



Optimize Your Refinery Processes with Elemental Analysis!



Welcome



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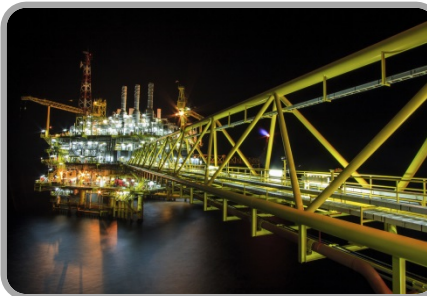
Dr. Gülüm Albut
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Optimize Your Refinery Processes with Elemental Analysis!

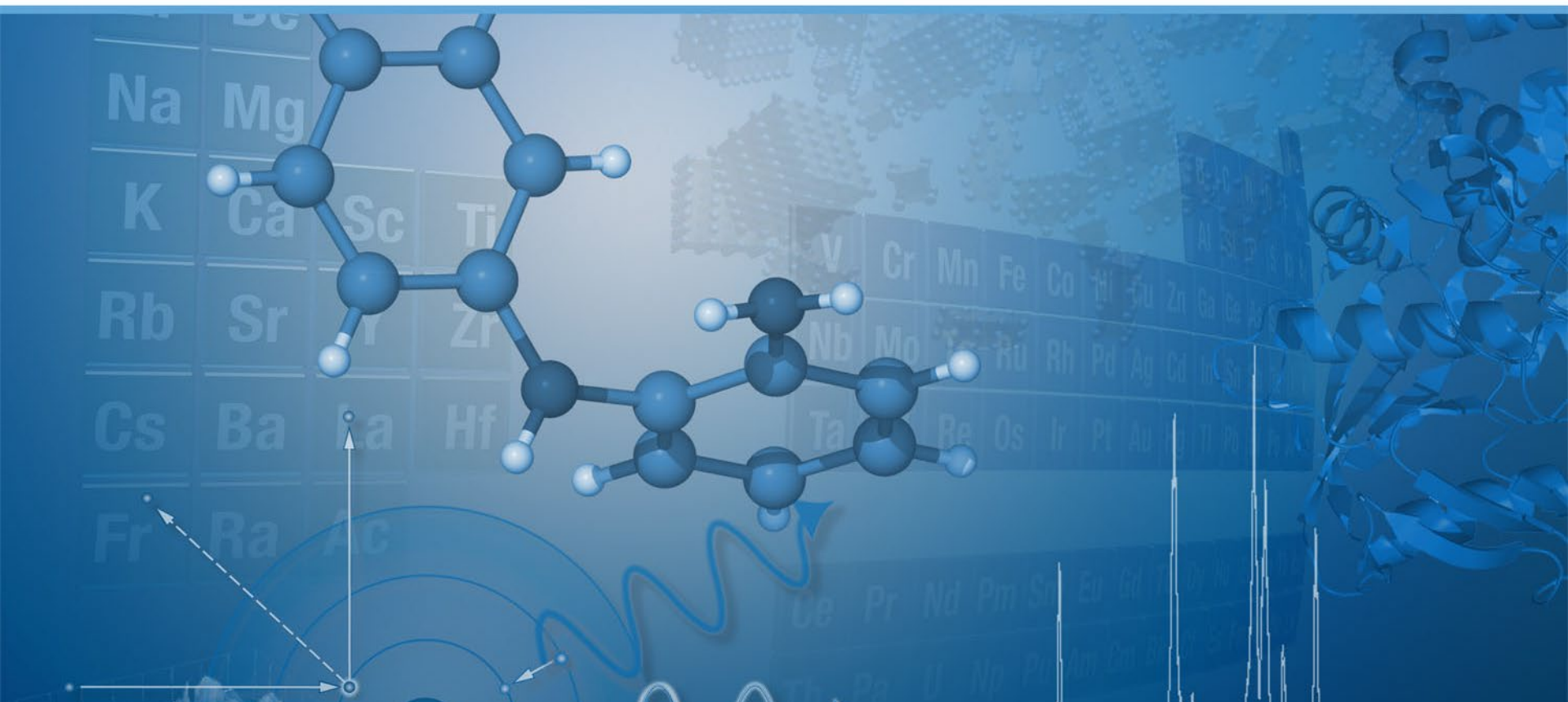


Today's Topics



- Today's Challenges in Refineries
- Why XRF (X-ray Fluorescence) Technology can Help in Refinery Processes
- Refinery Applications
- S2 POLAR Features & Benefits
- Summary

Today's Challenges in Refineries

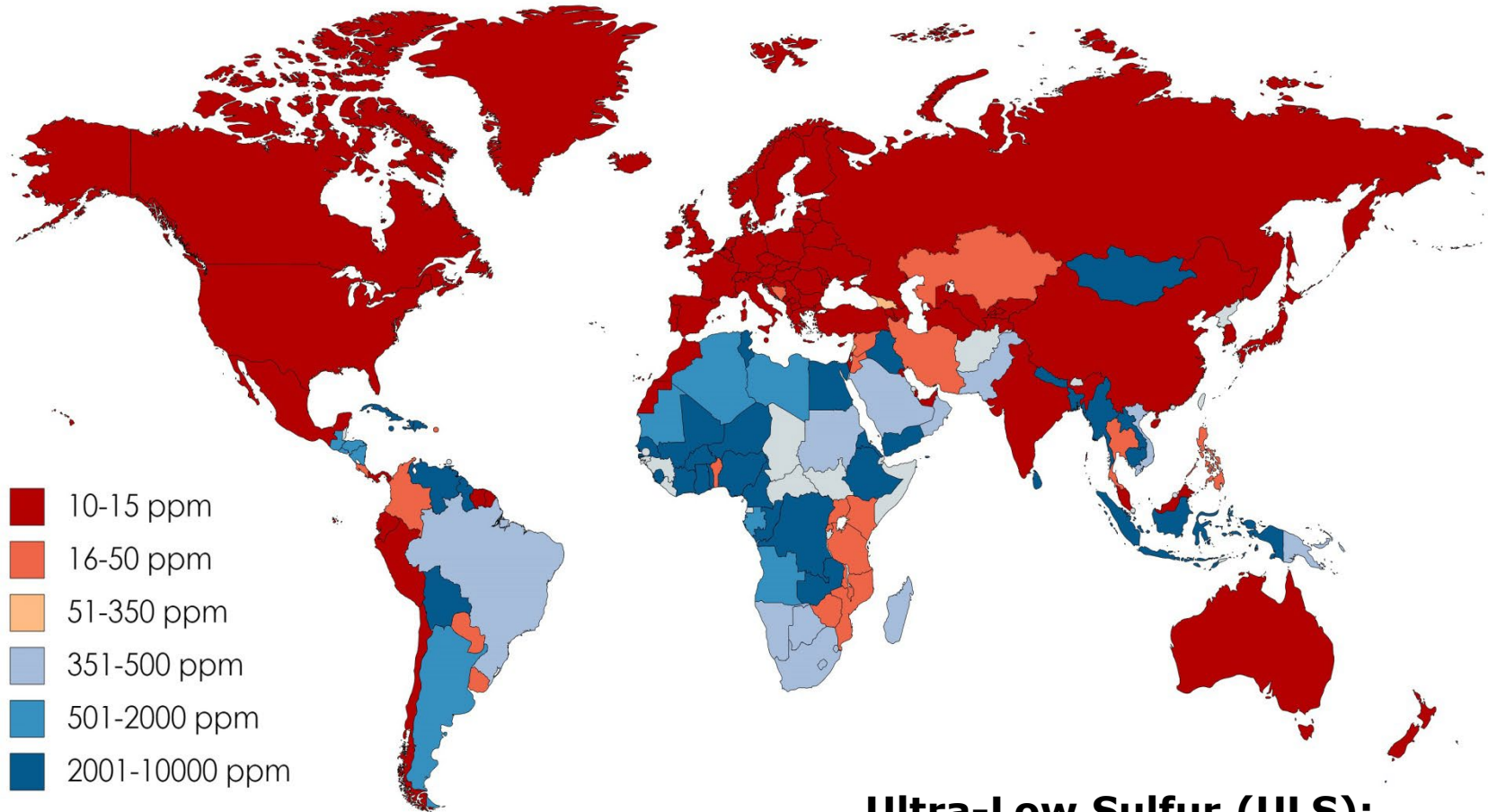


Today's Challenges in Refineries



- Stronger environmental regulations for sulfur in automotive and marine fuels (ULS, IMO 2020,...)
- Removing S is very costly

Sulfur Limits for On-Road Diesel, 2020



Detailed information on limits and regulations can be found at www.stratasadvisors.com.

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

Today's Challenges in Refineries



- Stronger environmental regulations for sulfur in automotive and marine fuels (ULS, IMO 2020,...)
- Removing S is very costly
- Current low crude oil demand and low oil price
- Huge impact on margin and profitability of refineries
- Results in even greater pressure to optimize processes, to minimize running costs and maximize product yield
- **Without close process control, processes quickly run too expensive**

How to Optimize Refinery Processes?



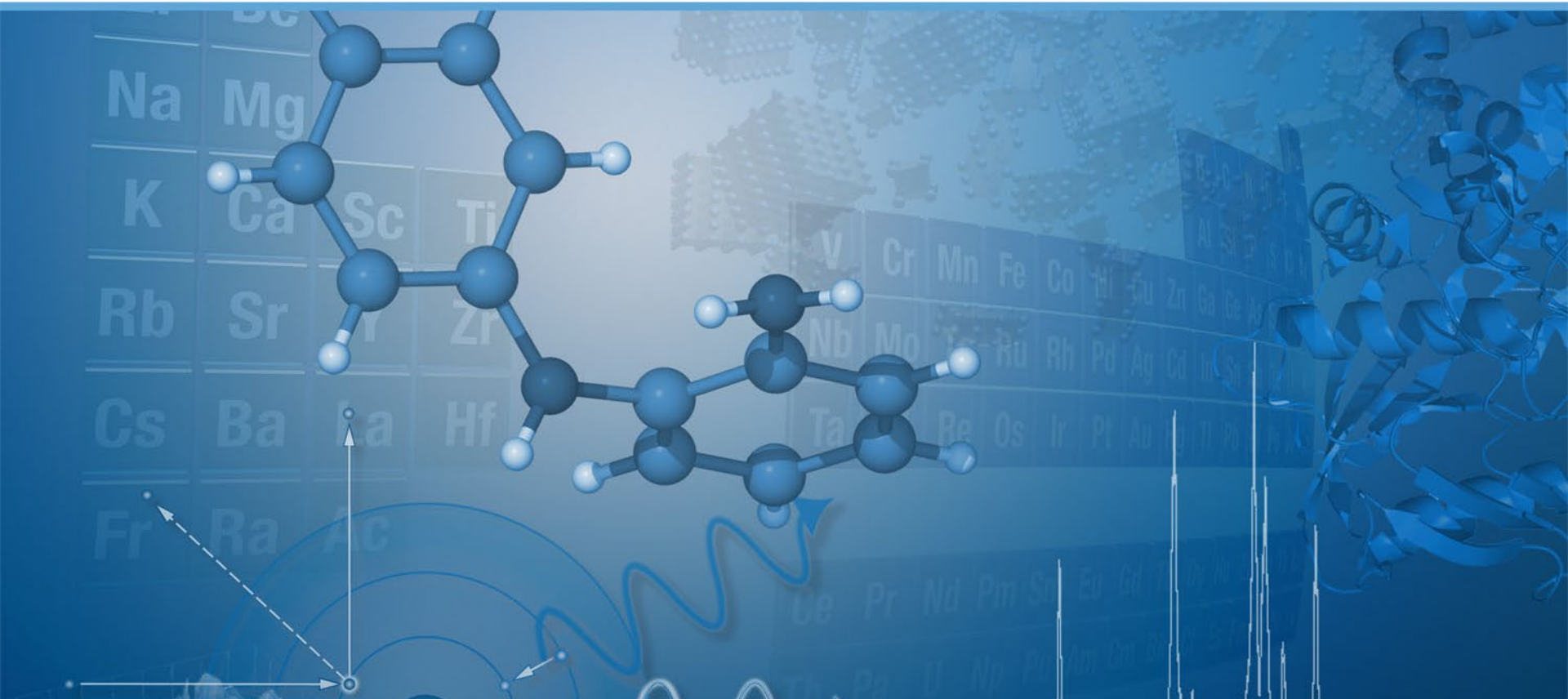
Close monitoring of elemental concentrations in

- raw materials,
- intermediates,
- process media,
- and final products.

With the right analytical tool that ideally should be:

- Easy to use
- Robust
- Short response time from sampling to result
- Low costs per sample

Why XRF (X-ray Fluorescence) Technology can Help in Refinery Processes



How does current Petrochemical Element Analysis often look like?



- Atomic Absorption Spectrometry (AAS)
 - Sample must be prepared/diluted
 - Requires daily instrument calibration
 - Requires nebulizer adjustment for organic solvents
 - Requires gases for flame or graphite tubes
 - Usually single element analysis
- Inductively Coupled Plasma Spectrometry (ICP-OES)
 - Similar to AAS, requires daily calibration and re-calibration
 - Requires expensive Argon gas for plasma
 - Adjustment of plasma gas conditions
- UV/VIS Spectroscopy (UV)
 - Requires reagents for UV reaction



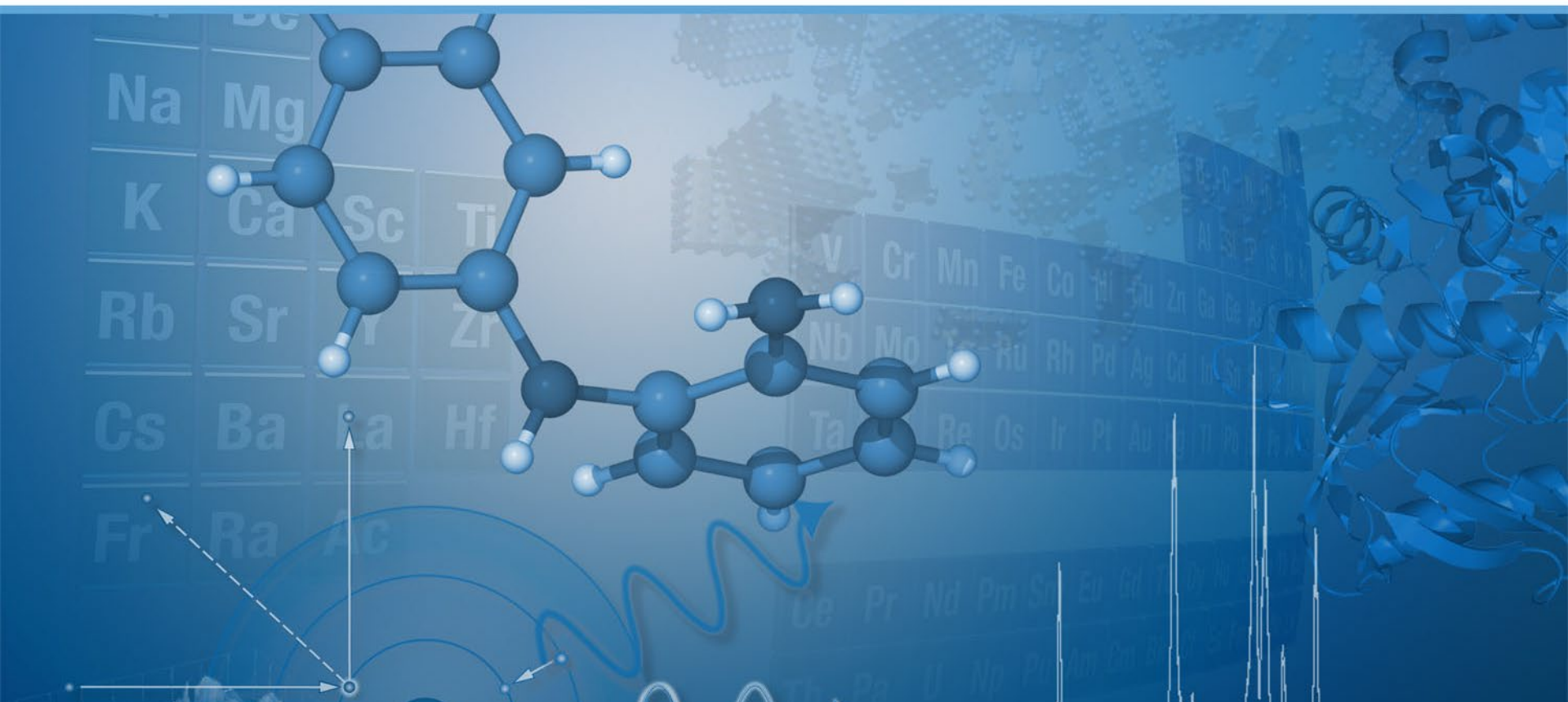
XRF (X-ray Fluorescence) Technology

Robust and easy to use

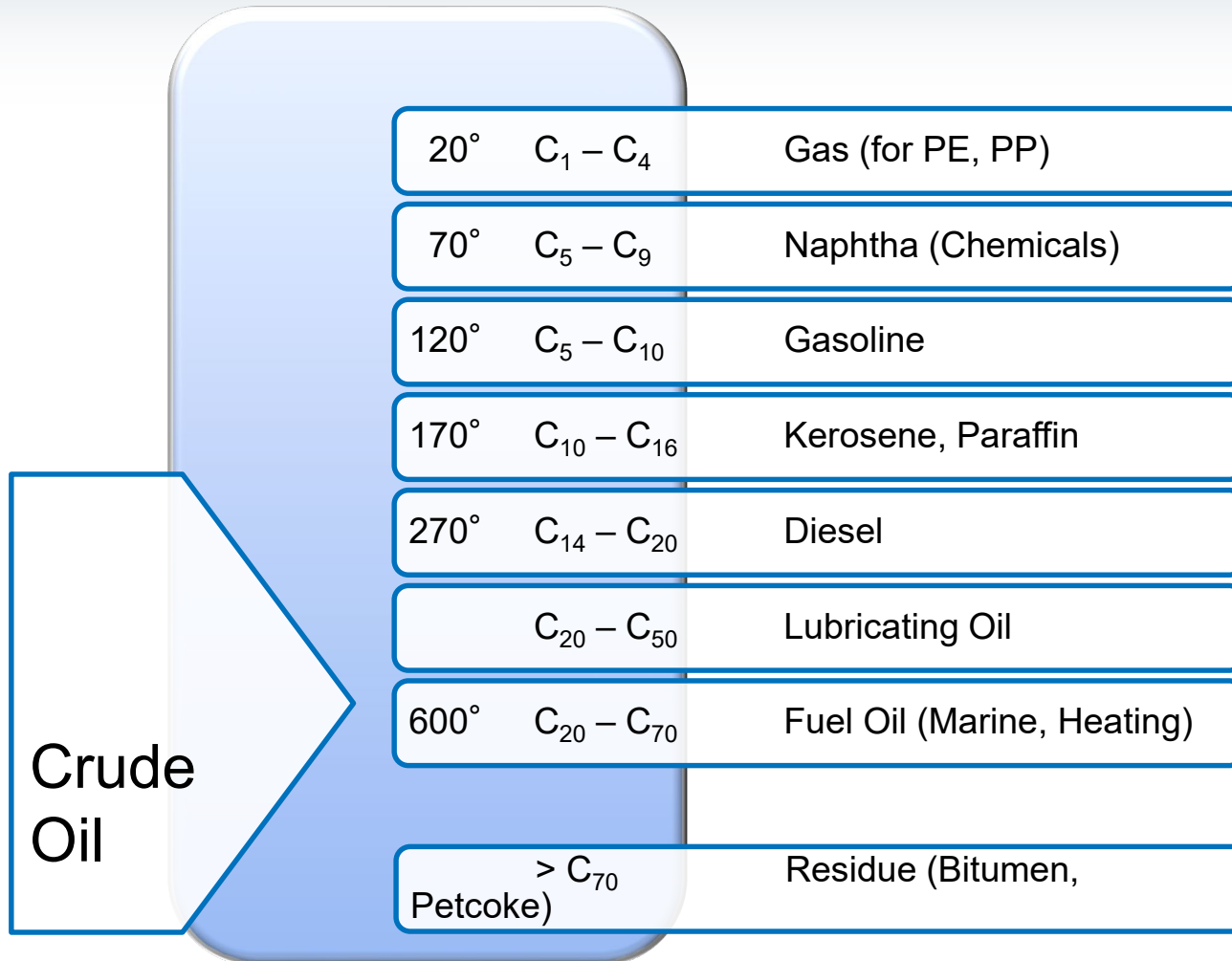


- XRF is a **robust, precise** technique and very **easy to use!**
 - 1.) **Prepare the sample cup**
 - 2.) **Fill the sample cup**
 - Place the cup on the balance
 - Fill with approx. 7 g of sample
 - 3.) **Load sample into the instrument**
- Done! **No dilution, no digestion!**
- **No daily calibration required!**
- Standard liquid cups guarantee **low costs per sample!**

Refinery Applications



Oil Refinery Products



Refinery Applications (1)

Monitoring **sulfur** in all kind of process media such as:

- **Crude oil** feedstock
- Intermediate cracking products at different process stages
- Fuel blending or final products at various sulfur levels from heating, jet and marine fuel to **Ultra-Low Sulfur (ULS)** in **automotive fuels** (-> removing S is costly)
- Comply with standards (ASTM...)

Monitoring **sulfur** in fuels along the downstream supply chain at:

- **Tank farms, pipelines**, petrol stations, custom control at harbors, and **service** and **inspection labs**



Refinery Applications (2)

Monitoring further important **elements** in refinery processes such as:

- **V**, **Ni**, and **Fe** for protection of Fluid Catalytic Cracking (FCC) or hydrotreater units
- **Cl** to minimize piping corrosion and to optimize desalter efficiency



Sulfur and Ultra-Low Sulfur (ULS) Petrochemical Sulfur Standards



Wavelength-dispersive XRF (WDXRF):

- **ASTM D2622**
- **ISO 20884**

Energy-dispersive XRF (EDXRF):

- **ASTM D7220**
- **ISO 13032**
- **ASTM D4294**
- **ISO 20847**
- **ISO 8754**



Sulfur and Ultra-Low Sulfur (ULS) Petrochemical Sulfur Standards



Wavelength-dispersive XRF (WDXRF):

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

Energy-dispersive XRF (EDXRF):

- **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 %)



S2 POLAR

High Performance Benchtop EDXRF for Petro Market



S2 POLAR

High Performance Benchtop EDXRF for Petro Market



ASTM D7220-12 (Reapproved: 2017)

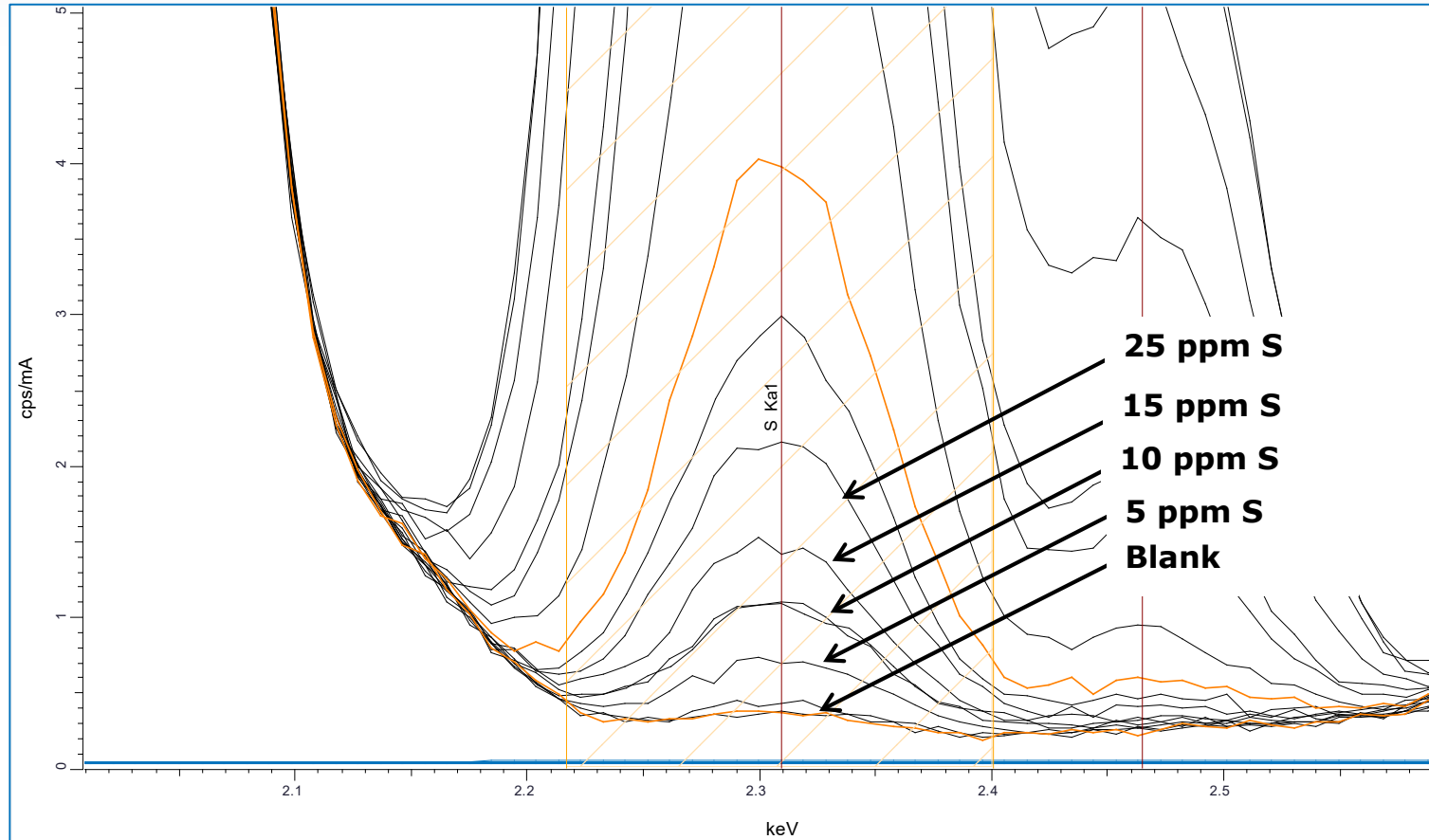


Designation: D7220 – 12

Standard Test Method for
Sulfur in Automotive, Heating, and Jet Fuels by
Monochromatic Energy Dispersive X-ray Fluorescence
Spectrometry¹

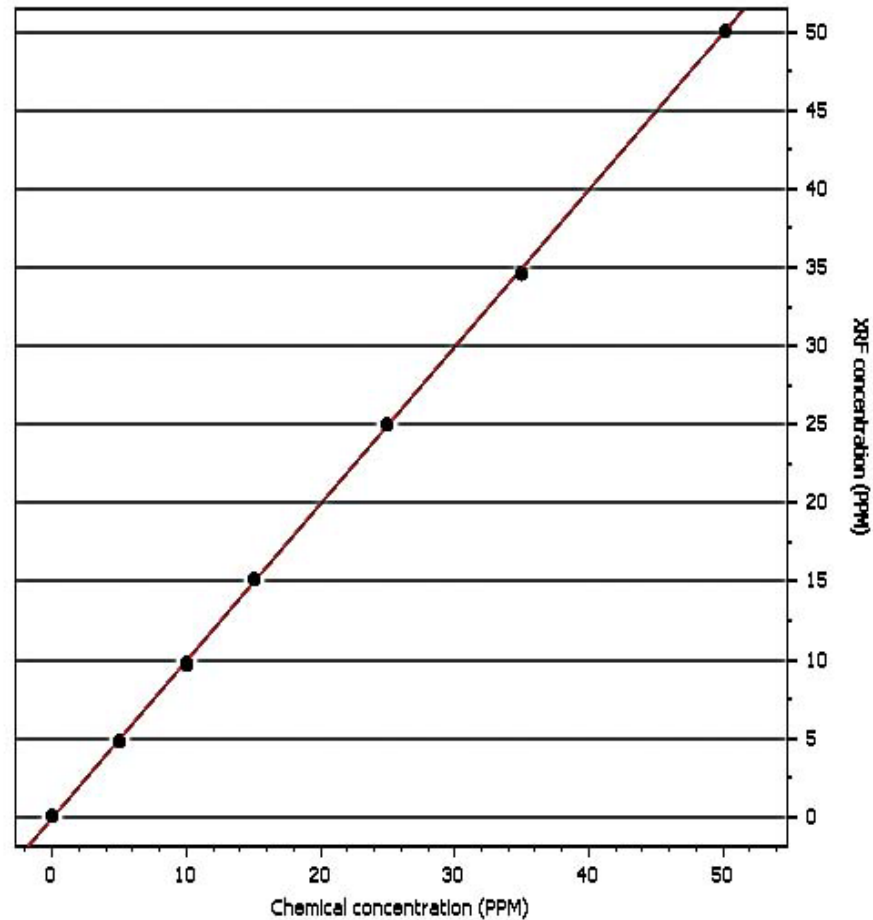
- ASTM International (American Society for Testing and Materials)
- Covers determination of sulfur in gasoline, diesel, diesel/biodiesel blends, kerosene, and jet fuel by **monochromatic EDXRF**
- For **Ultra-Low Sulfur (ULS)** levels
- Scope: **3 ppm** – 942 ppm S
- Defined repeatability (r) and reproducibility (R) limits have to be fulfilled
- Single measurements (no duplicates required)

ASTM D7220 - ULS in Gasoline S2 POLAR



Clear separation of different sulfur levels, including very low levels

ASTM D7220 – S in Gasoline S2 POLAR



Excellent calibration curve for ultra-low sulfur in the range of **0 to 50 ppm S**

Ultra-Low Sulfur (ULS) – Repeatability

S2 POLAR

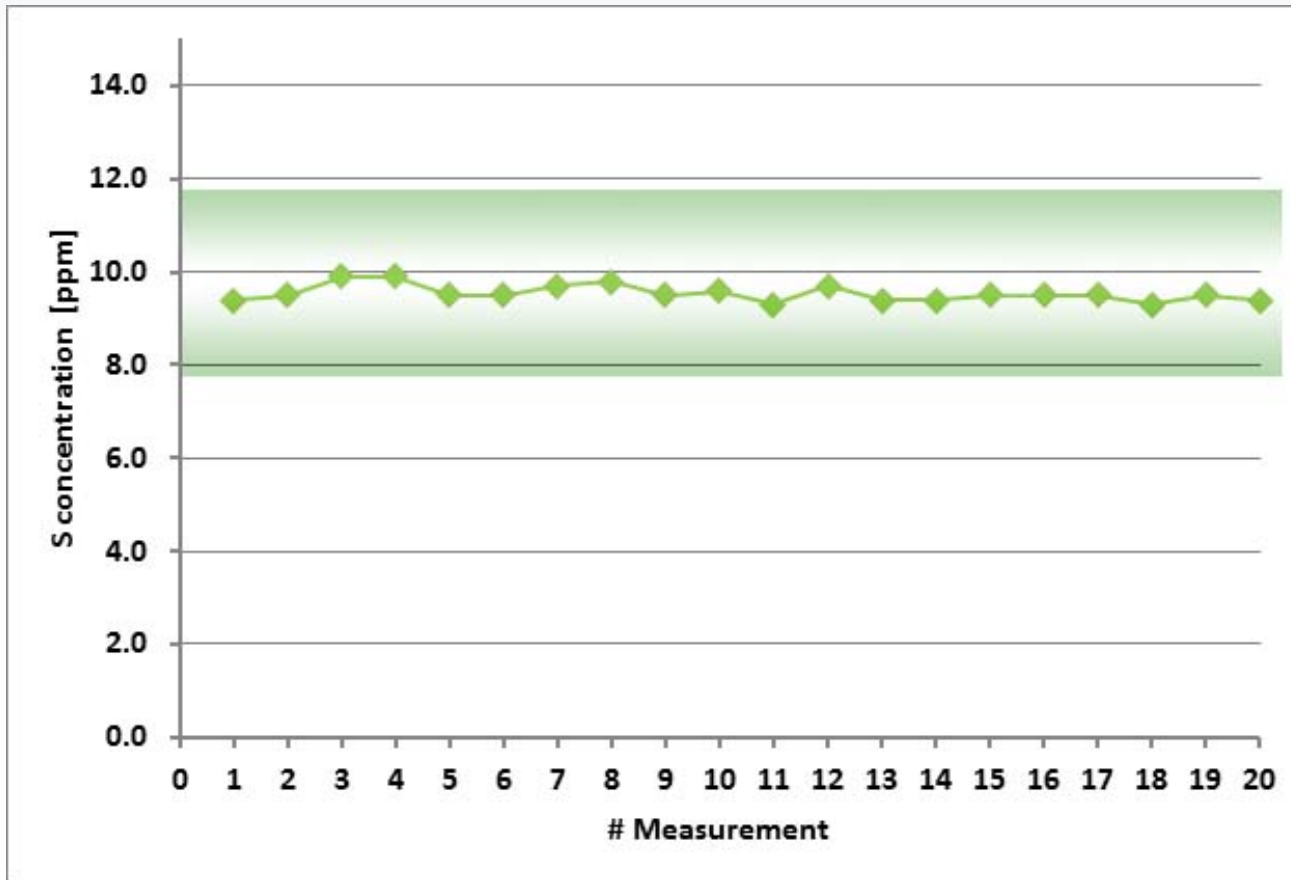


# Measurement	S [ppm]
1	10.1
2	10.0
3	10.2
4	10.9
5	10.4
6	10.4
7	10.3
8	10.4
9	10.1
10	10.2
Mean value	10.3
Abs. std. dev.	0.24
Rel. std. dev. [%]	2.34

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

 **Passed**

ASTM D7220 – Repeatability S2 POLAR

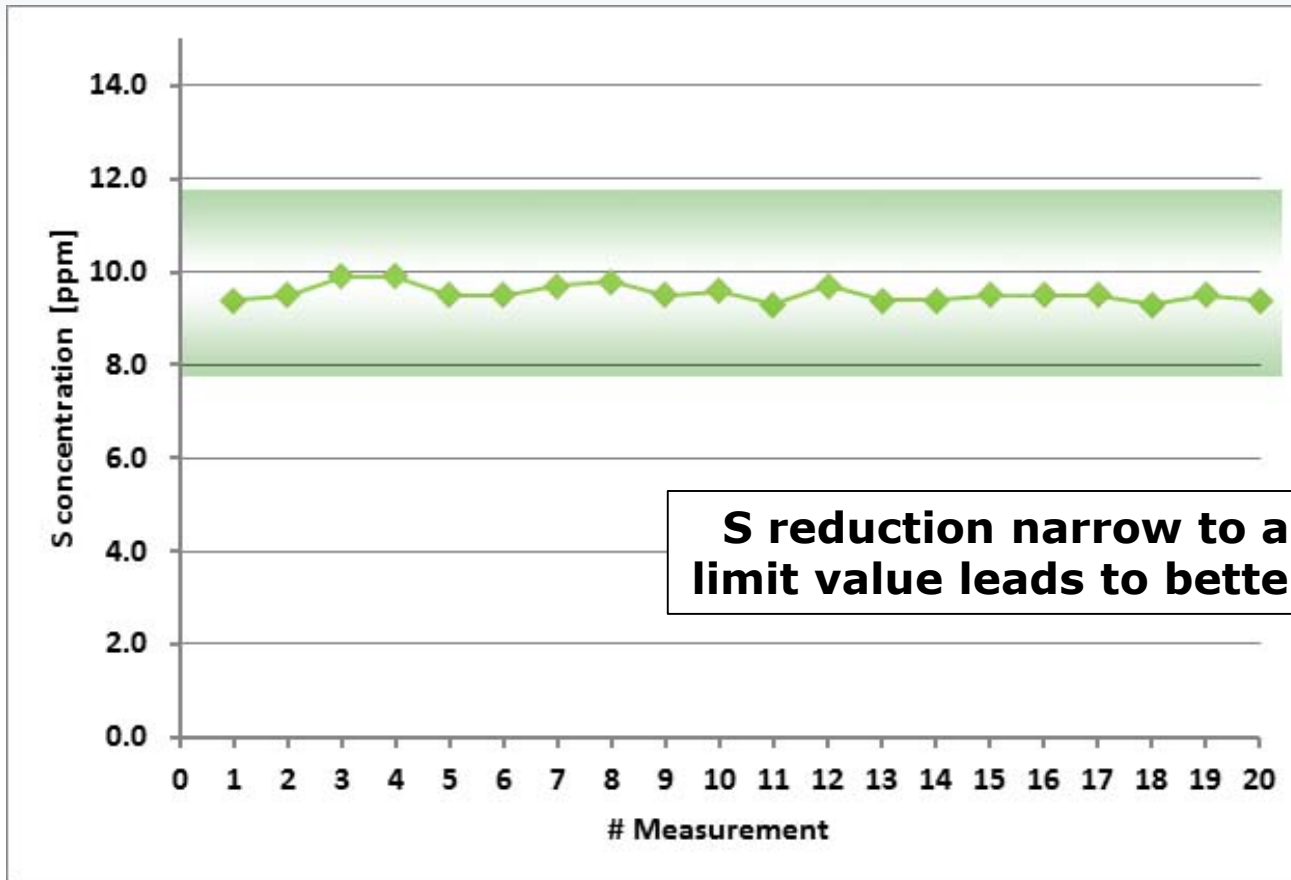


✓ Passed

Gasoline sample: 9.8 ppm S

Accepted difference between 2 measurements: ± 2.0 ppm S

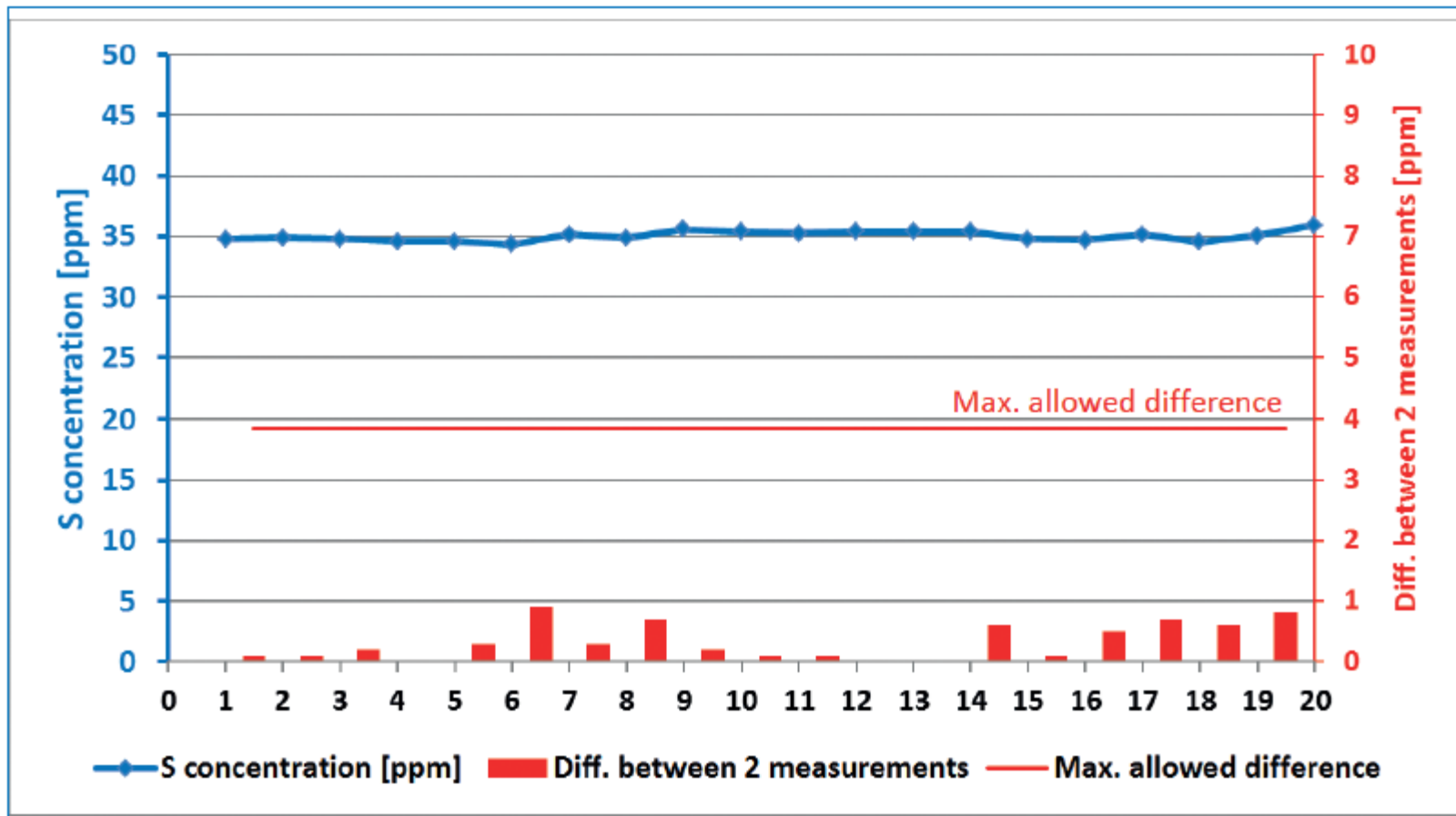
ASTM D7220 – Repeatability S2 POLAR



Gasoline sample: 9.8 ppm S

Accepted difference between 2 measurements: ± 2.0 ppm S

ASTM D7220 – 35 ppm QC Sample S2 POLAR



Repeatability of a gasoline sample, according to ASTM D7220

Passed

ISO 13032



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

ISO 13032 – Repeatability S2 POLAR



# Measurement	S [ppm]
1	11.5
2	11.2
3	11.7
4	11.1
5	11.5
6	11.4
7	11.1
8	11.3
9	11.6
10	11.3
Mean value	11.4
Abs. std. dev.	0.20
Rel. std. dev. [%]	1.72

- Gasoline sample
- Excellent repeatability for very low sulfur concentrations
- Defined limit for signal to background ratio easily fulfilled due to very low background of S2 POLAR
- Scope of ISO 13032:
8 to 50 ppm S in automotive fuels
- **Norm-compliant with ISO 13032**



ASTM D4294-16



Designation: D4294 – 16^{e1}

Standard Test Method for
Sulfur in Petroleum and Petroleum Products by Energy
Dispersive X-ray Fluorescence Spectrometry¹

- Covers determination of sulfur in petroleum and petroleum products by EDXRF
- For fuel, diesel, unleaded gasoline, lubricating base oil, crude oil, and similar petroleum products
- Scope: **16 ppm** – 4.6 % S
- 3 different concentration ranges:
 - 0 – 0.1 % S (0 – 1000 ppm) – Low range
 - 0.1 – 1.0 % S – Mid range
 - 1.0 – 5.0 % S – High range
- Defined repeatability and accuracy limits, duplicates <100 ppm S

S2 POLAR – S for Refineries

Ready-to-analyze 'One Button' Solutions




- Ready-to-analyze 'One Button' solutions
- Factory pre-calibrated methods
- Easy and straightforward to use
- Norm-compliance analysis immediately after installation
- Available for:
 - **ASTM D7220**
 - **ASTM D4294**
 - ASTM D7751
 - ASTM D6481

ASTM D2622-16



Designation: D2622 - 16

Standard Test Method for
Sulfur in Petroleum Products by Wavelength Dispersive
X-ray Fluorescence Spectrometry¹

- Covers determination of sulfur in petroleum products by **WDXRF**
- For petroleum products, diesel, gasoline, jet fuel, residual oil, lubricating base oil, crude oil, biodiesel
- Scope: **3 ppm** – 4.6 % S
- 3 different concentration ranges:
 - 0 – 1000 ppm S – Low range
 - 0.1 – 1.0 % S – Mid range
 - 1.0 – 5.0 % S – High range
- **WDXRF S6 JAGUAR and S8 TIGER**  **Passed**

Petrochemical Sulfur Standards Overview



	ASTM D2622	ISO 20884	ASTM D7220	ASTM D4294	ISO 13032	ASTM D5453
Applied technique	WDXRF	WDXRF	Mono-chromatic EDXRF	EDXRF	EDXRF	UV
S concentration range	3 ppm - 4.6 %	5 - 500 ppm	3 - 942 ppm	16 ppm - 5 %	8 - 50 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 - 1000 ppm 0.1 - 1.0 % 1.0 - 5.0 %	0 - 50 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	Petroleum products, diesel, gasoline, jet fuel, residual oil, lubricating base oil, crude oil, biodiesel	Automotive fuels, diesel, gasoline, biodiesel	Total sulfur in light hydrocarbons, spark ignition engine fuel, diesel, engine oil
Bruker XRF norm compliance	S6 JAGUAR, S8 TIGER	S6 JAGUAR, S8 TIGER	S2 POLAR	S2 POLAR, S2 PUMA	S2 POLAR	

It's not all about Sulfur...

More Refinery Applications



Fluid Catalytic Cracking Units



Monitoring elements important for the **protection** and **efficiency improvement** of Fluid Catalytic Cracking (**FCC**) or hydrotreater units such as:

- Lower levels of **vanadium (V)** and **nickel (Ni)**, as these elements deactivate the catalysts
- **Iron (Fe)** as corrosion byproduct to minimize impact on FCC, can lead to pump and exchanger fouling

ASTM D8252-19



Designation: D8252 - 19^{e1}

Standard Test Method for
Vanadium and Nickel in Crude and Residual Oil by X-ray
Spectrometry¹

- Covers determination of **total vanadium and nickel in crude and residual oil** by XRF
- Vanadium and nickel, along with sulfur, occur naturally in crude oil, and their concentrations vary depending on the geographical region of the oil deposits
- Nickel and vanadium are critical due to their impact on refining process efficiency, contamination risk of the cracking catalysts
- and pipelines have set specifications for Ni and V in their common stream sweet crude

ASTM D8252-19

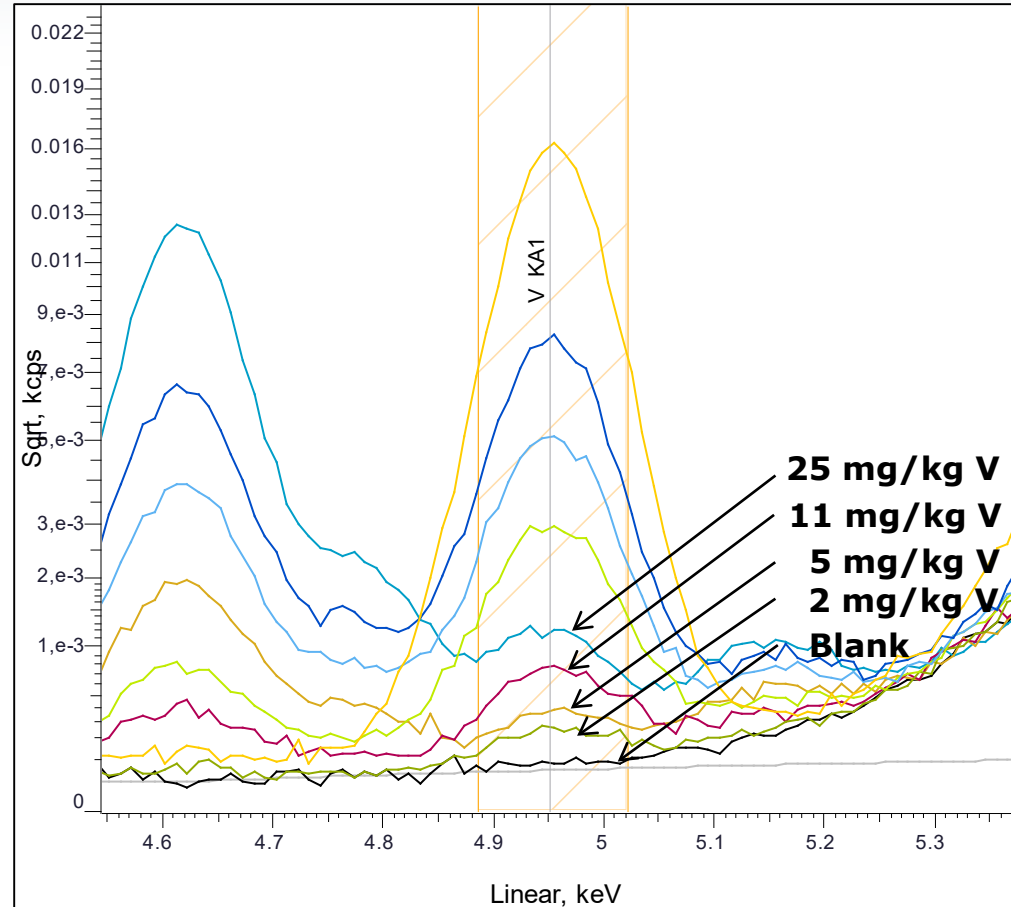
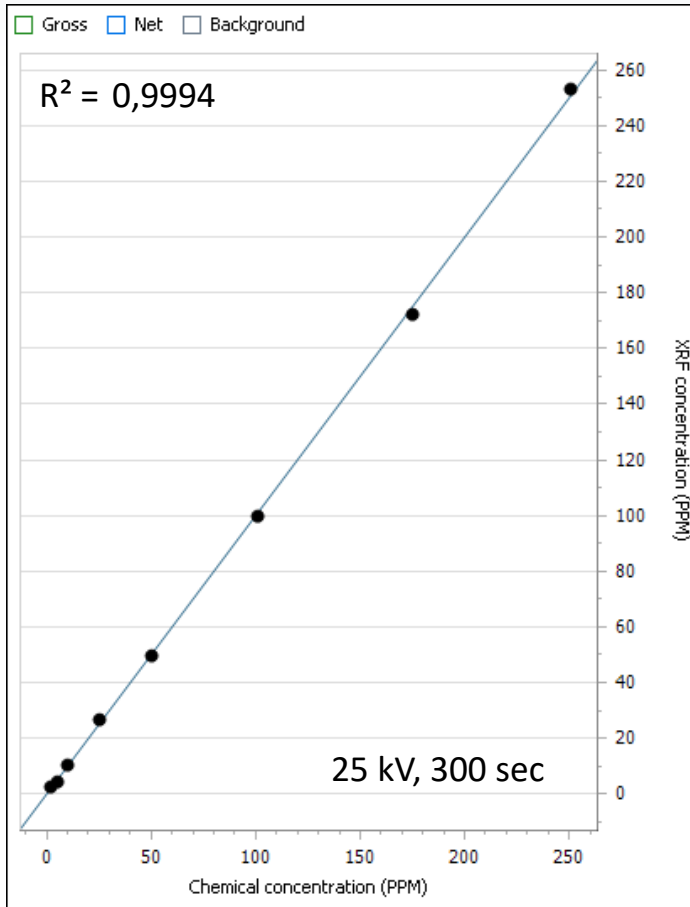


Designation: D8252 - 19^{e1}

Standard Test Method for
Vanadium and Nickel in Crude and Residual Oil by X-ray
Spectrometry¹

- These elements rapidly **deactivate the catalysts that are used in the catalytic cracker (FCC) and hydrotreater units,**
- Might catalyze **undesirable side reactions (such as carbonization), and devalue any residual material** in which it may be isolated (**such as coke**)
- Defined repeatability (r) and reproducibility (R) limits have to be fulfilled for 1.9 to 50 mg/kg V and 2.2 to 50 mg/kg Ni
- Single measurements (no duplicates required)

Vanadium in Crude Oil – 0–100 mg/kg S2 POLAR



Clear separation of different V levels, including low levels

ASTM D8252 – V Repeatability S2 POLAR



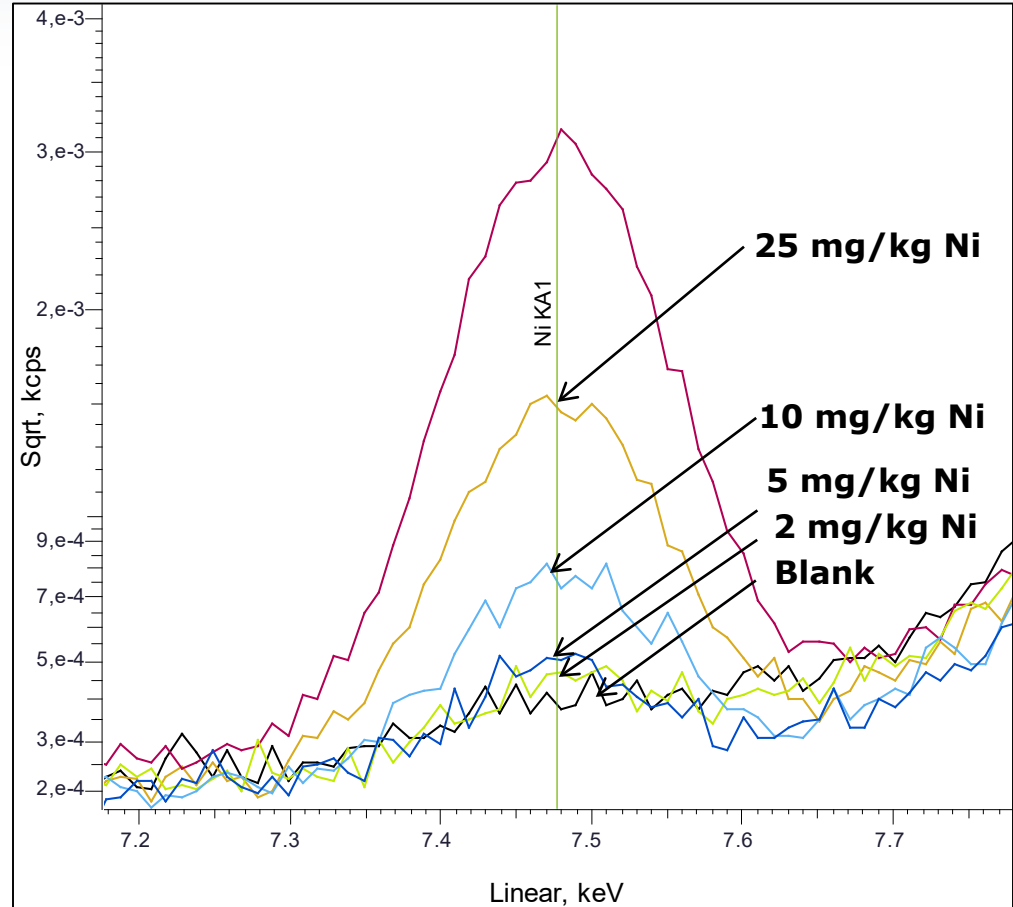
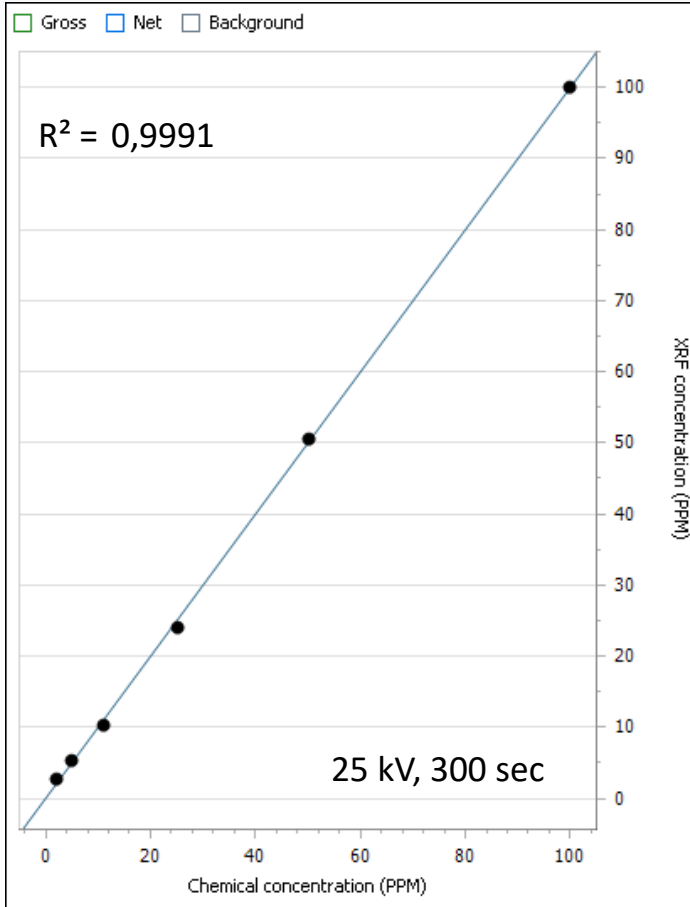
	V [mg/kg]
Rep 01	54.2
Rep 02	53.8
Rep 03	54.6
Rep 04	54.6
Rep 05	55.1
Rep 06	55.3
Rep 07	54.5
Rep 08	54.4
Rep 09	55.0
Rep 10	55.0
Mean	54.7
Abs. Std. Dev.	0.43
Rel. Std. Dev. [%]	0.79

- 55 mg/kg V oil standard
- Excellent repeatability for vanadium
- **Norm-compliant with ASTM D8252**



Accepted difference between 2 measurements: ± 3.5 mg/kg V

Nickel in Crude Oil – 0 – 100 mg/kg Ni S2 POLAR



Clear separation of different Ni levels, including low levels

ASTM D8252 – Ni Repeatability S2 POLAR



	Ni [mg/kg]
Rep 01	51.6
Rep 02	50.3
Rep 03	50.8
Rep 04	51.0
Rep 05	50.0
Rep 06	50.7
Rep 07	50.9
Rep 08	51.3
Rep 09	50.7
Rep 10	51.1
Mean	50.8
Abs. Std. Dev.	0.44
Rel. Std. Dev. [%]	0.86

- 50 mg/kg Ni oil standard
- Excellent repeatability for nickel
- **Norm-compliant with ASTM D8252**



Accepted difference between 2 measurements: ± 3.6 mg/kg Ni

Corrosion of Piping/ Desalter Optimization



Monitoring lower levels of **chlorine (Cl)**

- to minimize impact of corrosion of piping (due to formation of **corrosive hydrochloric acid** at higher temperatures)
- to optimize **desalter** performance
 - Desalter used as first step to remove salt from crude
 - Remaining salt could cause water hydrolysis -> HCl

ASTM D4929-17

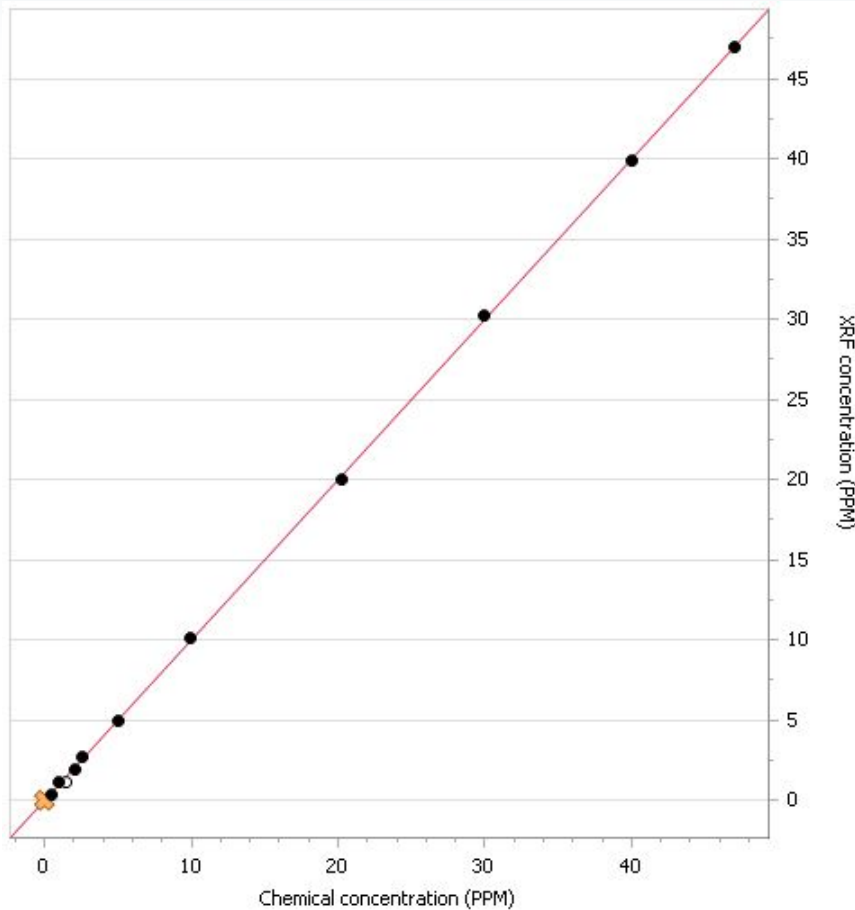


Designation: D4929 – 17

Standard Test Method for
Determination of Organic Chloride Content in Crude Oil¹

- Covers determination of organic **chloride in crude oil** by XRF
- Organic chlorides break down during fractionation and produce hydrochloric acid (HCl), which has a **corrosive effect**
- **Organic chlorides naturally are not present in crude oils** and **usually result from cleaning operations** at production sites, pipelines, or tanks
- Several pipelines have set specification limits for organic chlorides and trade contracts often specify that no organic chloride is present in the crude oil
- Requires some sample preparation prior to Cl determination

ASTM D4929 - Chlorine in Crude Oil S2 POLAR

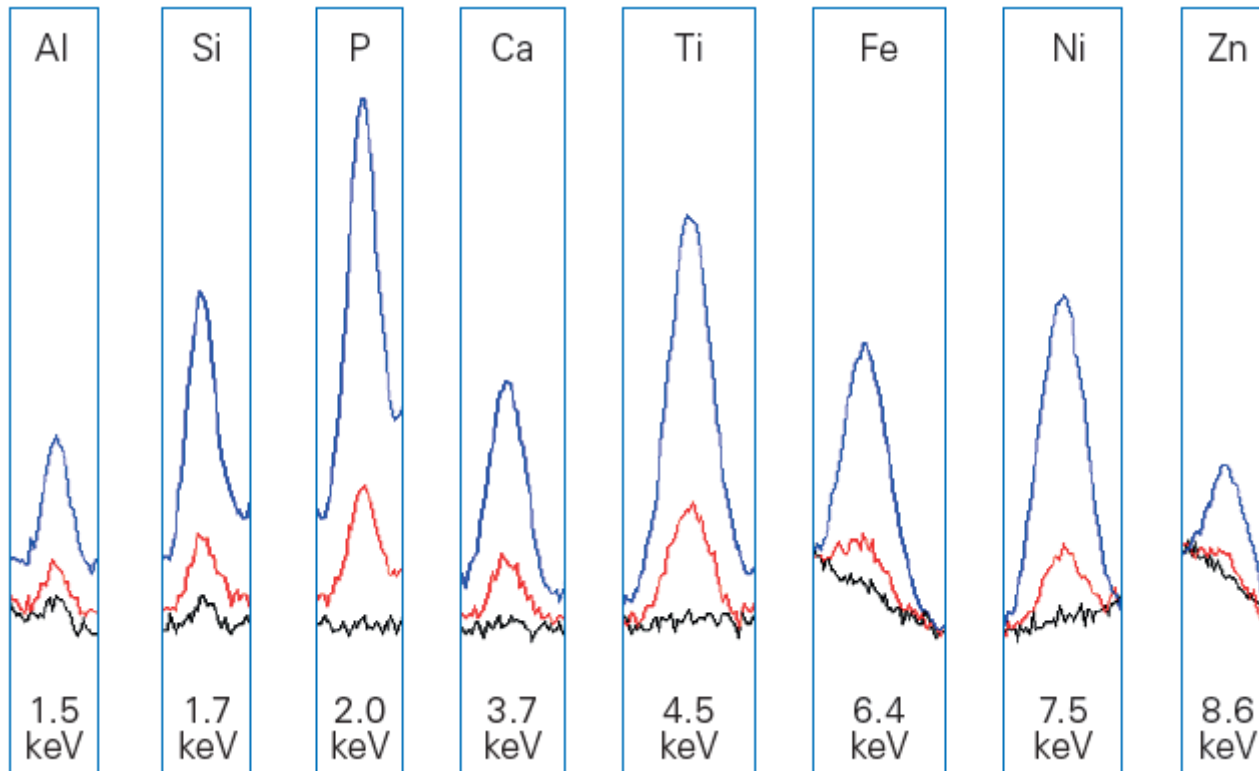


- Analysis of **low levels of organic chlorine** for corrosion monitoring and desalter control
- **1 to 100 ppm Cl**
- Norm-compliant with **ASTM D4929**



Excellent accuracy also at low Cl concentrations

Multi-element Capability S2 POLAR



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

SampleCare™ Cup S2 POLAR

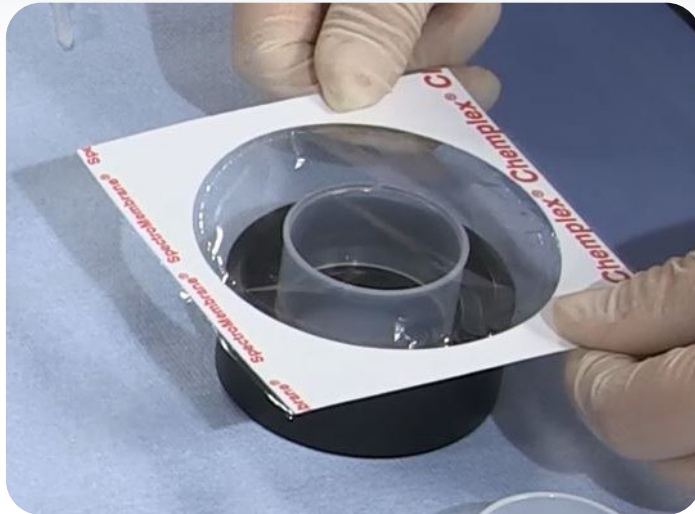


Liquid sample cup (Ø 40 mm)

SampleCare™ cup (Ø 51 mm)



Liquid Cup Preparation Tool S2 POLAR

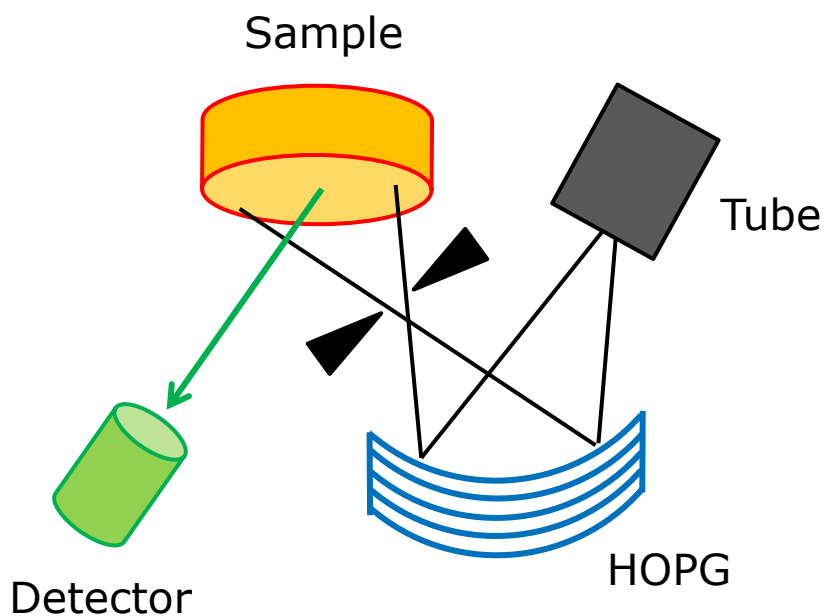


- Tool for easy and efficient preparation of liquid cups
- Used for sample liquid cups (Ø 40 mm) and SampleCare cups (Ø 51 mm)
- Easy and straightforward!

S2 POLAR



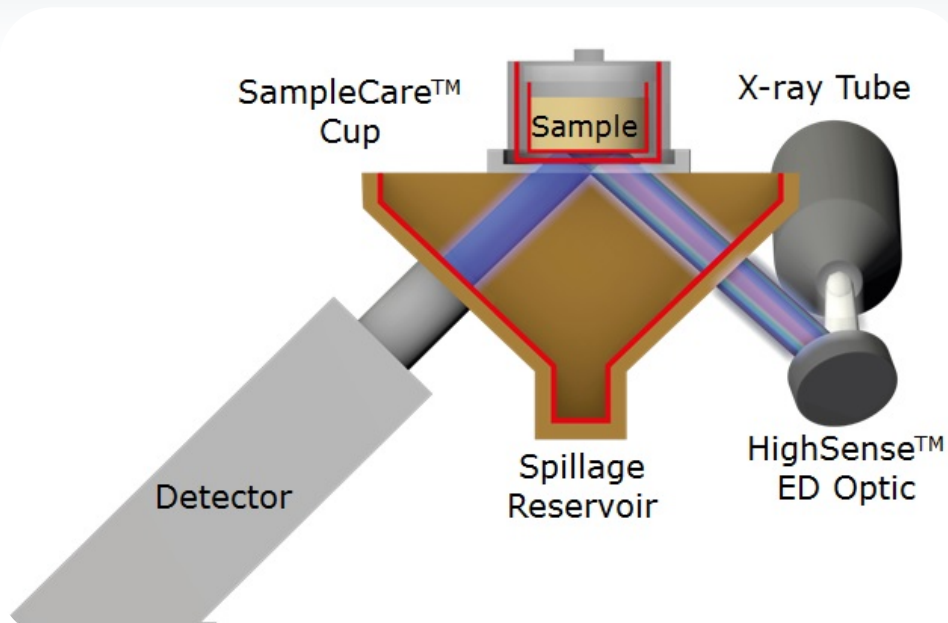
HighSense™ Beam Path S2 POLAR



- Polarizing HighSense™ beam path
- HighSense™ ULS SDD
- Powerful 50 W, 50 kV
- Perfect excitation conditions for **petrochemical products** (fuels, oils, polymers = light matrices)
- Reduced background due to polarization
- Results in **excellent LLDs**

HOPG: Highly oriented pyrolytic graphite

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 farms
 - oil terminals

TouchControl™ S2 POLAR




- Large touchscreen user interface
- Intuitive and easy-to-use
- 'One Button' solutions
- Enable users with minimal training to run routine samples
- Multilingual:
English, German, French,
Spanish, Portuguese, Italian,
Russian, Chinese, Japanese

German Type Approval / NF C 74-100 S2 POLAR



Bundesamt für Strahlenschutz



Bauartzulassung nach Röntgenverordnung
Type Approval Pursuant to the German X-Ray Ordinance (RöV)

Zulassungsschein
Bauartzeichen BfS 14118 V RÖV
Certificate of Type Approval No. BfS 14118 V RÖV

I. Bauartzulassung
Type Approval

Gemäß den §§ 8 bis 12 in Verbindung mit Anlage 2 Nr. 3 der Verordnung über den Schutz vor Schäden durch Röntgenstrahlung (Röntgenverordnung - RöV) ist die Bauart der im Folgenden bezeichneten Vorrichtung mit den dazugehörigen Angaben zugelassen.

Vorrichtung: Röntgenfluoreszenzspektrometer
Kategorie/Device: Vollschutzgerät gem. § 2 Nr. 25 RöV

Typ / Firmenbezeichnung: S2 POLAR
Modell, trade name:

Inhaber der Zulassung / Hersteller der Vorrichtung:
Holder of the type approval / Manufacturer of the device
BRUKER AXS GmbH
Östliche Rheinbrückenstraße 49
76187 Karlsruhe

Zugelassene Verwendung: Das Vollschutzgerät ist zur Materialanalyse zugelassen.
Approved purpose of use

Befristung der Zulassung: Die Zulassung ist auf 10 Jahre befristet, gem dem Datum der Erteilung.
Expiration

Technische Angaben
Technical Information

Maximale Betriebswerte: Röhrenspannung 50 kV (Gleichspannung)
Maximum operating values: Röhrenleistung 50 W

Röntgenröhre / X-Ray tube

Typ / type: VF-50J-PD
Anodenmaterial: Palladium (Pd)
Acrode material:

Hersteller / Manufacturer: Varix Imaging Corporation, Inc.
1676 Pioneer Road, Salt Lake City
Utah 84104, U.S.A.



CERTIFICAT DE CONFORMITE
N° 2450423-24 R1 A LA NORME NF C 74-100
Certificate of conformity N° 2450423-04 R1

Identification de l'article : Groupe radiogène de radiologie industrielle composé d'un générateur haute tension type UX50P50X4786 et d'un tube radiogène type VF-50J-PD, intégré au système par rayons « X » modèle S2 POLAR (A36X).

Références : NF C 74-100 de juin 1981 et NF C 74-100 ADD 3 de juin 1984

Fabricant / Manufacturer : BRUKER AXS GmbH
Östliche Rheinbrückenstraße 49
76187 Karlsruhe

Fourni par / Delivered by : BRUKER AXS GmbH
Östliche Rheinbrückenstraße 49
76187 Karlsruhe

Demandeur du certificat / Applicant : BRUKER AXS GmbH
Östliche Rheinbrückenstraße 49
76187 Karlsruhe

BRUKER France S.A.S.
4 Allée H. Lorentz
77420 Champs Sur Marne

Au vu des résultats et des remarques figurant dans les rapports d'essai n° 2450423-24 R1 et n° 2450423-17C, l'article testé est déclaré conforme aux exigences du document de référence dans les limites du domaine défini dans le bulletin d'identification et des références citées dans le document « A36-X1-X47-R03.xls ».

On the basis of the results and remarks contained in the test reports n° 2450423-24 R1 and n° 2450423-17C, the item tested is in conformity with the requirements of the above referenced document inside the limits defined in the "identification bulletin" and references cited in the document "A36-X1-X47-R03.xls".

Osny, le 18 mars 2019


Yann Foucher, Responsable Technique

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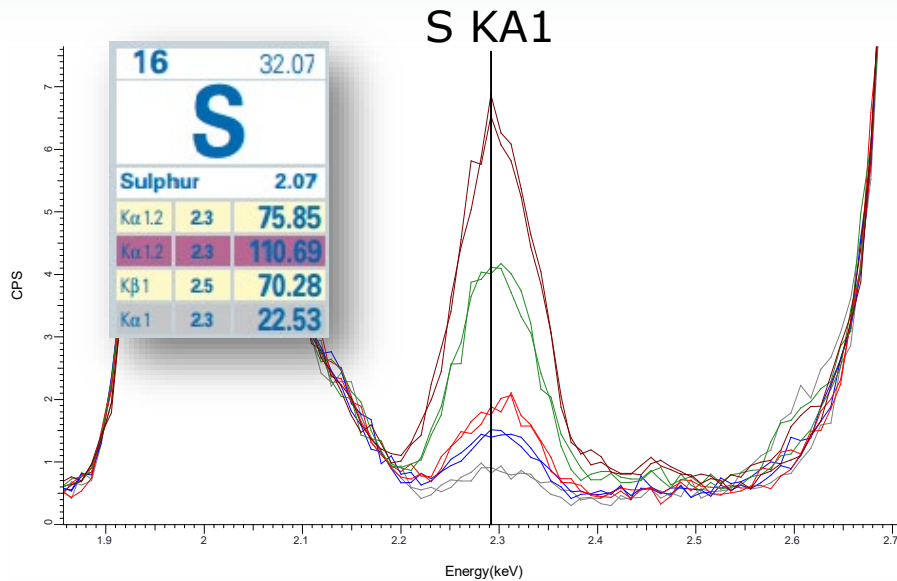
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- **German Type Approval** and Vollschutz according to BfS RöV
- **Approval for France** (NF C 74-100) and **Spain**
- Fully radiation-protected system
- High voltage **30 kV max.** (optionally), simplify regulatory efforts in certain countries:
- France/Belgium/Luxembourg
- Italy/Austria
- Taiwan

Refinery Applications

S2 POLAR



- Covers **Ultra-Low Sulfur (ULS)** in fuels up to % S in crude oil
- Norm-compliant sulfur analysis:
 - **ASTM D7220**
 - **ISO 13032**
 - **ASTM D4294**
 - ISO 20847
 - ISO 8754
 - IP 336, 496, 532, JIS K2541-4
- **ASTM D8252: V, Ni + Fe**
- **ASTM D4929: Cl**



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 for Refineries (1)



One instrument does it all
for refineries:

- From Ultra-Low Sulfur (**ULS**) in fuels to % in crudes
- **S reduction narrow to allowed limit value leads to better margin**
- Norm-compliant to international standards **ASTM D7220, D4294, D4929, D8252, ISO 13032,...**

S2 POLAR for Refineries (2)



Advantages of monitoring:

- **Ni, V** can damage the Fluid Catalytic Cracking (FCC) and hydrotreater unit
- **Fe** as corrosion byproduct has a negative impact at FCC
- **Cl** causes **HCl** formation resulting in piping **corrosion**
- **The S2 POLAR combines excellent analytical performance in a single powerful benchtop instrument.**

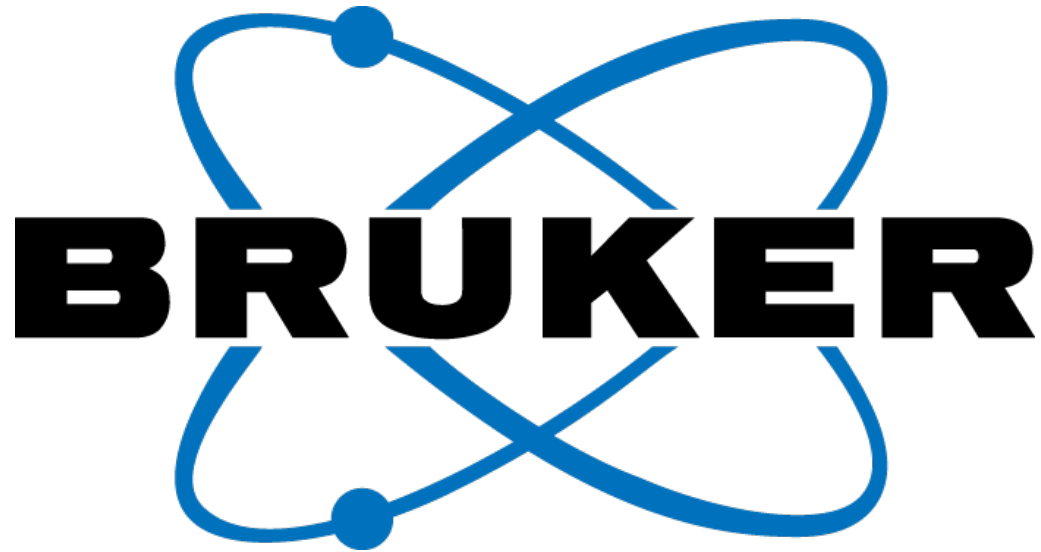
S2 POLAR for Refineries



Questions



Thank you!



Innovation with Integrity