 TIGER

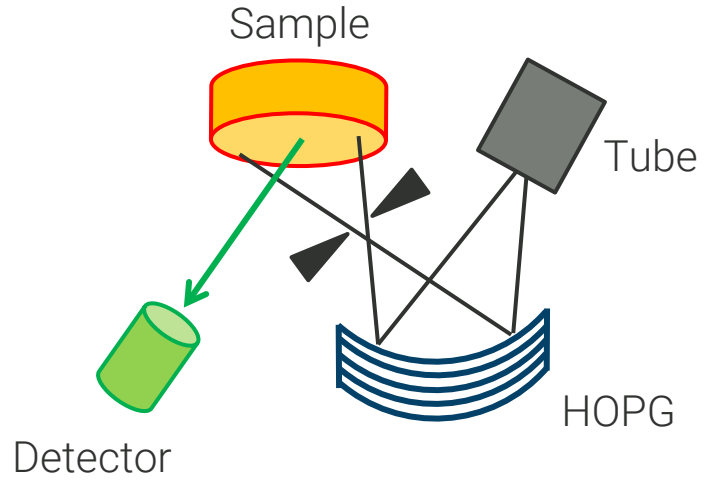
With 1, 3 or 4 kW

EDXRF Excitation Techniques
Direct Excitation vs. Polarized Excitation

Direct excitation



S2 POLAR



Direct excitation:

- Leads to very high intensity
- But also to higher background intensity

Polarized excitation:

- Reduced background due to polarization
- Improved signal to background ratio (better LLD)

Petrochemical Standards (1)
Ultra-Low Sulfur (ULS) Range

	ASTM D2622	ISO 20884	ASTM D7220	ASTM D5453
Applied technique	WDXRF	WDXRF	Monochromatic EDXRF	UV
S conc. range	3 ppm - 4.6 %	5 - 500 ppm	3 - 942 ppm	1 - 1000 ppm
Calibration ranges	0 - 1000 ppm 0.1 - 1.0 % 1.0 - 5.0 %	0 - 60 ppm 60 - 500 ppm	0 - 50 ppm 50 - 1000 ppm	0 - 10 ppm 5 - 100 ppm 100 - 1000 ppm
Scope …	Petroleum products, diesel, gasoline, jet fuel, residual oil, lubricating base oil, crude oil, biodiesel	Automotive fuels, diesel, gasoline, biodiesel	Automotive fuels, heating and jet fuels, including biodiesel blends	Total sulfur in light hydrocarbons, spark ignition engine fuel, diesel, engine oil
Bruker norm compliance	S6 JAGUAR, S8 TIGER	S6 JAGUAR, S8 TIGER	S2 POLAR	

Petrochemical Standards (2)
Low Sulfur Range

	ISO 13032	ASTM D6334	ASTM D4294	ISO 20887	ISO 8754
Applied technique	EDXRF	WDXRF	EDXRF	EDXRF	EDXRF
S conc. range	8 - 50 ppm	15 - 940 ppm	16 ppm - 5 %	30 - 500 ppm	300 ppm - 5 %
Calibration ranges	0 - 50 ppm	0 - 100 ppm 100 - 1000 ppm	0 - 1000 ppm 0.1 - 1.0 % 1.0 - 5.0 %	0 - 500 ppm	0.03 - 0.10 %, 0.10 - 0.5 %, 0.5 - 2.0 %, 2.0 - 5 %
Scope …	Automotive fuels, diesel, gasoline, biodiesel	Gasoline and gasoline-oxygenate blends	Petroleum products, diesel, gasoline, jet fuel, residual oil, lubricating base oil, crude oil, biodiesel	Sulfur content of gasolines, incl. those containing up to 2.7 % (m/m) oxygen, and diesel fuels, incl. those containing up to 5 % (V/V) fatty acid methyl ester	For petroleum products such as naphtha, unleaded motor gasolines, middle distillates, residual fuel oils, base lubricating oils and components
Bruker norm compliance	S2 POLAR	S6 JAGUAR, S8 TIGER	S2 POLAR, S2 PUMA	S2 POLAR, S2 PUMA	S2 POLAR, S2 PUMA

Petrochemical Standards (3)
Additonal Elements

	ASTM D8252	ASTM D4929	ASTM D5059	ASTM D6376
Applied technique	XRF	M-WDXRF, M-EDXRF, EDXRF	XRF	WDXRF
Application	Vanadium and Nickel in Crude and Residual Oil	Organic Chloride Content in Crude Oil	Pb in Gasoline, incl. Mn with 2020 update	Determination of Trace Metals in Petroleum Coke
Calibration ranges	1.9 - 50 ppm V 2.2 - 50 ppm Ni	0 - 100 ppm Cl	Part C: 0.0026 - 1.32 g Pb/L (= 2.6 ppm - 1320 ppm Pb); Part D (new): Mn in aviation gasoline 25 - 250 mg Mn/L	50 - 500 ppm Na 50 - 500 ppm Al 20 - 500 ppm Si 0.10 - 7.0 % S 20 - 500 ppm Ca 10 - 200 ppm Ti 20 - 2000 ppm V 10 - 200 ppm Mn 20 - 1000 ppm Fe 20 - 500 ppm Ni
Scope …	Crude and residual oil	Crude oil	Gasoline	Petroleum coke
Bruker norm compliance	S2 POLAR, S2 PUMA	S2 POLAR, S2 PUMA	S2 PUMA S6 JAGUAR	S6 JAGUAR, S8 TIGER

Low sulfur in automotive fuels
Analysis with XRF in refineries and downstream

- Most precise and close control of low levels possible by WDXRF
- Several calibrations for each matrix with ASTM D
- Internal standards (EN ISO) for just one method for all matrices
- Polarized EDXRF for smaller labs and downstream
- Enhanced analytical performance with lower COV compared to direct EDXRF
- Better handling of various matrices, e.g. biofuels, compared to FT-IR, AAS and other methods
- Atmospheric purge vs reduced pressure to enhance analytical performance and reliability for volatile samples

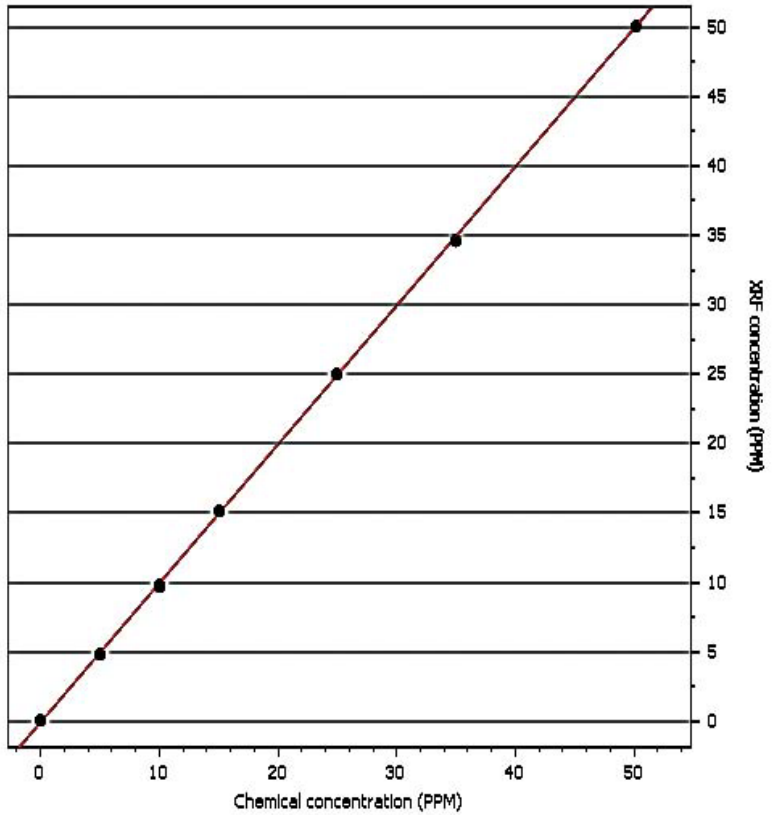
S2 POLAR
High Performance Benchtop EDXRF for Petro Market

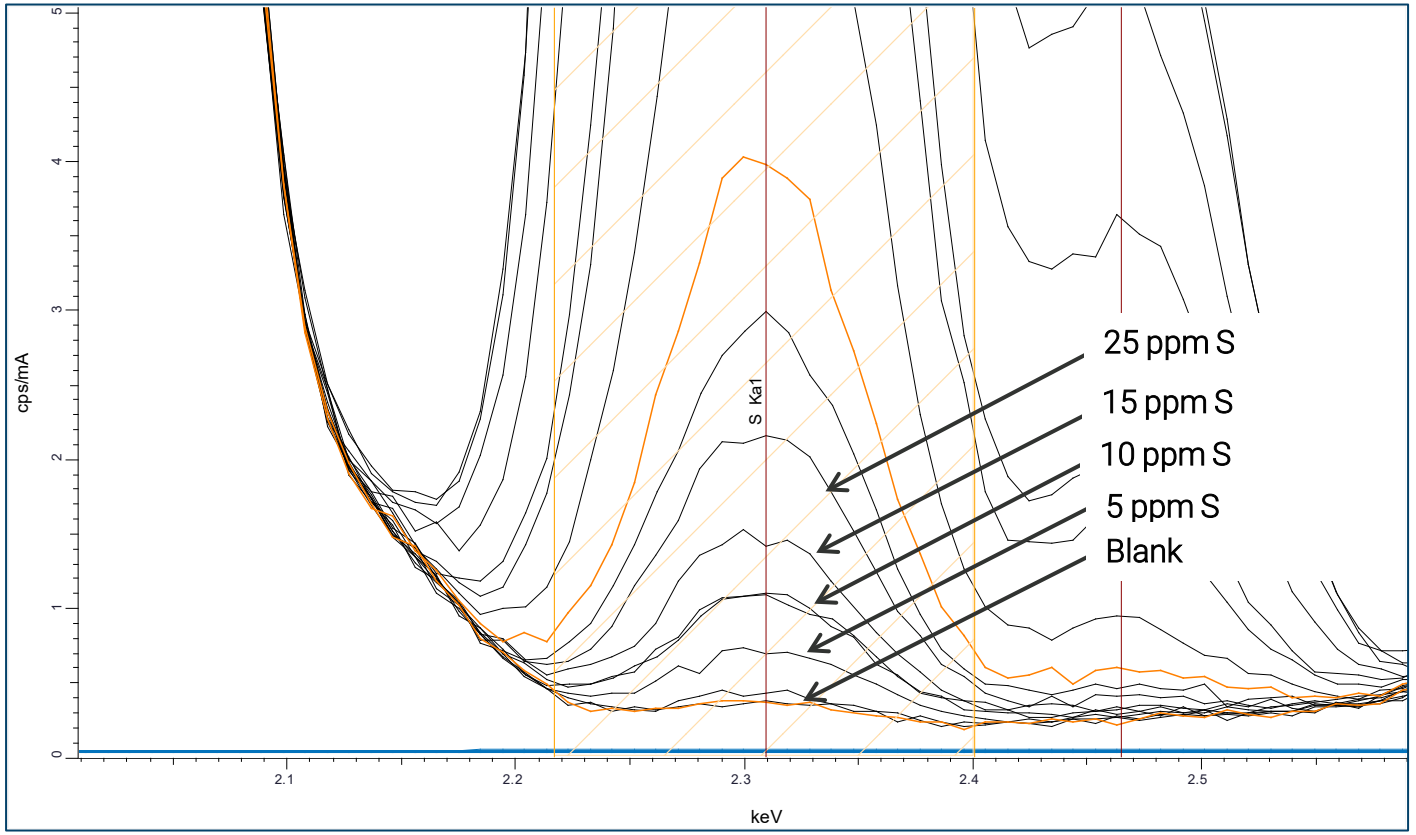
- Process control in the refinery
- Quality Control in downstream at tank farms or shipping stations

- Small size for small labs, low cost of ownership
- Quick sample preparation w/o any chemicals involved
- Ease-of-use w/ TouchControl for shift workers
- Robust technology w/ little maintenance
- One-time calibration
- Norm compliant, for various matrices

ASTM D7220 – Ultra-Low Sulfur in Gasoline S2 POLAR

- Excellent calibration curve for ultra-low sulfur in the range of 0 to 50 ppm with a clear separation of different sulfur levels





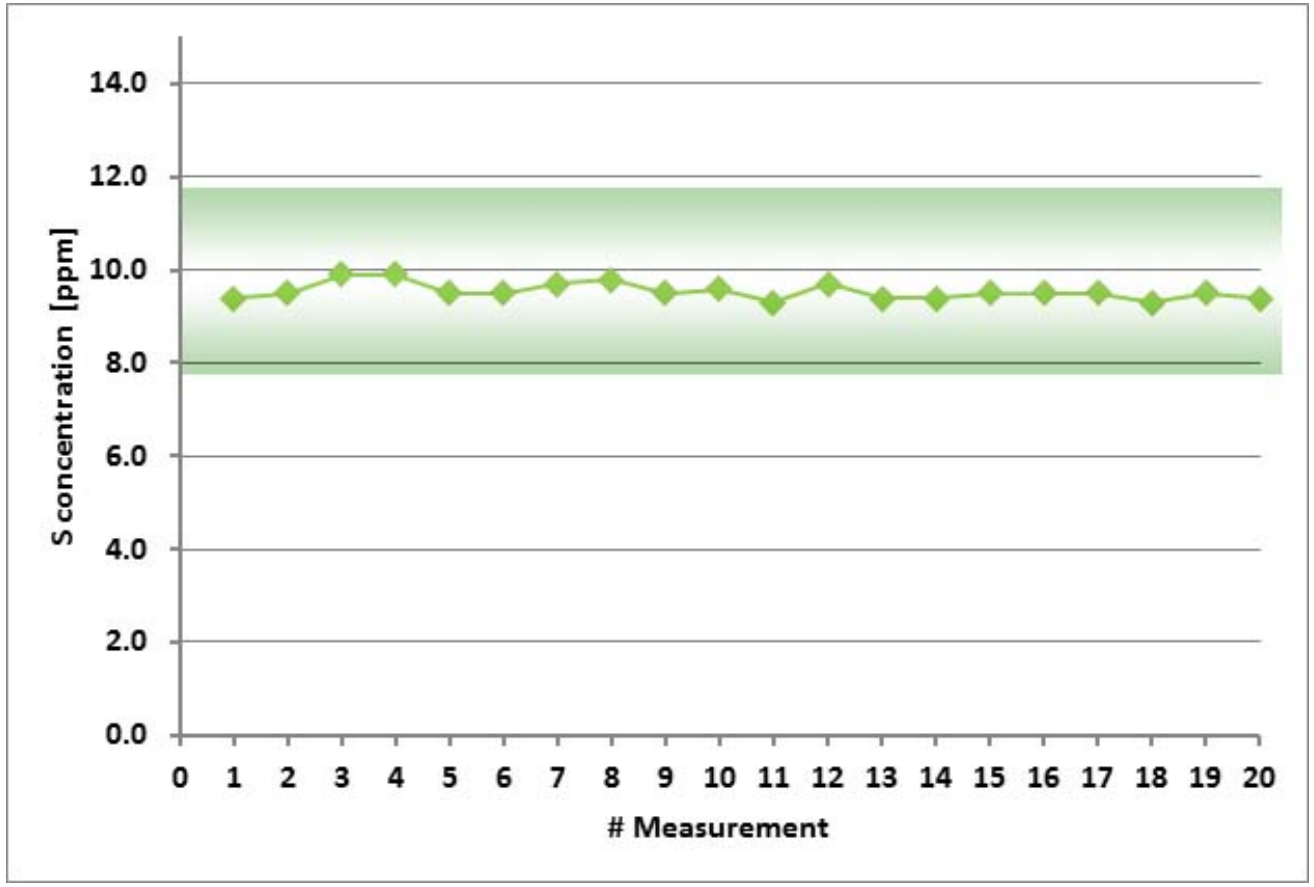
Ultra-Low Sulfur (ULS) – Repeatability S2 POLAR

- 10 ppm S gasoline sample
- Excellent repeatability for very low sulfur concentrations
- Norm-compliant with ASTM D7220
- Scope of ASTM D7220: 3 to 942 ppm S in automotive fuels
- LLD: 0.7 ppm (300 s, with SampleCare™ cup)

# Measurement	S [ppm]
1	10.1
2	10.0
3	10.2
4	10.9
5	10.4
6	10.4
7	10.3
8	10.4
9	10.1
10	10.2
Average	10.3
Std.Dev.	0.24
Rel.Std.Dev.	2.34%

ASTM D7220 – Ultra-Low Sulfur in Gasoline S2 POLAR

- Gasoline sample (9.8 ppm S) with excellent repeatability at such low concentration level



✓ Passed

Accepted difference between 2 measurements: ±2.0 ppm S

ISO 13032
S2 POLAR

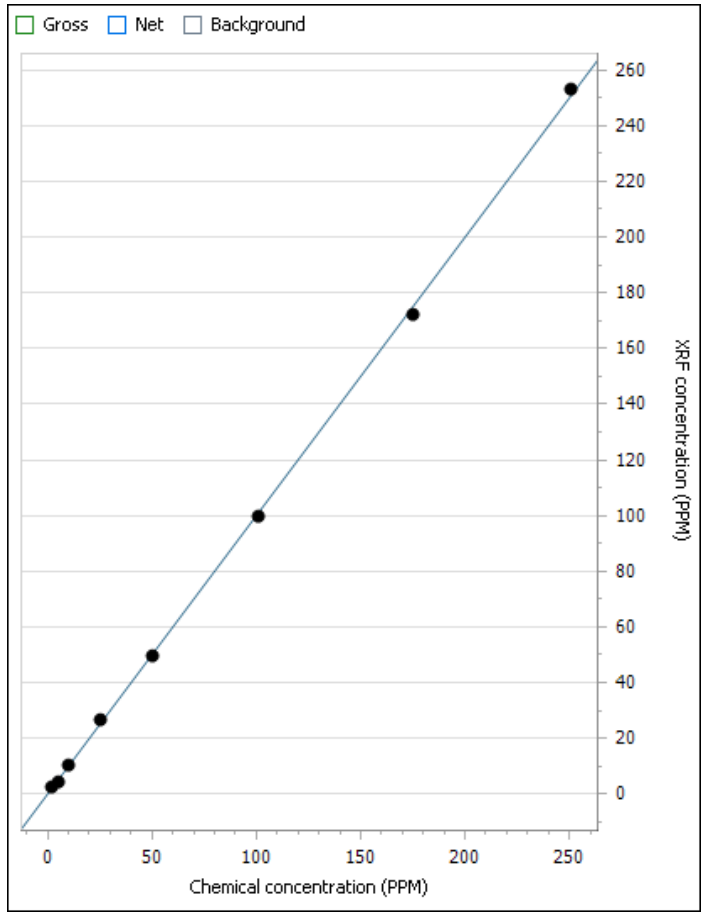
ISO 13032-12(2018)

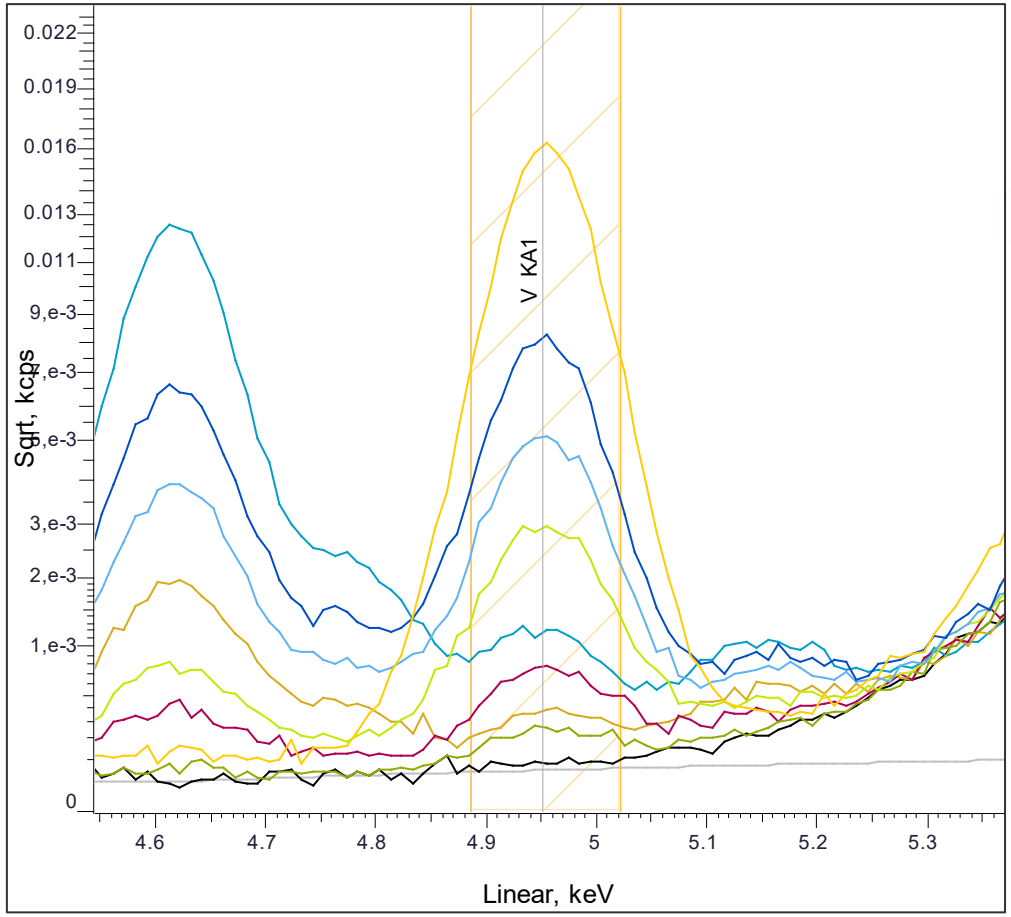
**Petroleum products –
Determination of low concentration of sulfur in automotive fuels –
Energy-dispersive X-ray fluorescence spectrometric
method (ISO 13032:2012)**

- Covers determination of low S in automotive fuels by EDXRF
- Scope: 8 ppm – 50 ppm S
- Duplicates are required
- Defined repeatability (r) and reproducibility (R) limits have to be fulfilled
- Defined limit for Signal to Background ratio for 10 ppm S sample

✓ Passed by S2 POLAR

ASTM D8252 - V in Crude Oil
S2 POLAR





Passed

Clear separation of different V levels, including low levels

ASTM D8252 - Repeatability QC Sample S2 POLAR

	Date	V [ppm]	Ni [ppm]	Fe ppm]
Rep 01	13.11.2020 16:09	48.4	47.7	50.0
Rep 02	13.11.2020 16:22	48.7	47.3	51.0
Rep 03	13.11.2020 16:31	48.0	49.2	50.4
Rep 04	13.11.2020 16:45	48.9	47.8	49.3
…	…	…	…	…
Rep 17	13.11.2020 18:59	48.5	49.3	51.2
Rep 18	13.11.2020 19:08	49.1	49.1	51.5
Rep 19	13.11.2020 19:17	48.7	46.8	50.5
Rep 20	13.11.2020 19:26	49.4	48.9	50.6
Mean value		**48.99**	**48.14**	**50.35**
Abs. Std. Dev.		**0.54**	**0.80**	**0.95**
Rel. Std. Dev. [%]		**1.10**	**1.67**	**1.89**
Cert. value		**50.0**	**50.0**	**50.0**

Excellent repeatability for all elements

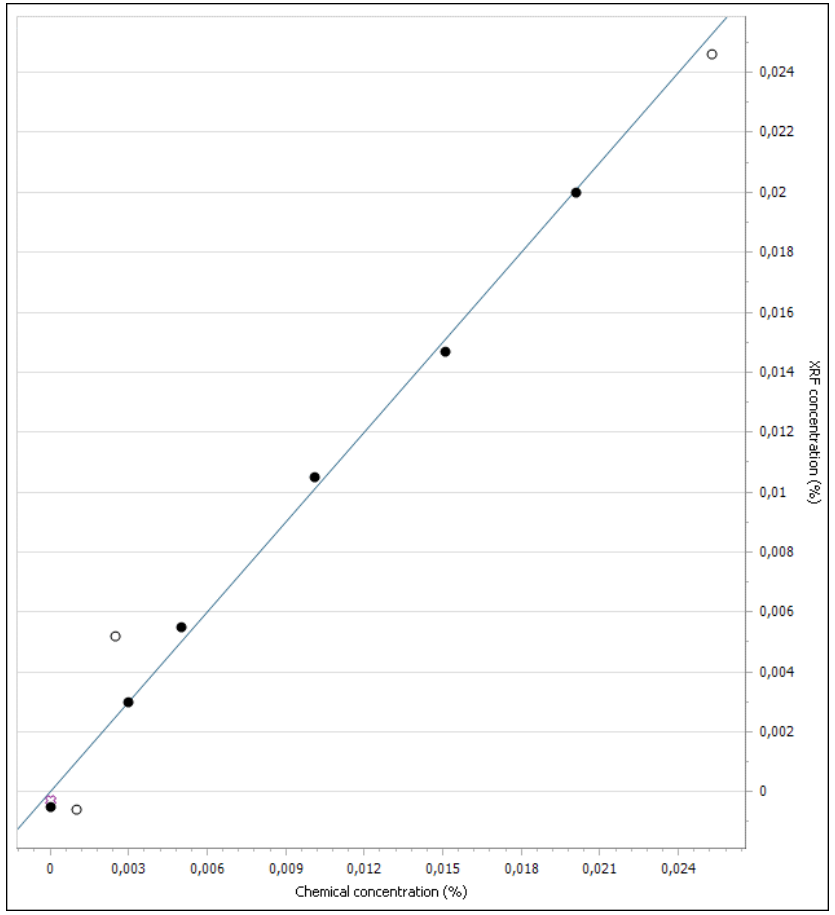
✓ Passed

Heavy Fuel Oil Application (HFO)
S2 POLAR

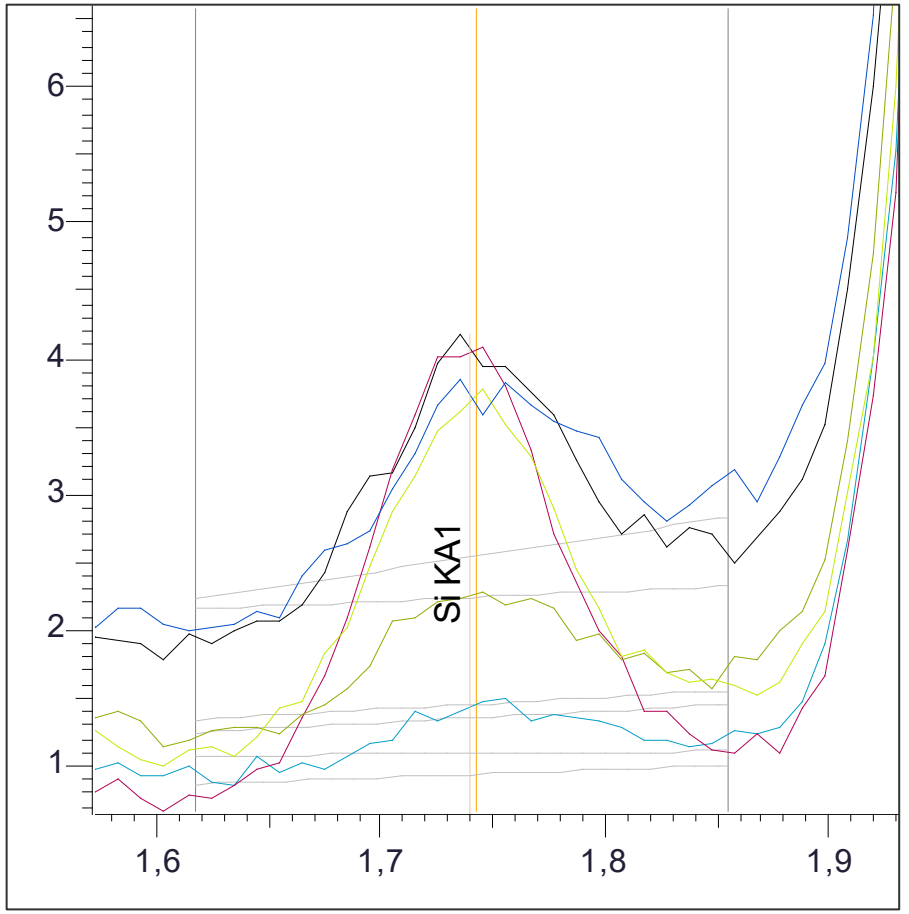
Std.	Ca [%]	Fe [%]	Ni [%]	P [%]	S [%]	Si [%]	V [%]	Zn [%]	CH2 [%]	Al [%]
Std 1	0.0010	0.0251	0.0050	0.0020	4.9997	0.0050	0.0075	0.0010	94.9500	0.0005
Std 2	0.0075	0.0100	0.0005	0.0005	1.9996	0.0101	0.0300	0.0002	97.9300	0.0100
Std 3	0.0100	0.0000	0.0000	0.0010	0.5063	0.0000	0.0354	0.0050	99.4400	0.0010
Std 4	0.0030	0.0051	0.0075	0.0050	3.9993	0.0253	0.0050	0.0040	95.9400	0.0025
Std 5	0.0040	0.0151	0.0101	0.0075	0.3000	0.0201	0.0000	0.0015	99.6300	0.0075
Std 6	0.0000	0.0075	0.0040	0.0101	1.0098	0.0030	0.0100	0.0075	98.9400	0.0050
Std 7	0.0050	0.0200	0.0020	0.0040	0.7254	0.0151	0.0010	0.0000	99.2100	0.0150
Std 8	0.0005	0.0010	0.0010	0.0000	0.1001	0.0010	0.0201	0.0020	99.8700	0.0000
Std 9	0.0020	0.0005	0.0150	0.0025	2.4997	0.0050	0.0005	0.0005	97.4700	0.0025
Std 10	0.0150	0.0025	0.0025	0.0015	2.9998	0.0025	0.0025	0.0010	96.9700	0.0050

Set of standards for HFO calibration, covering all key elements for refinery processes

Silicon in Heavy Fuel Oil (HFO)
S2 POLAR



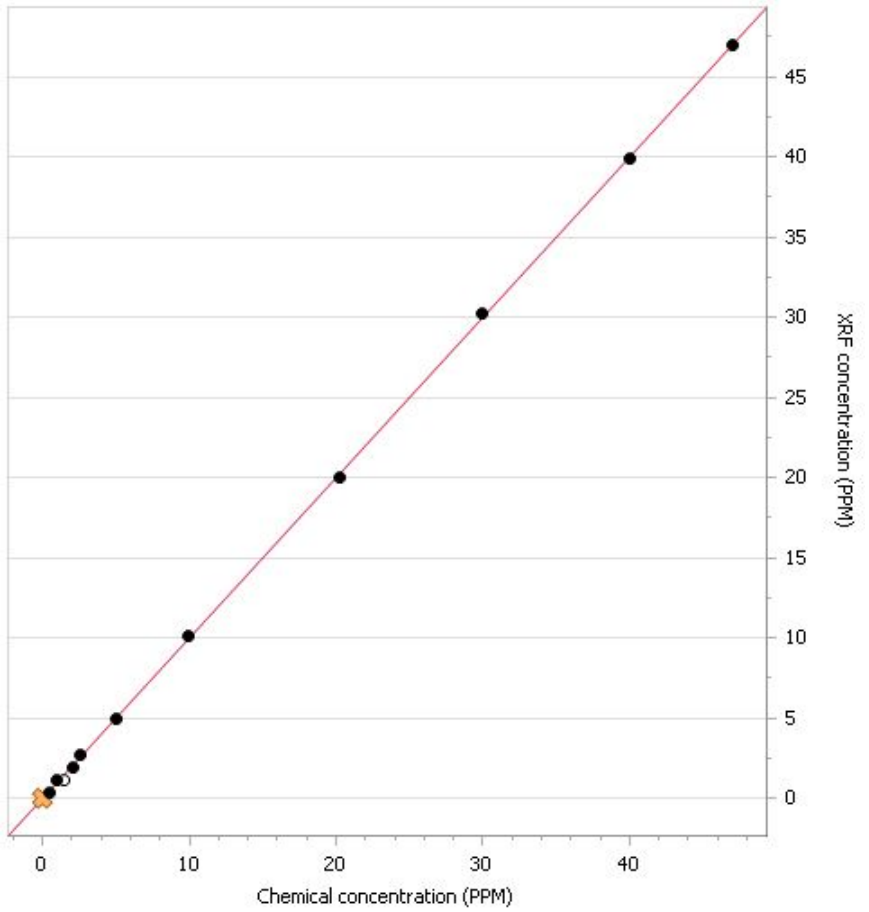
Si calibration between 0 – 250 ppm Si



Clear separation of low Si levels (0 – 250 ppm Si)

Chlorine in Crude Oil – ASTM D4929C
S2 POLAR

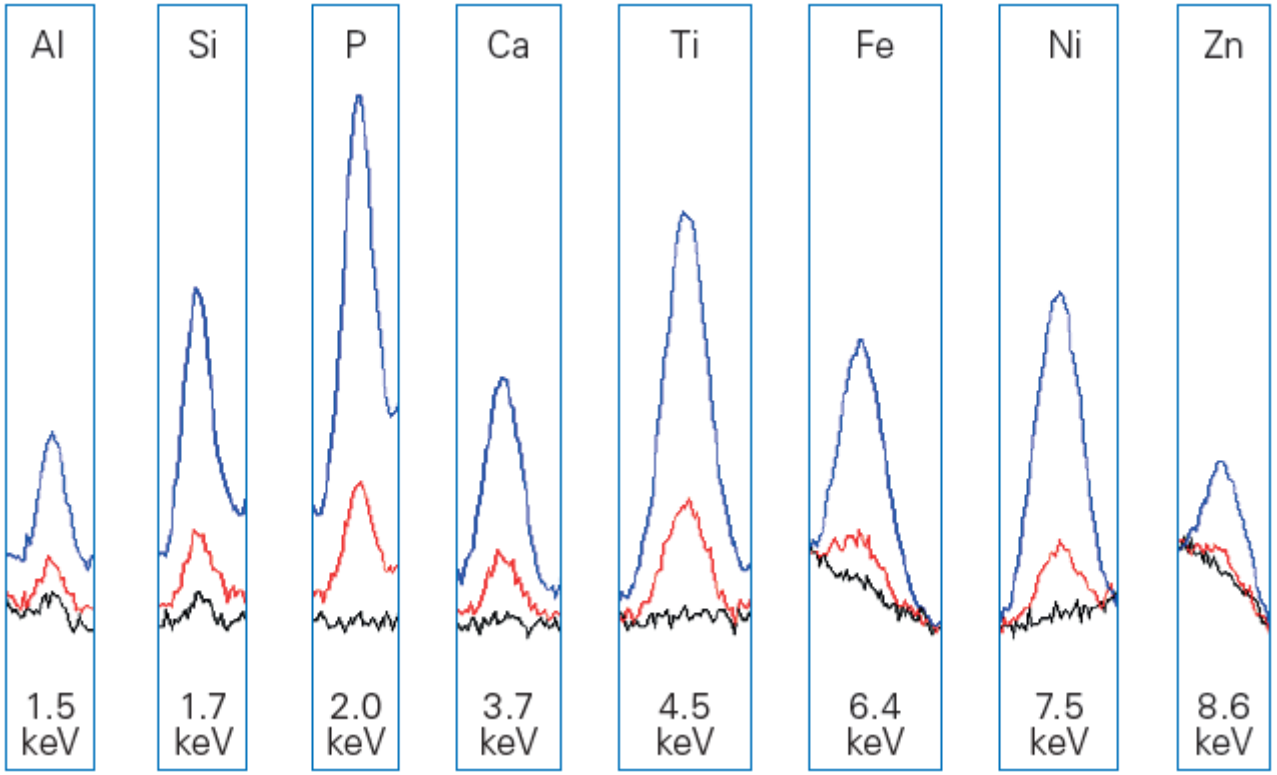
- Analysis of **low levels of organic chlorine** for corrosion monitoring and desalter control
- Concentration range: **1 to 100 ppm** Cl
- Norm-compliant with **ASTM D4929C**



Excellent accuracy also at low Cl concentrations

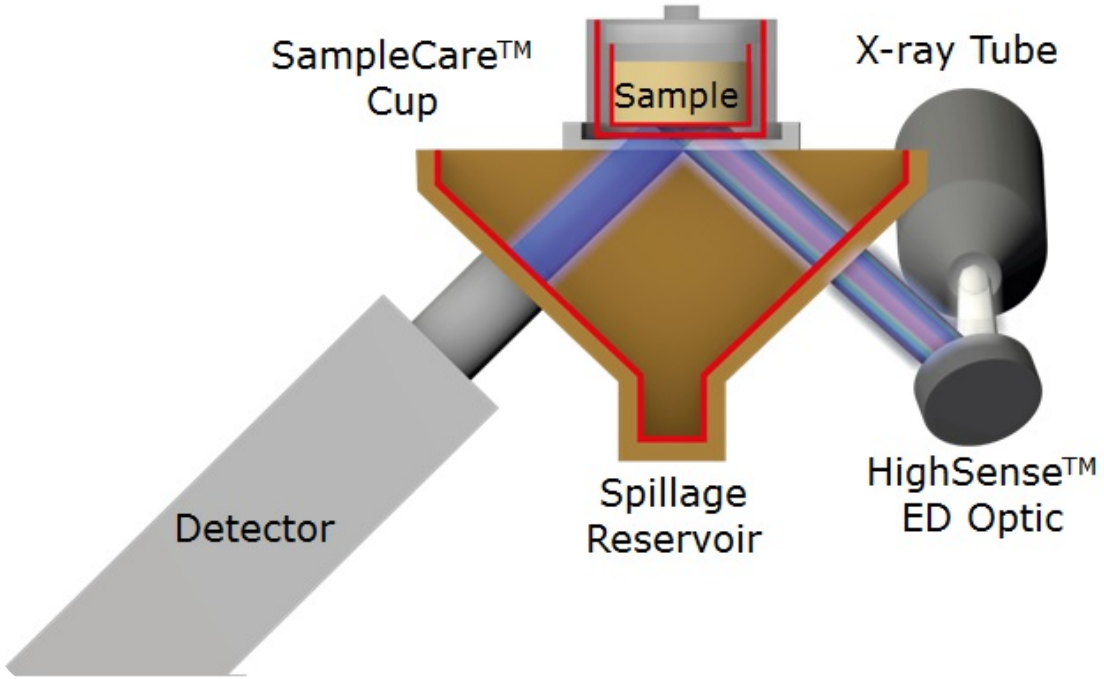
✓ Passed

Multi-element Capability
S2 POLAR



Selected elements of overlaid multi-element oil standards
(Black: blank sample, red: 10 ppm, blue: 100 ppm)

SampleCare™ Technology S2 POLAR



- SampleCare™ cup prevents leakages of liquid samples
- Protects important system components
- Measurement chamber with large spillage reservoir
- S2 POLAR **SampleCare™** Technology **guarantees** highest instrument **uptime**
- Important for high throughput industrial labs

Small Footprint
S2 POLAR

- Very small, compact footprint
- For space-saving analysis in labs
- Also important for on-site process control with limited space in refineries, tank terminals, depots
- Ready-to-analyze ‘One Button’ solutions, e.g.
- ASTM D7220, D4294, ISO 13032
- ASTM D8252, D4929C
- ASTM D7751, D6481

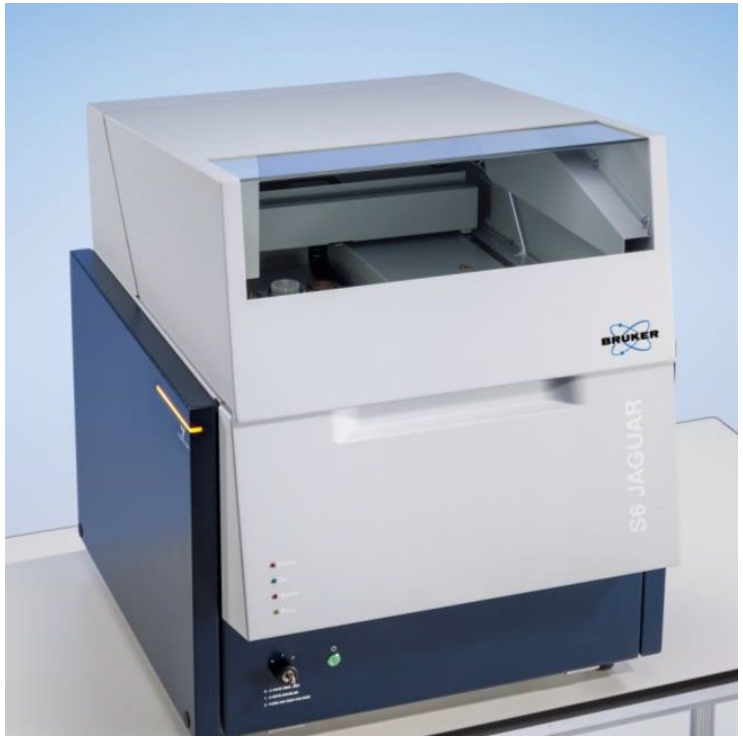
One instrument does it all for refineries:

From Ultra-Low Sulfur (ULS) in fuels to % in crudes

Norm-compliant to ASTM D7220, D4294, ISO 13032, 20847, 8754

ASTM D 2622 for Low Sulfur based on WDXRF

- WDXRF is defined as international standard, delivering best detection limit, robustness and precision
- But limited no of samples and/or applications doesn‘t justify budget for high power, floorstanding units
- Compact mid power instruments, like S6 JAGUAR can be configured from single element units to multi-purpose

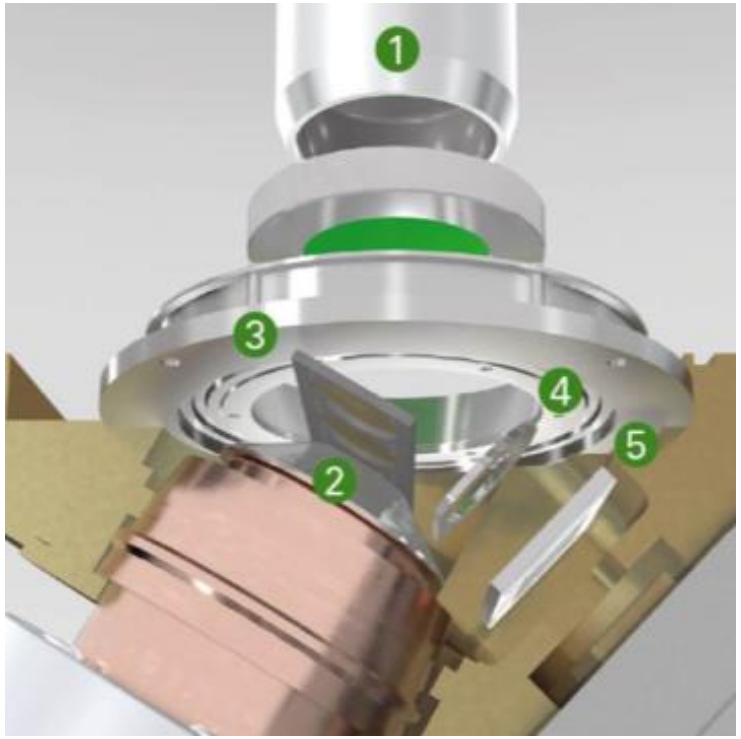


Unit w/ Autochanger for higher productivity

Single Loader for immediate analysis

S6 JAGUAR
SampleCare™: High Instrument Uptime & Low cost of operation

- High instrument uptime due to unique protection during loading and unloading
- Two contamination shields to protect tube window and goniometer
- Unique Vacuum Seal with high transmission window for goniometer protection
- Low helium consumption
  - Flushing of sample chamber only
  - Goniometer chamber remains in vacuum all the time



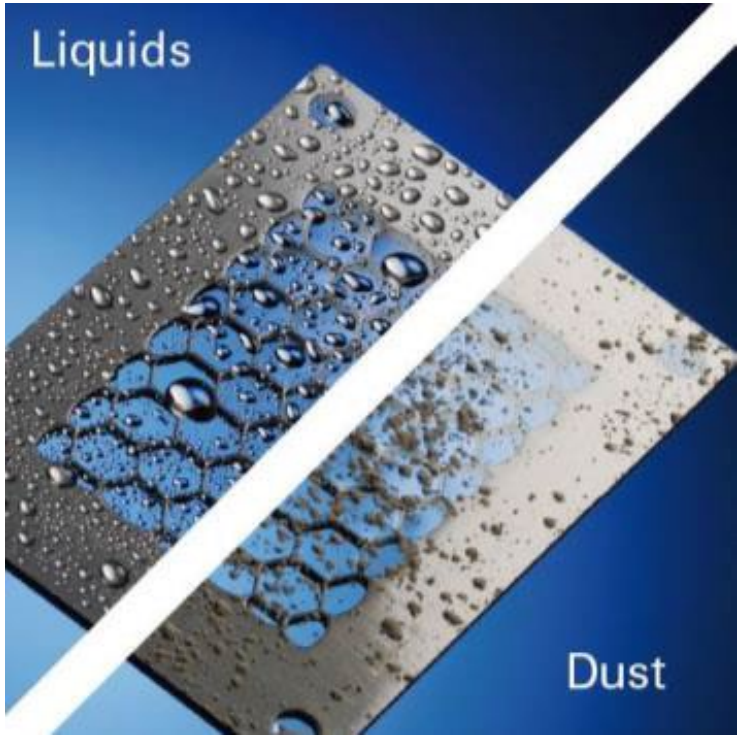
1 Grabber with automatic sample detection

2 Tube shield

3 Filter changer

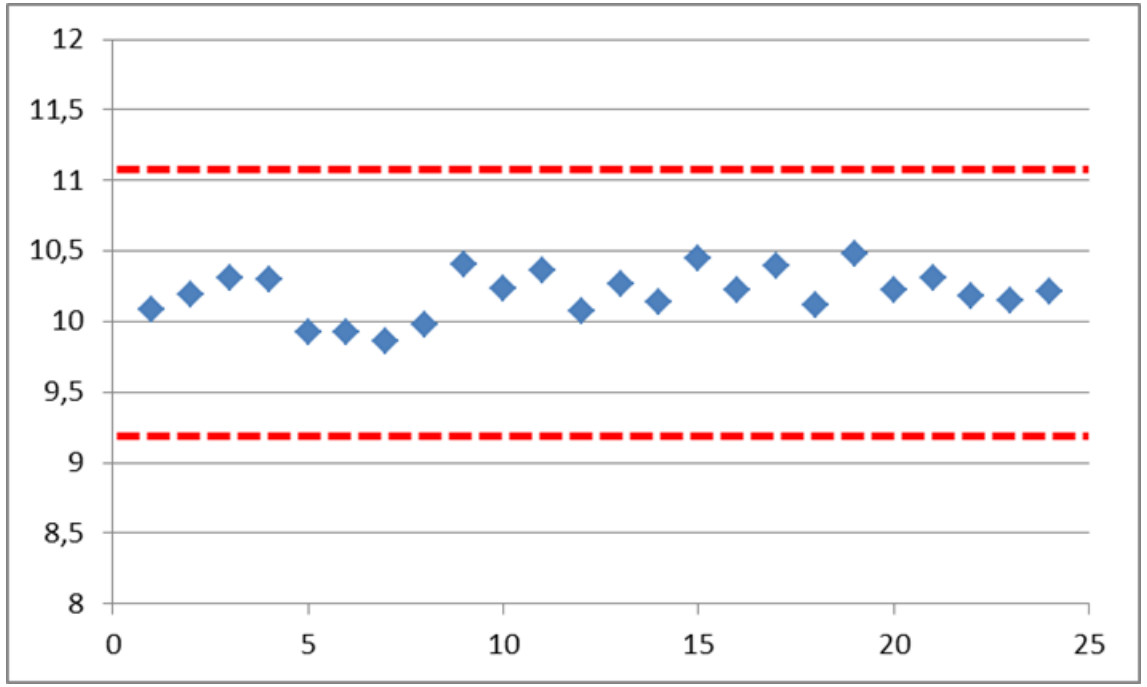
4 Mask holder

5 Vacuum seal



Unique High Transmission Vacuum Seal

S6 JAGUAR Performance
ASTM D 2622 - 10



- 25 fold repetition
- 200 s M.T. in total
  - **Manual** (30 (simple licensing) or 50 kV)
  - Vacuum
  - **Helium flushing**
  - **One** crystal **(Ge)**
  - **One** detector

- 10 ppm gasoline repro, better than enforced

S6 JAGUAR Performance
ASTM D 2622 - 10

Number	c S [ppm]	Differ [ppm]	Max allowed Diff [ppm]
# 1	10.09		
# 2	10.19	0.1	0.93
# 3	10.31	0.12	0.93
# 4	10.3	-0.01	0.93
…	…	…	…
# 22	10.31	0.09	0.93
# 23	10.18	-0.13	0.93
# 24	10.15	-0.03	0.93
# 25	10.21	0.06	0.93
Mean Value [ppm]	**10.20**		
Std Dev]ppm]	**0.16**		
RSD [ppm]	**1.61**		

- Max allowance between two consecutive measurements
  - 0.93 ppm
- Typical
  - 0.3 ppm max
- LLD 0.73 ppm

“Our S6 JAGUAR is optimally configured for doing ULS analysis in automotive fuels acc. to ASTM D 2622. The data quality is comparable to big WDXRF at lower cost of ownership. The radiation license procedure was easy due to the 30 kV option.”

S6 JAGUAR

- Sold to refineries and downstream for low S with preference on WD
- Multi-Instrument deals

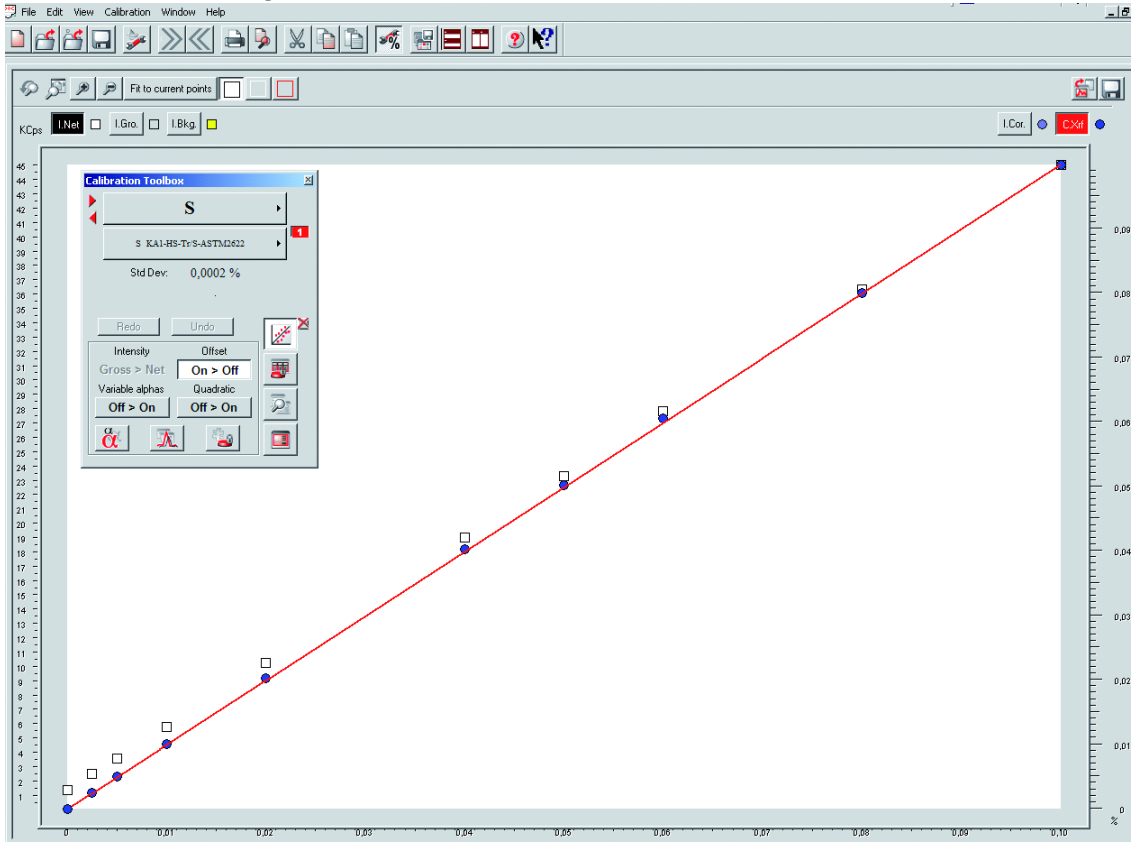
“The S6 JAGUAR WDXRF has become an indispensable tool in our QC lab. The quick analysis of our lubricating products acc. to ASTM D 2622 and D 6443 with low cost of operation is unique. We have recommended the instrument in our company globally”

Low sulfur in automotive fuels ASTM D 2622 with the S8 TIGER Series

- High sample load, multiple applications from fuels, oils, coke, catalysts,…
- Precise and close control of low levels possible by WDXRF
- Several calibrations for each matrix with ASTM D
- Internal standards (EN ISO) for just one method for all matrices
- Enhanced analytical performance with lower COV compared to EDXRF
- Better handling of various matrices, e.g. biofuels, compared to FT-IR, AAS and other methods
- Atmospheric purge vs reduced pressure to enhance analytical performance and reliability for volatile samples

S8 TIGER 4 kW
Maximum precision and throughput

Straight calibration curve based on CRM
Fit for every matrix



Best precision reduces cost for S removal in crude oil, production close to limit of 10 ppm

High power WDXRF S8 TIGER with 4 kW excitation power offers:

- Very low detection limits down to 0.2 ppm
- High sample throughput of more than 30 samples per hour
- Optimal precision with less than 1.5% variation at 10 ppm

- The better precision enables to reduce Sulfur to just below the limit, savings in refinery process

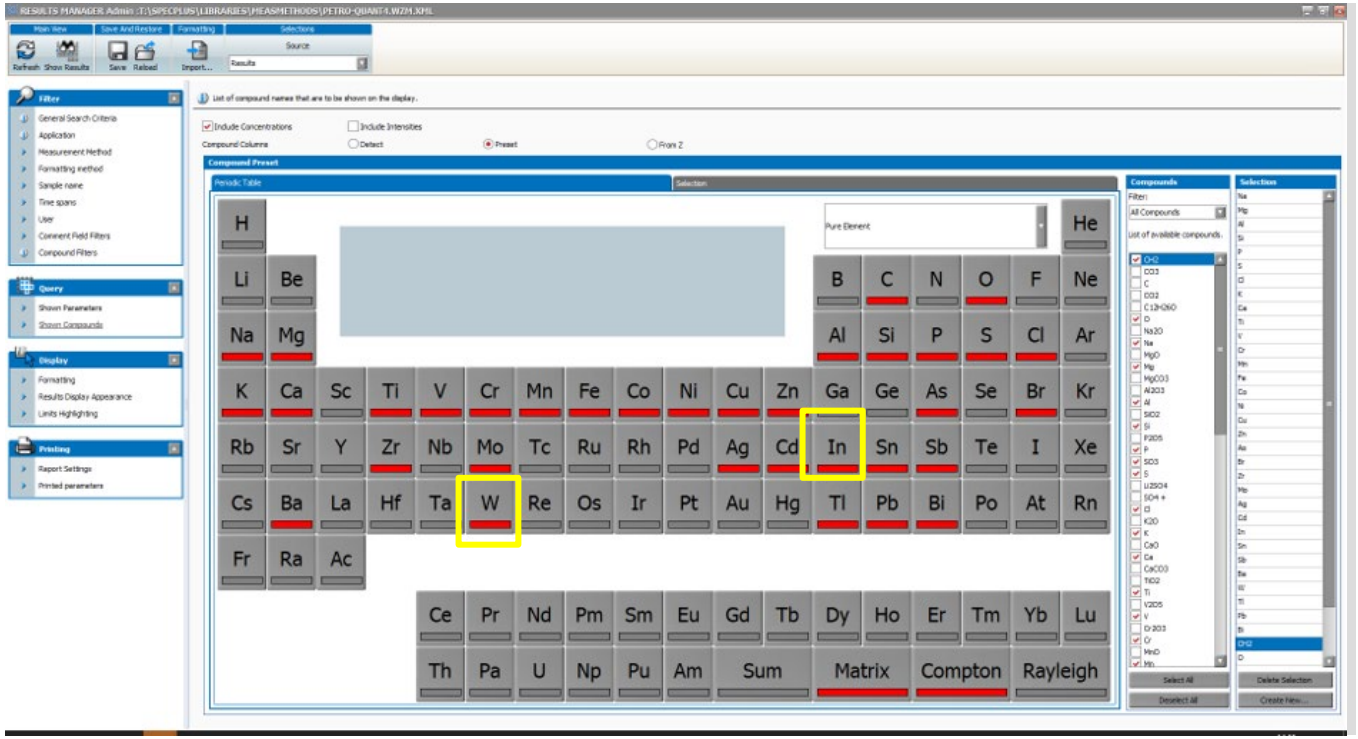
S8 TIGER News
XRF - Solutions for Industry and Research

Ready-To-Analyze Solutions for optimal Performance

- Factory Setup
- Quick start into Routine
- Ease-of-Use
- Best Results
- Bruker Expertise built in

PETRO-QUANT
Unique Solutions for Petrochemicals

- Universal petrochemical calibration up to 34 elements in hydrocarbon-based matrices – straight out of the box
  NEW: 2 additional elements: W and In as additives and contaminants
- Methods for best detection w/o DuraBeryllium™ Tube shield and w/ Tube shield for highest instrument uptime



Ready – To – Analyze Solutions for all petrochemical applications:

- in refineries, lubricant manufacturing, oil blending, engine development
- In plastics and polymer production

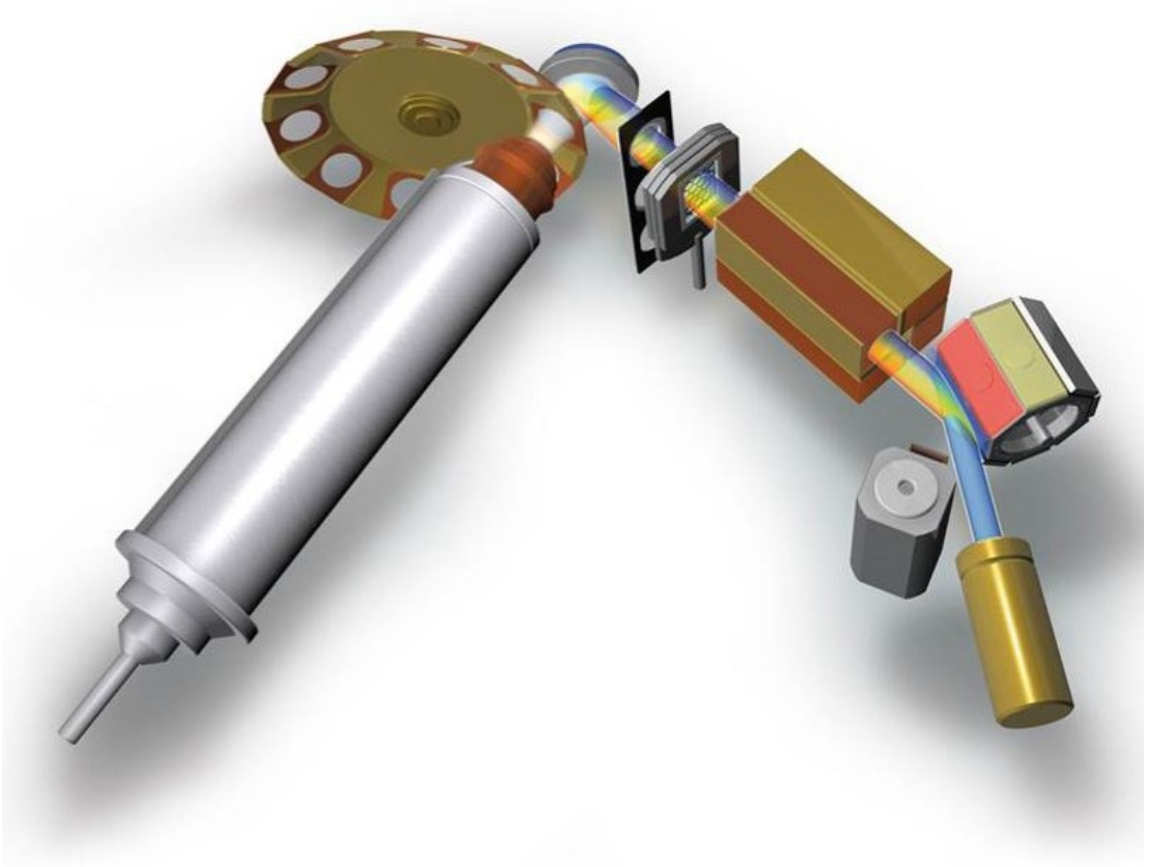
PETRO-QUANT
Unique Solutions for Petrochemicals

Universal Calibration for:

- Matrix: 95% or more hydrocarbons
- Elements: natural contaminants and technical additives
- Optimized sample prep for liquids and polymers
- Concentration ranges:
  S, Cl: LLD to 5% (heavy fuels and metal working fluids)
  Mg, P, S, Ca and Zn: up to several thousand PPM (additives)
  Ni, V and wear metals: max several hundred PPM (traces)

Performance

- LLD´s: a few ppm's, typically less than 1 PPM
- accuracy: a few ppm
- precision: a few ppm



PETRO-QUANT
Ultimate Analytical Performance

Universal Calibration for petrochemicals

based on SPECTRA*plus*:

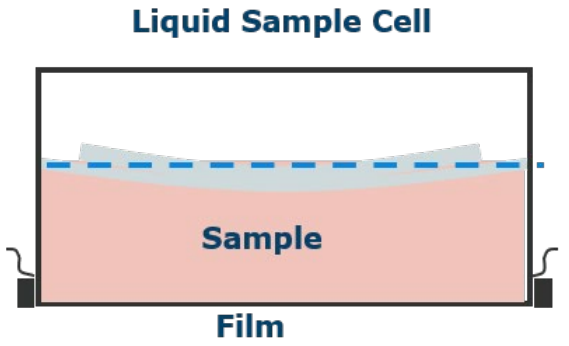
- Variable alpha (Fundamental Parameter) model for wide concentration ranges
- Automatic selection of best lines for high concentrations (S, Cl) and severe line overlaps (As, Tl, Pb, Bi)
- Aut-O-matic: Quantification of light matrix
- Geometric Correction of Wedge Effect
- Meniscus Correction

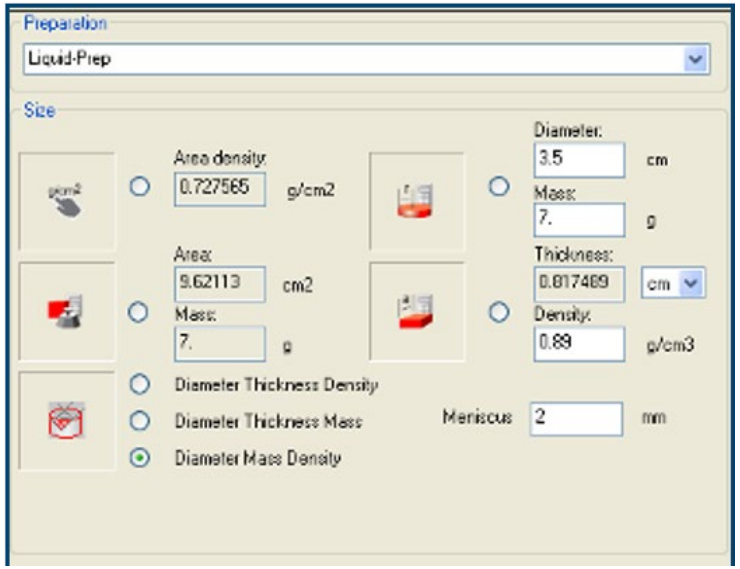
PETRO-QUANT
Ultimate Analytical Performance

Geometric Correction of Wedge Effect and Meniscus Correction

- Liquid samples often exhibit the meniscus effect, where the top surface of the liquid is concave instead of flat
- This will introduce errors in the calculation of the composition (wrong sample height)

- Meniscus Effect Correction for liquid samples:
- Insert size of the meniscus effect in the ApplicationWizard





BRUKER's Strength
Complete Product Range for Refineries

S8 TIGER

- For high demanding central labs

S6 JAGUAR

- For petrochemical labs
- e.g. ASTM D2622 and ASTM D6443

S2 POLAR

- For petro applications, incl. Ultra-Low Sulfur
- Multi-element refinery and oil applications
- Small and compact, along distribution channel

S2 PUMA

- For wear metals in lubricating oils

ALPHA FT-IR

- For biodiesel (FAME) analysis

S2 POLAR
Fuel - Analyzer

Any Questions?

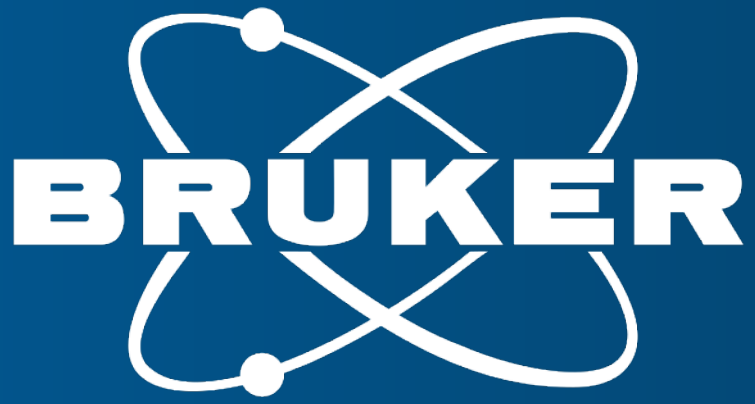
Learn more about matrix influences on HC,

matrix correction and how to handle these in lubricants

In our 2.6.2021 webinar – Sign Up Now!

Thank you!

Kai Behrens Frank Portala Adrian Fiege



Innovation with Integrity