Trace Elemental Analysis in Petroleum and Energy by ICP-OES/ICPMS

PRESENTED BY

Trace Element Analysis (TEA) Sci Spec Team

What’s Petroleum

6
C
Carbon

1
H
Hydrogen

7
N
Nitrogen

16
S
Sulfur

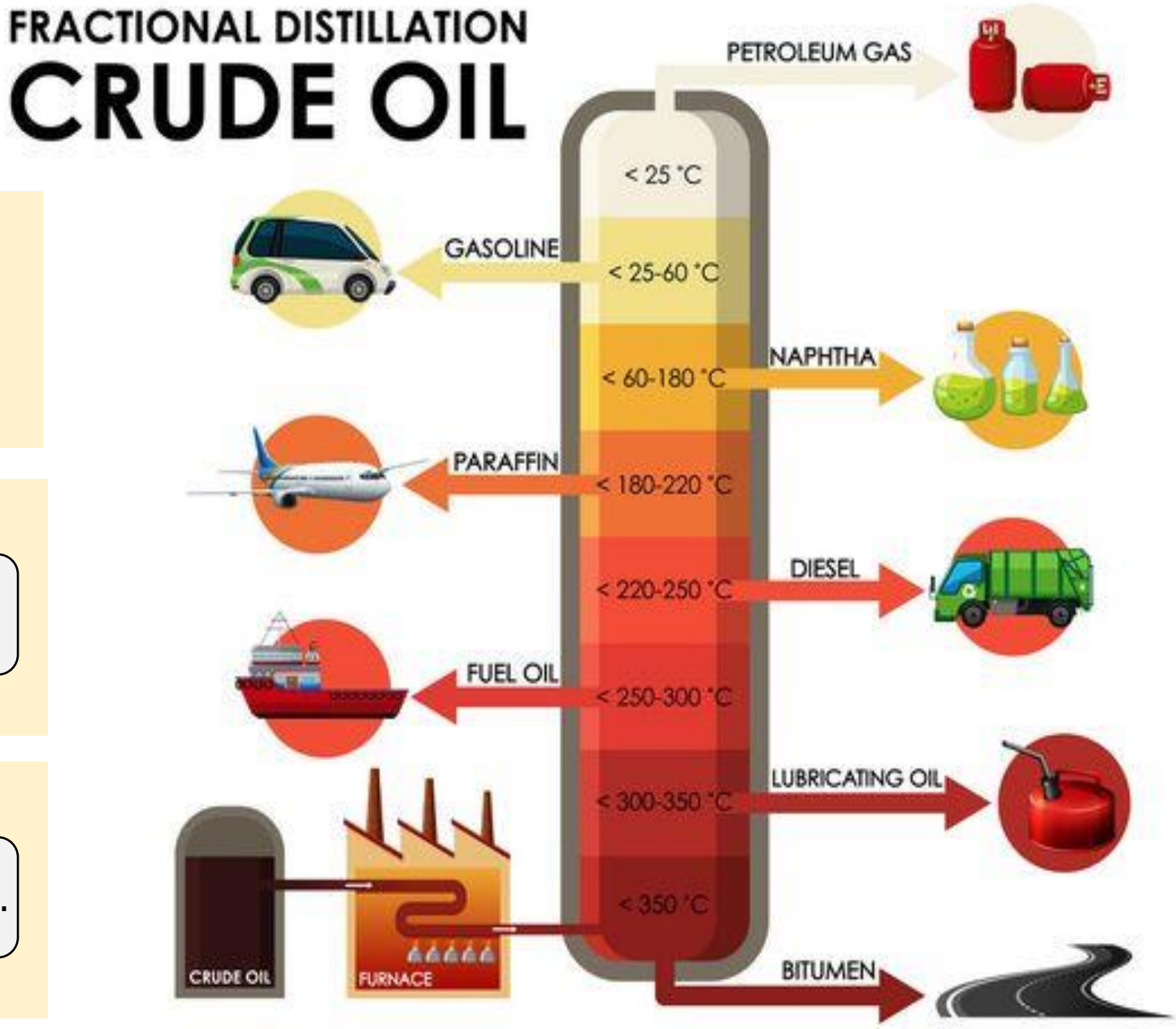
Basic steps for crude oils refinery

- Separation
- Conversion
- Treatment

Crude oil > **Furnace** Liquids and vapor > **Distillation** Petroleum fractions

Intermediate distillate component > **Streams** Finished product

Finished product > **Refinery technician** Treatment to achieve specification.



Why should we test the Oil and Petroleum products?

Designation: D7691 – 16

Standard Test Method for Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[1]

Designation: D 5185 – 09

Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[1]

Designation: D7111 – 16

Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[1]

Designation: D8110 – 17

Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[1]

ASTM INTERNATIONAL

Standards Worldwide

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Trace Metals in Organics by ICP-MS

UOP Method 1005-14

Scope

This method is for determining the concentrations of aluminum (Al), arsenic (As), calcium (Ca), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), gallium (Ga), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), sodium (Na), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr), in organic matrices such as crude petroleum, asphalts, vacuum tower bottoms, vacuum gas oils, atmospheric gas oils, diesel and jet fuels and their blending components, pyrolysis oils, and fatty acid derivatives by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The lower limits of quantitation for the above elements, are listed in Table 1. Determination of additional elements is possible if they are compatible with other analytes during digestion.

Table 1
Lower Limits of Quantitation, mg/kg (mass-ppm)

Al	0.02	K	0.03	Pd	0.01
As	0.01	Li	0.01	Pt	0.01
Ca	0.03	Mg	0.02	Sn	0.01
Cd	0.01	Mn	0.01	Sr	0.01
Co	0.01	Mo	0.01	Ti	0.03
Cr	0.01	Na	0.06	V	0.01
Cu	0.01	Ni	0.01	Zn	0.01
Fe	0.02	P	0.50	Zr	0.01
Ga	0.01	Pb	0.01		

Alternatively, many of the elements listed above can be determined using UOP Method 389, "Trace Metals in Organics by ICP-OES." Some of the elements listed above may be analyzed by Atomic Absorption Spectroscopy (AAS). See UOP Method 391, "Trace Metals in Petroleum Products or Organics by AAS," for specific metals and their range of quantitation. Metals known to be non-volatile may be analyzed by UOP Method 407, "Trace Metals in Organics by Dry Ashing - ICP-OES." Many of these elements can be determined in kerosene using ASTM Method D7111, "Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)."

References

ASTM Specification D1193, "Reagent Water," www.astm.org

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

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Trace Metals in Organics by ICP-OES

UOP Method 389-10

Scope

This method is for determining the concentrations of aluminum (Al), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), sodium (Na), strontium, (Sr), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn) in organic matrices such as crude petroleum, asphalts, vacuum tower bottoms, vacuum gas oils, atmospheric gas oils, diesel and jet fuels and their blending components, pyrolysis oils, and fatty acid derivatives by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The lower limits of quantitation for the above elements, except palladium, are listed in Table 1; see *Note*.

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Al	0.05	Li	0.03	Pb	0.04
Ca	0.08	Mg	0.04	Pt	0.01
Co	0.02	Mn	0.01	Sn	0.10
Cr	0.04	Mo	0.01	Sr	0.01
Cu	0.01	Na	0.04	Ti	0.03
Fe	0.09	Ni	0.03	V	0.01
K	0.05	P	0.11	Zn	0.03

Determination of additional elements is possible if they are not volatilized during the ashing step and do not form insoluble sulfates. Two different reagents are used in sample preparation, depending upon the sample matrix.

Alternatively, some of the elements listed above may be analyzed by Atomic Absorption Spectroscopy (AAS). See UOP Method 391, "Trace Metals in Petroleum Products or Organics by AAS," for specific metals and their range of quantitation. Metals known to be non-volatile may be analyzed by UOP Method 407, "Trace Metals in Organics by Dry Ashing - ICP-OES."

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UOP Method 407, "Trace Metals in Organics by Dry Ashing - ICP-OES," www.astm.org

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UOP Method 389-10

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IP 547/07 BSI BS EN 14538 : 2006 BS 2000-547 : 2006

EUROPEAN STANDARD **EN 14538**

NORME EUROPÉENNE

EUROPÄISCHE NORM June 2006

ICS 67.200.10

English version

Fat and oil derivatives — Fatty acid methyl ester (FAME) — Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES)

Produits dérivés des corps gras - Esters méthyliques d'acides gras (EMAG) - Détermination de la teneur en Ca, K, Mg et Na par spectrométrie d'émission optique avec plasma à couplage inductif (ICP OES)

Erzeugnisse aus pflanzlichen und tierischen Fetten und Ölen - Fettsäure-Methylester (FAME) - Bestimmung von Ca, K, Mg und Na durch optische Emissionsspektralanalyse mit induktiv gekoppeltem Plasma (ICP OES)

This European Standard was approved by CEN on 10 May 2006.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Spain, Sweden, Switzerland and United Kingdom.

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 14538:2006 E

547.1

IP 587/11 BSI BS EN 15944 : 2010 BS 2000 : 587 : 2010

EUROPEAN STANDARD **EN 15944**

NORME EUROPÉENNE

EUROPÄISCHE NORM November 2010

ICS 75.100

English Version

Liquid petroleum products - Determination of nickel and vanadium content - Inductively coupled plasma optical emission spectrometry method (ICP OES)

Produits pétroliers liquides - Détermination de la teneur en Nickel et vanadium - Méthode directement par spectrométrie d'émission atomique à couplage inductif par plasma (SOD-PCI)

Flüssige Mineralölerzeugnisse - Bestimmung des Gehaltes an Nickel und Vanadium - Optische Emissionsspektralanalyse mit induktiv gekoppeltem Plasma (ICP OES)

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 15944:2010: E

587.1

IP 592/11

Determination of lead, nickel, chromium, copper, zinc, arsenic, cadmium, thallium, antimony, cobalt, manganese and vanadium in burner fuels derived from waste mineral oils — Inductively coupled plasma mass spectrometry method

1 Scope

This standard specifies a method for the determination of the concentration of lead, nickel, chromium, copper, zinc, arsenic, cadmium, thallium, antimony, cobalt, manganese and vanadium present in burner fuels derived from waste mineral oils, by inductively coupled plasma mass spectrometry (ICPMS).

Element	Range mg/kg
Vanadium	1-6
Nickel	1-6
Zinc	20-900
Lead	1-50
Cadmium	1-6
Antimony	1-6
Thallium	1-6
Manganese	1-20
Arsenic	1-6
Cobalt	1-6
Chromium	1-6
Copper	3-70

NOTE 1 — For the purposes of this standard, the terms "% (m/m)" and "% (V/V)" are used to represent respectively the mass fraction and the volume fraction.

NOTE 2 — This procedure presents concentrations of elements and internal standards to the instrument generally in the 1 ng/g to 50 ng/g range. Both higher and lower concentrations of elements in samples can be measured by this method. The low concentration limits are dependent on the sensitivity of the ICPMS instrument, the dilution factor and the cleanliness of the reagents and equipment used for the sample digestion. The high concentration limits are determined by the product of the maximum concentration of analyte used for the calibration, and the sample dilution factor.

Note 3 — The description of waste mineral oils that are acceptable inputs for the production of Processed Fuel Oil is given in Appendix B of the Environment Agency's Quality Protocol for Processed Fuel Oil.

WARNING — The use of this standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety and environmental problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health and environmental practices and determine the applicability of regulatory limitations prior to use.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IP 475, *Manual sampling.*

3 Principle

A test portion is digested with nitric acid in a sealed quartz or PTFE vessel in a microwave oven. The solution is diluted with high purity water and introduced into an ICP mass spectrometer by use of a peristaltic pump, and the count rates for specified isotopes of the elements of interest are measured. Element concentrations are determined from calibration curves prepared from solutions of multi-element standards in 2 % nitric acid, analysed in the same manner as the samples. A multi-element internal standard is used to compensate for matrix effects and/or instrument drift. The multi-element internal standard may be added to the sample solutions and standards or added on-line to the ICPMS instrument using the peristaltic pump.

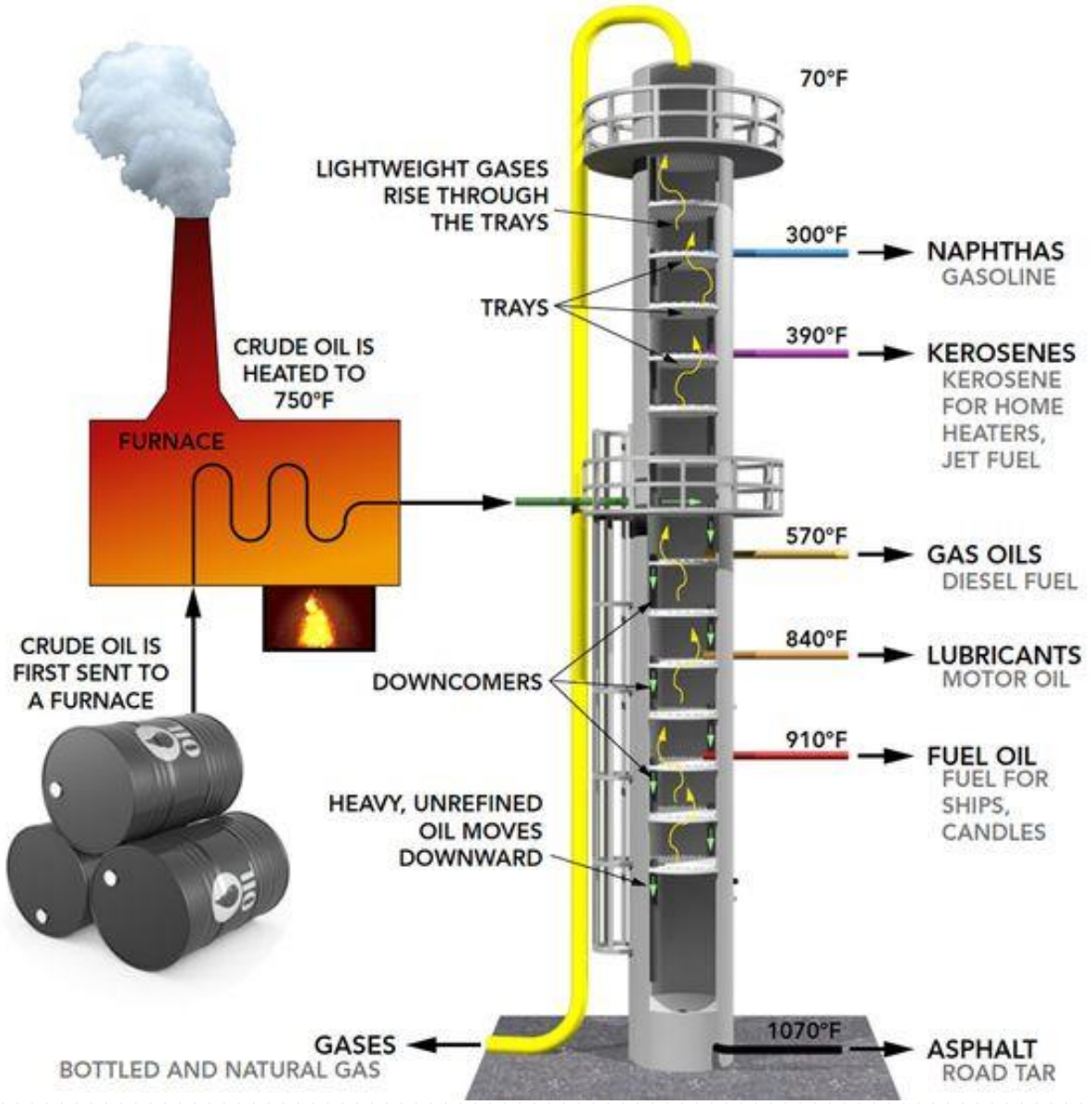
592.1

What's the importance of quality crude oil?

ASTM D7691

Trace elements in crude oil can have an adverse effect.

- Refractory damage in furnace from Vanadium compound.
- Catalysts poisoned such as Iron, Lead, and Arsenic.
- Excessive atmospheric emission in combustion fuel.
- Superficial fusion on the fire brick by concentrating sodium compound.
- Some organometallic compounds are volatile which can lead to the contamination of distillate fractions and a reduction in their stability or malfunctions of equipment when combusted.



Why should we analyze Lubricating oils?

ASTM D4951

Detergents

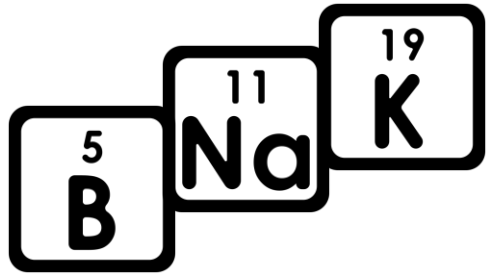
Antioxidants

Antiwear agents

To achieve the specification of the lubricating product determine!!

Why should we analyze used Lubricating oils?

ASTM D5185



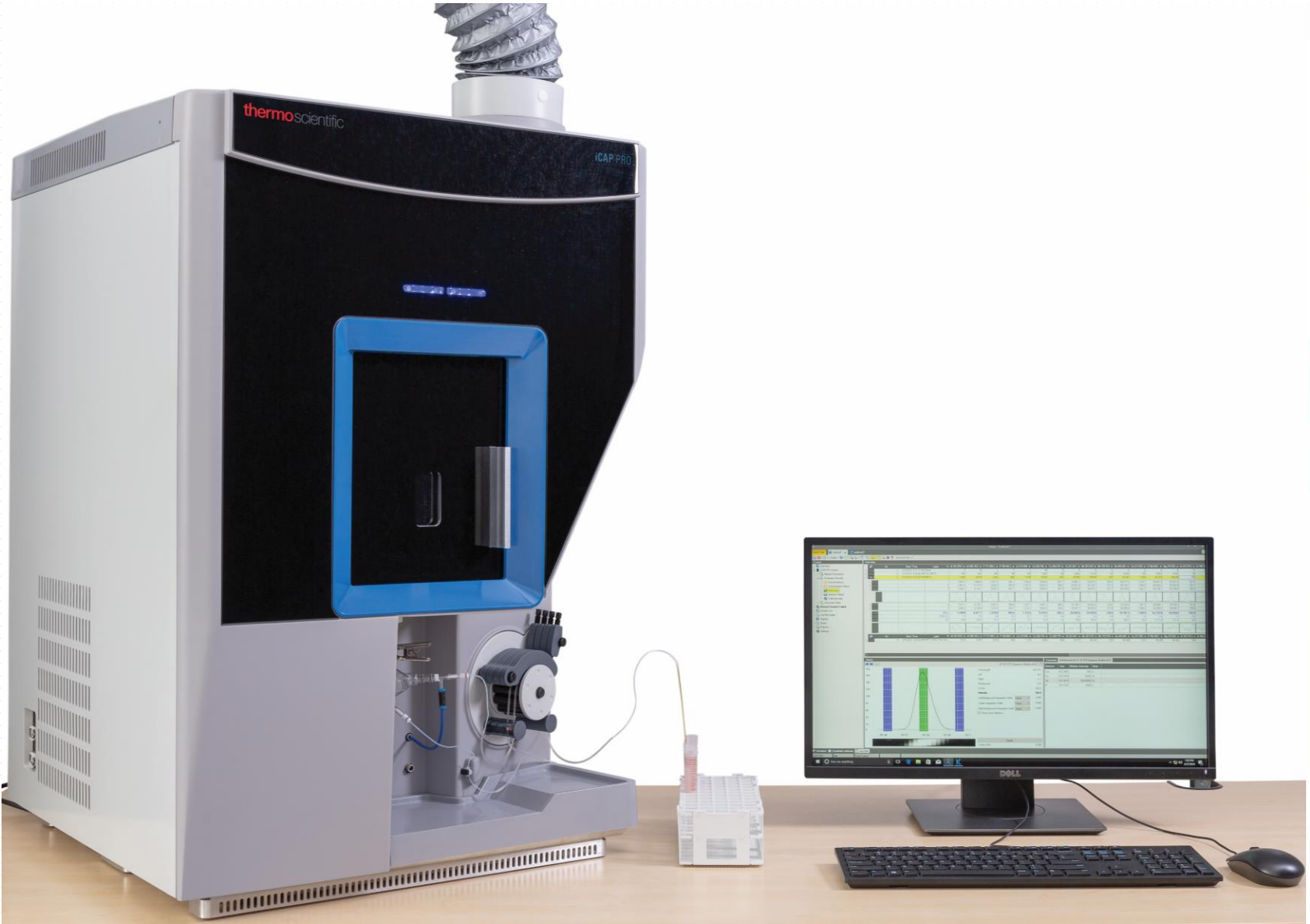
ASTM D7111

The impact of contamination in Middle Distillation fuels?

What is the effect of the contaminant in light and middle distillate fuels

ASTM D8110

- Petroleum condensate and naphtha are derived products from crude oils.
- Petroleum condensate and naphtha are important raw materials for the petrochemical industry. It use in production of ethylene, propene, benzene, toluene, and xylenes.
- Naphtha is a colorless liquid that comprises a mixture of paraffinic, olefinic, naphthenic and aromatic with 5 to 15 carbon atom.
- The petrochemical naphtha can be obtained from direct distillation of petroleum.
- It's very important feedstock for gasoline formulation.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iCAP PRO


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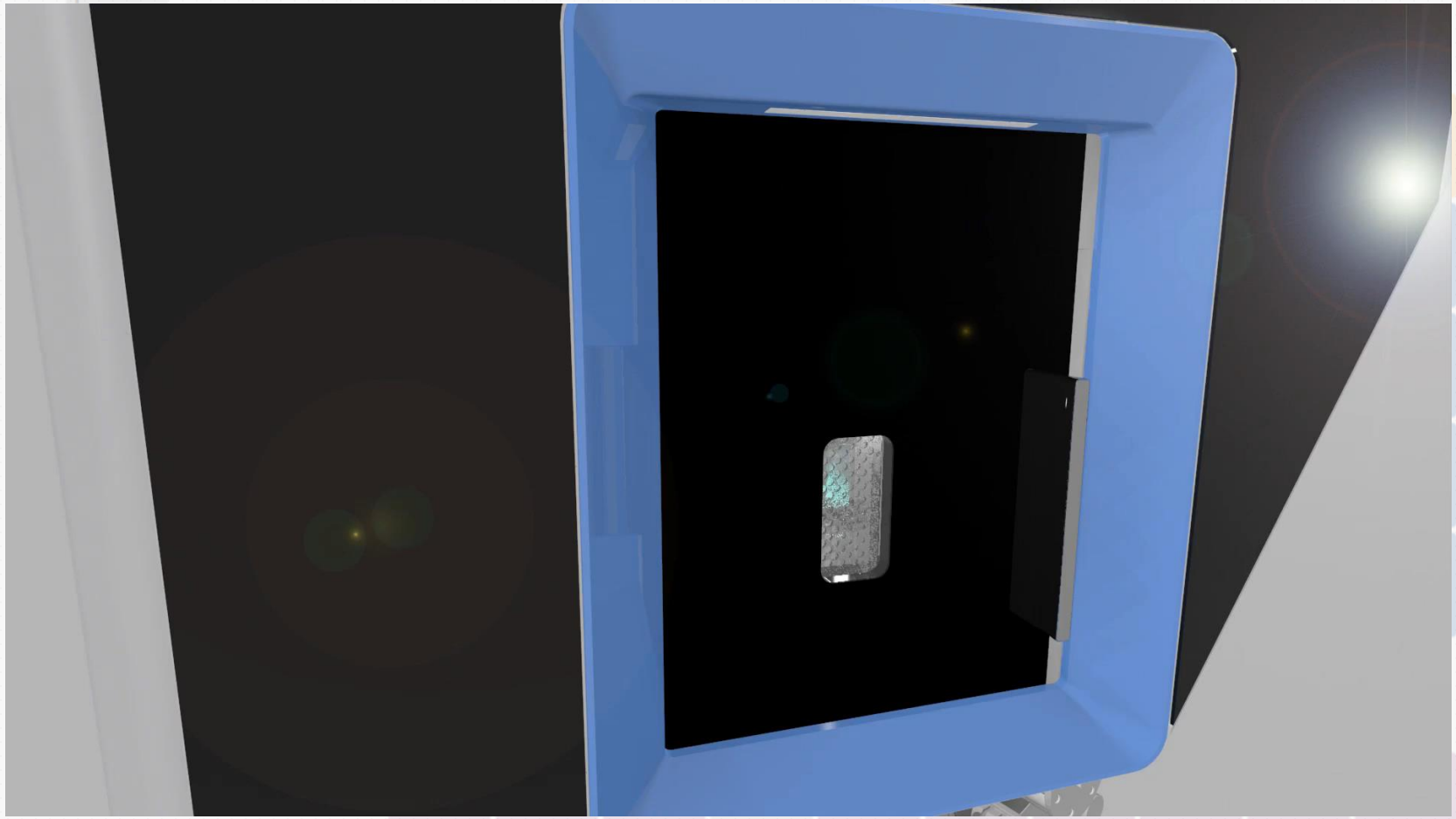
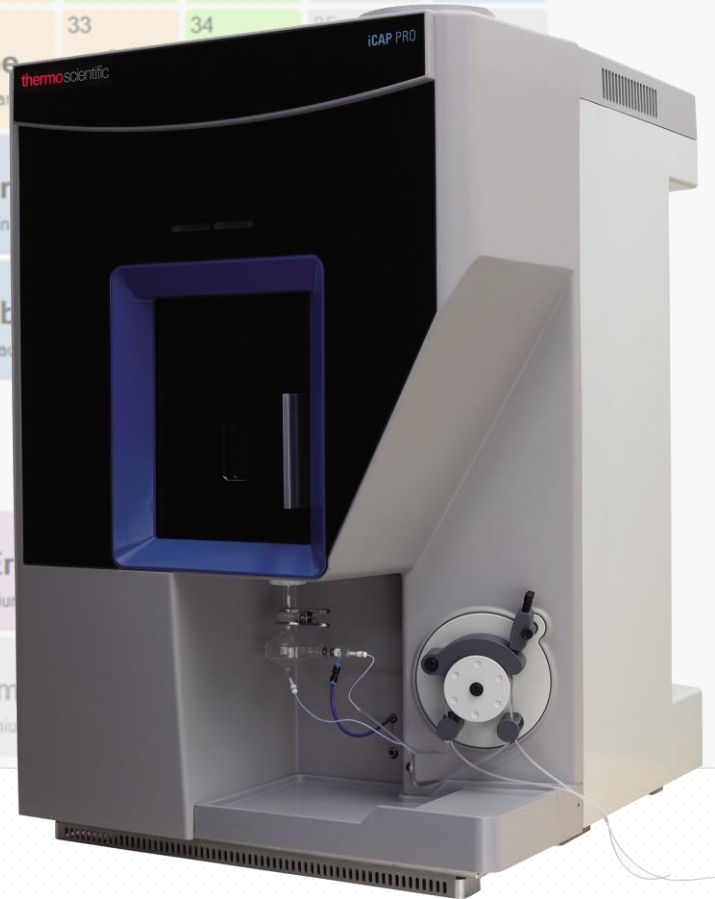
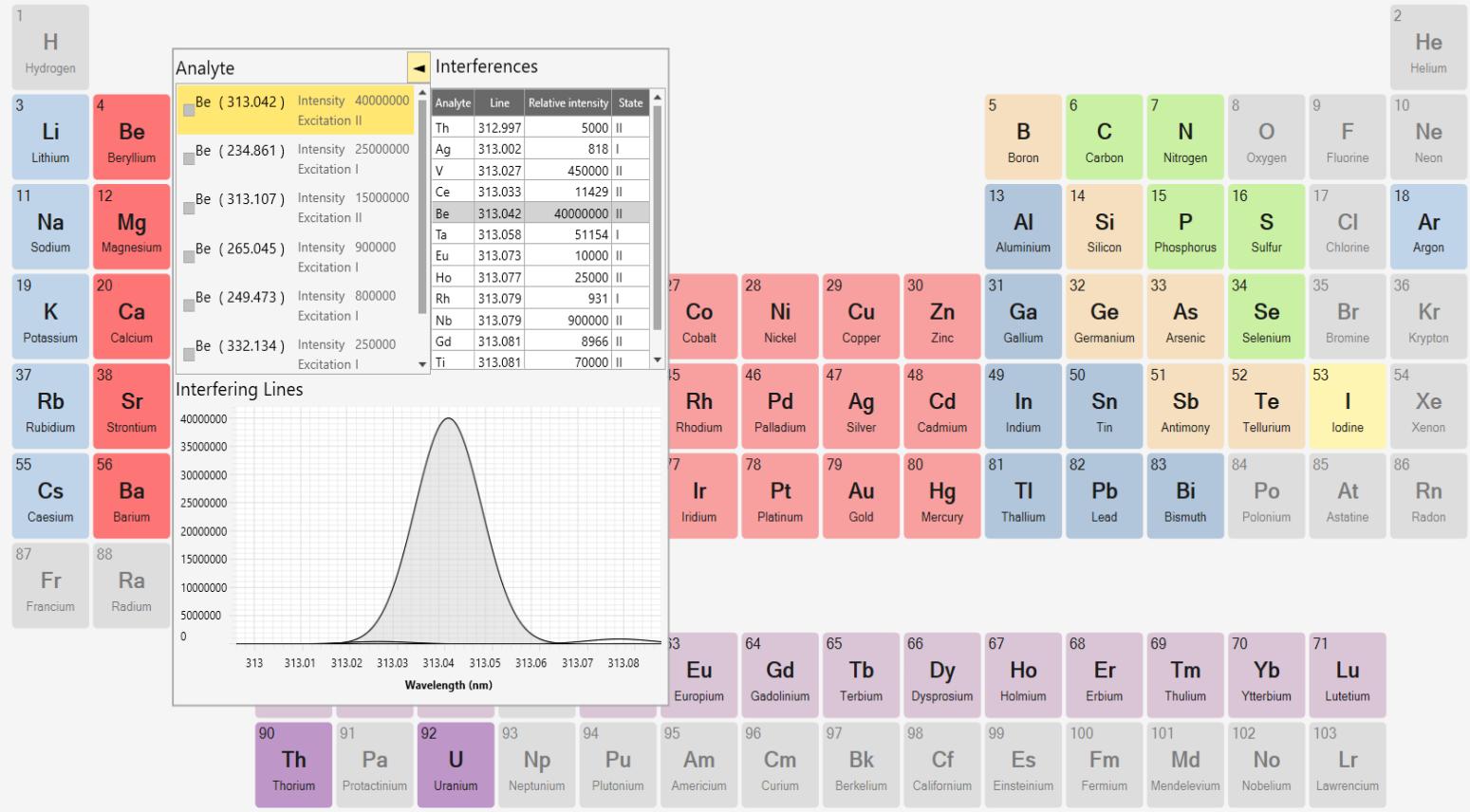
iCAP RQplus

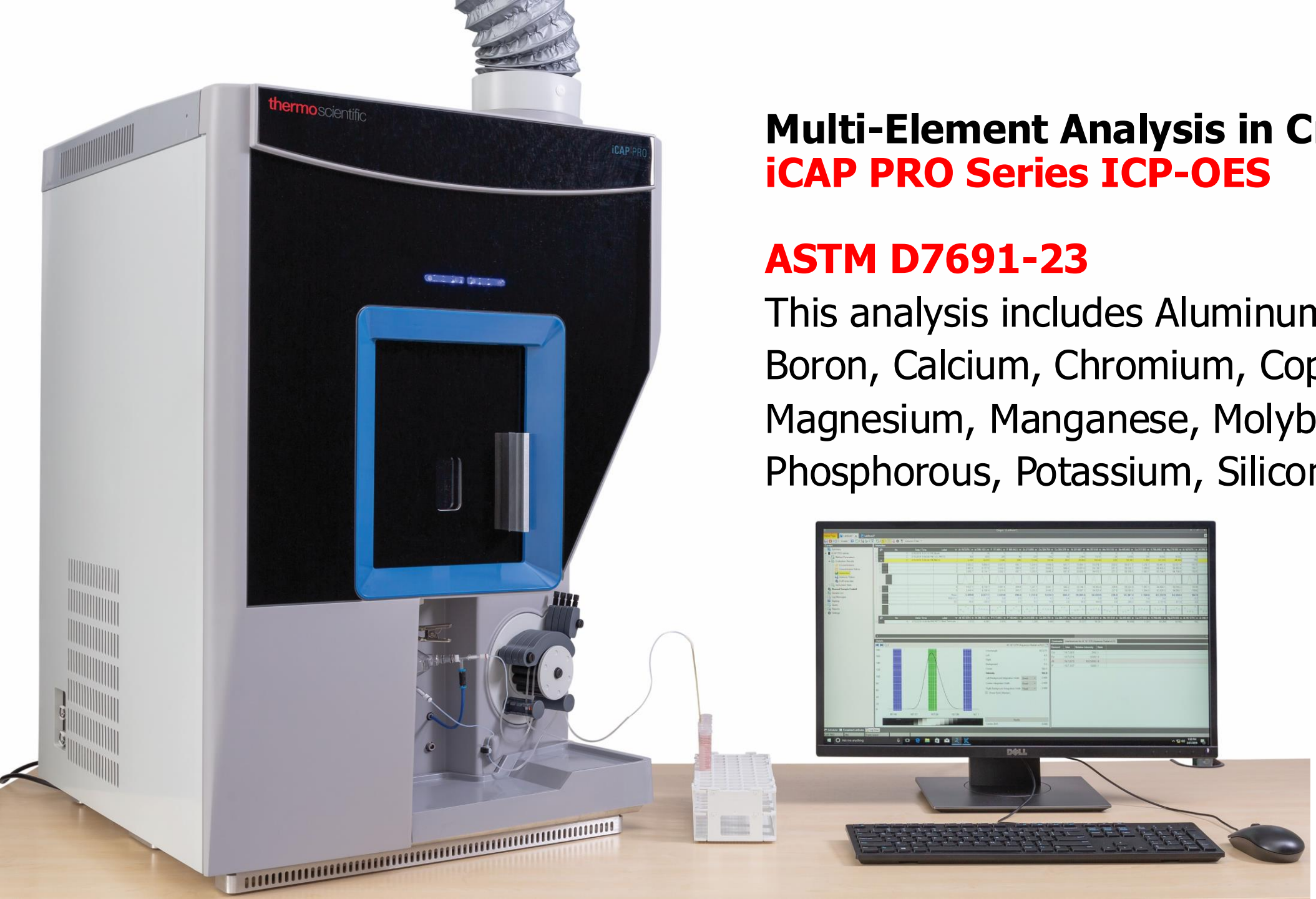



iCAP PRO
thermoscientific

Analytes



CID Detector



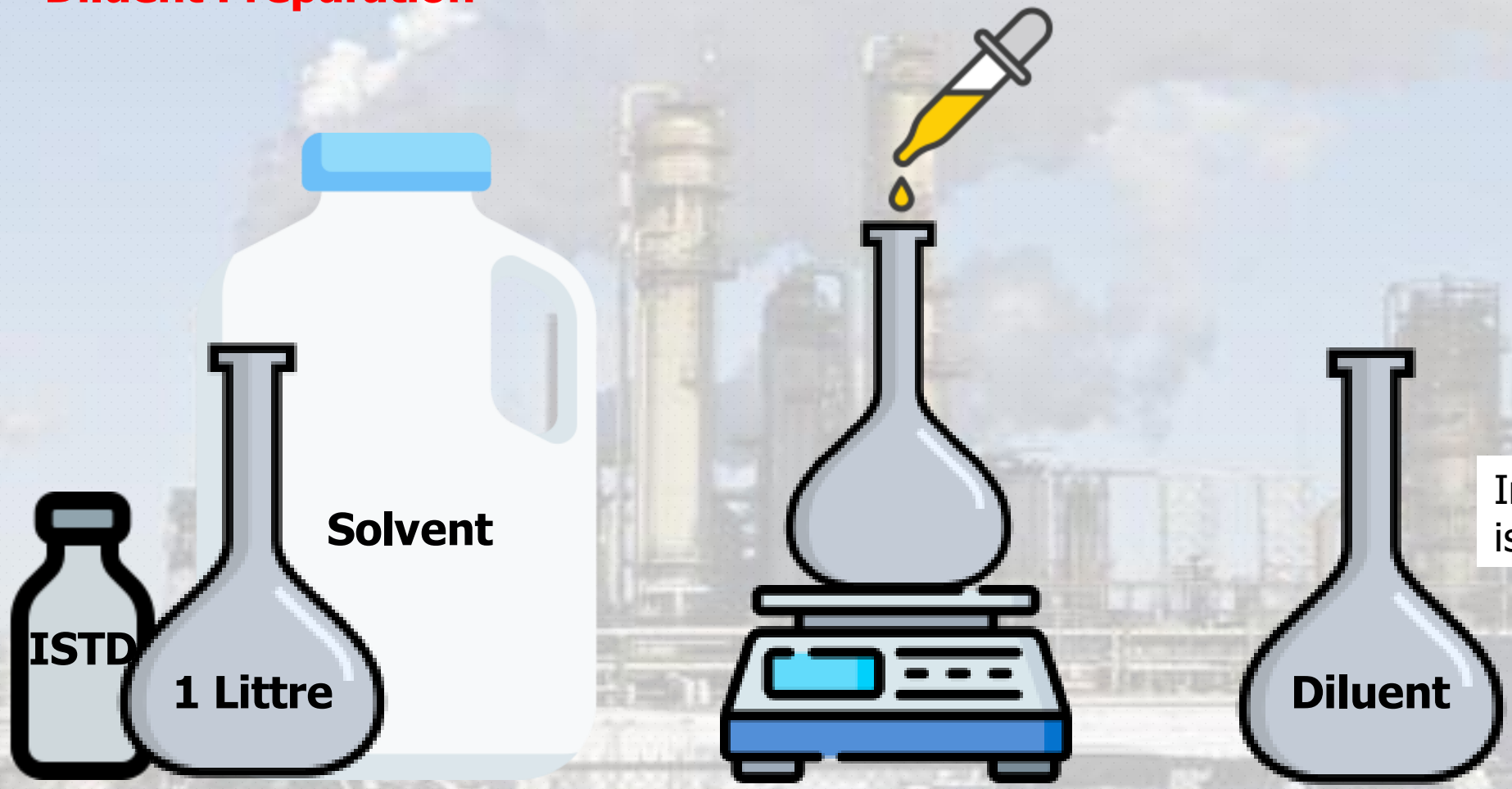
Multi-Element Analysis in Crude Oils by iCAP PRO Series ICP-OES

ASTM D7691-23

This analysis includes Aluminum, Barium, Boron, Calcium, Chromium, Copper, Lead, Magnesium, Manganese, Molybdenum, Phosphorous, Potassium, Silicon, Zinc

ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

Diluent Preparation

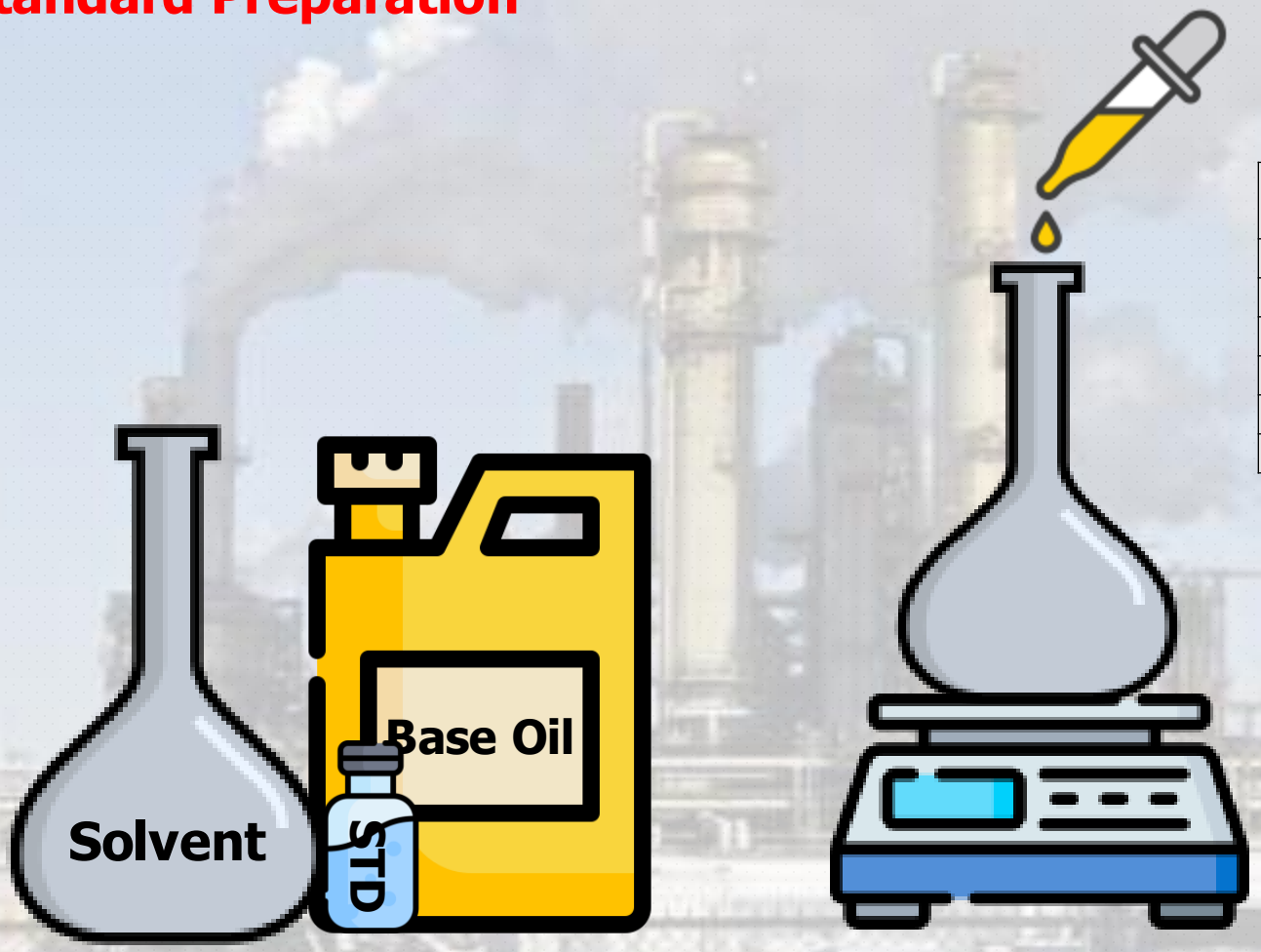


Internal Standard concentration is about 10 – 20 mg/kg

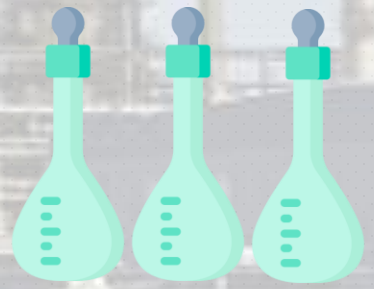
ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

Standard Preparation

- **Standard x grams**
- **Base oil 4x from standard**
- **Diluent 45x from standard**



Calibration point	Organometallics Standard (g)	Base oil (g)	Diluent (g)	Final concentration (mg/kg)
1	0.20	5	50	2
2	0.40	5	50	4
3	0.60	5	50	6
4	0.80	5	50	8
5	1.00	5	50	10
QC	0.50	5	50	5



ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

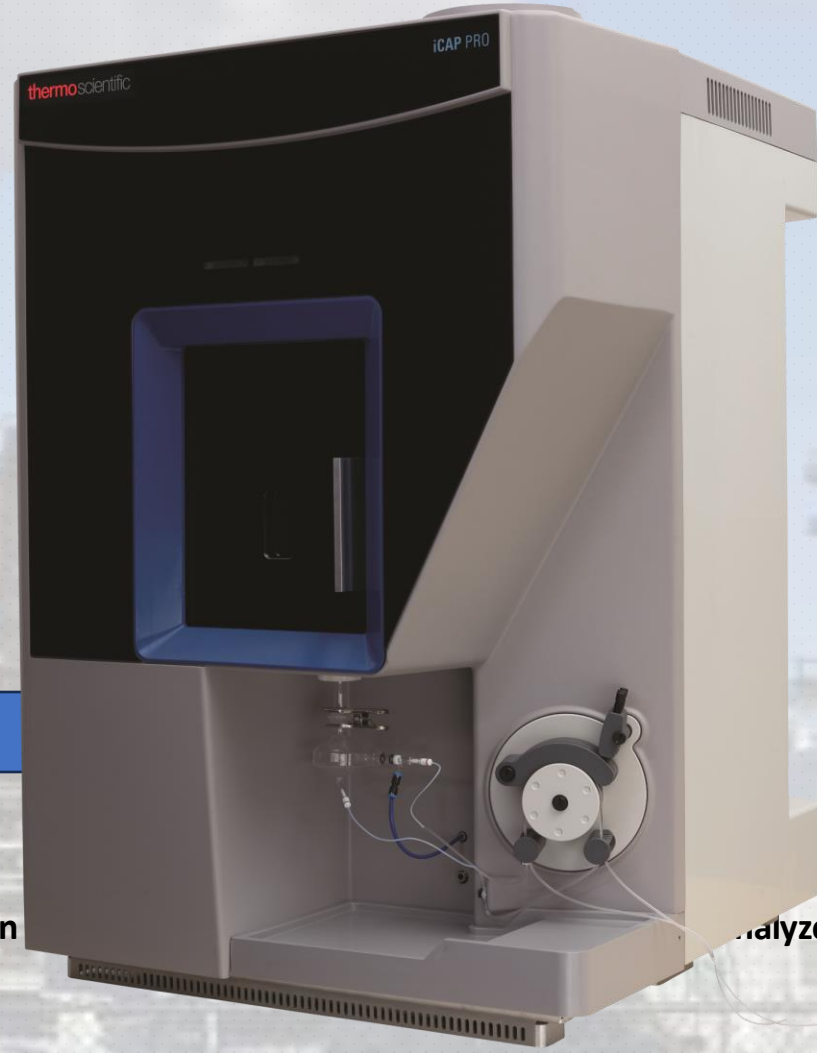
Sample handling and preparation

*** It is not required when the sample is at a low pour point.***

50 – 60 °C

Heat the specimen at 50 – 60 °C

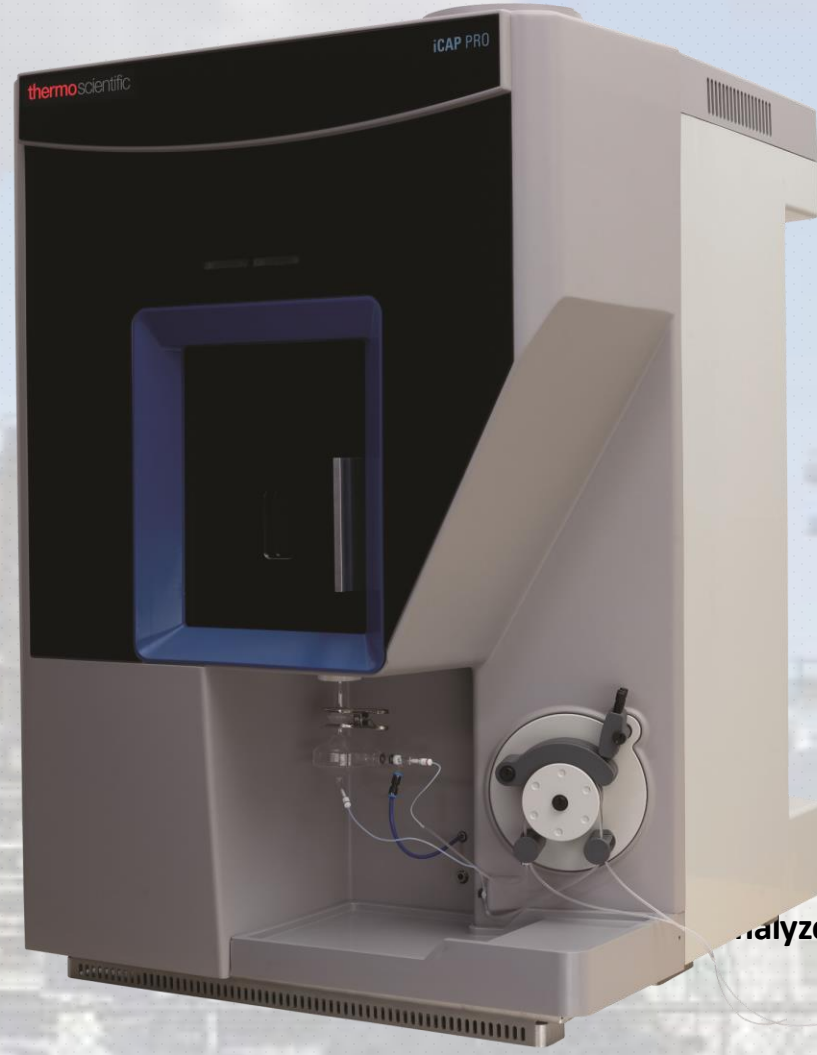
Mix to homogenize the specimen



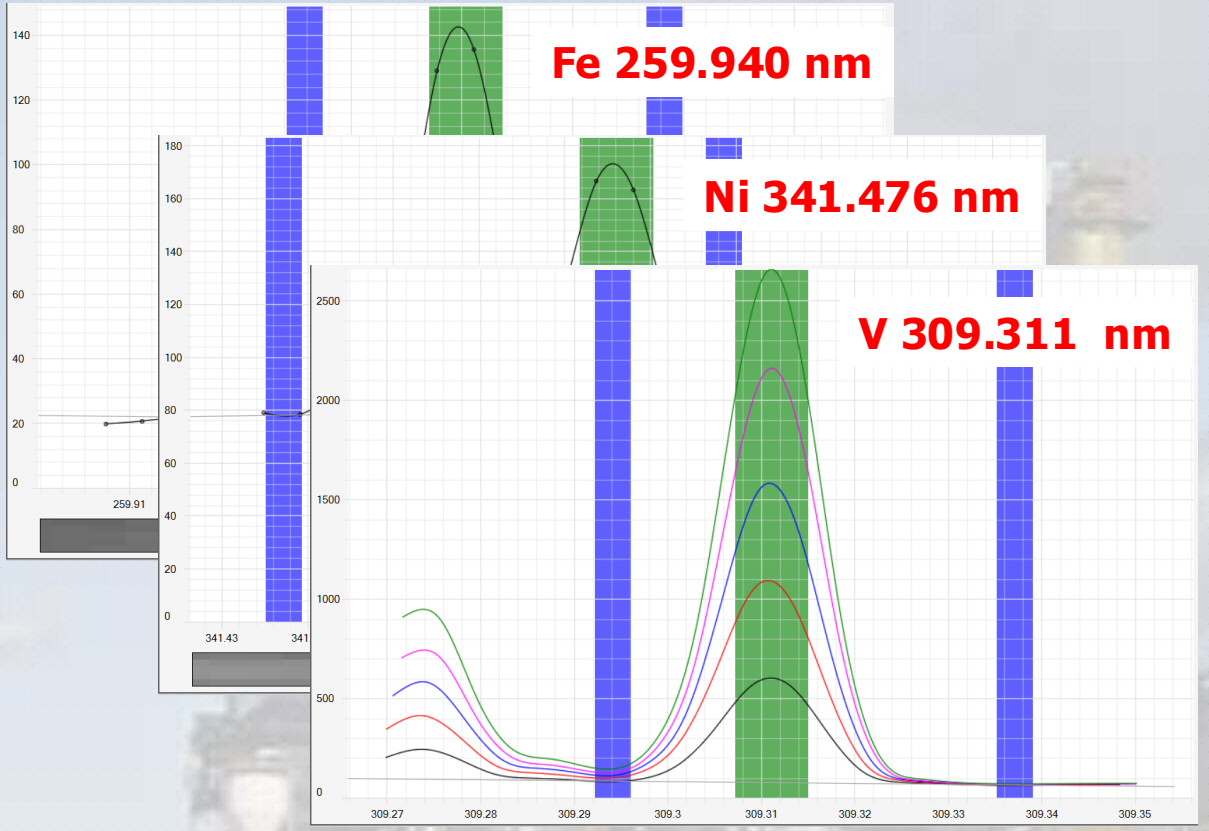
ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

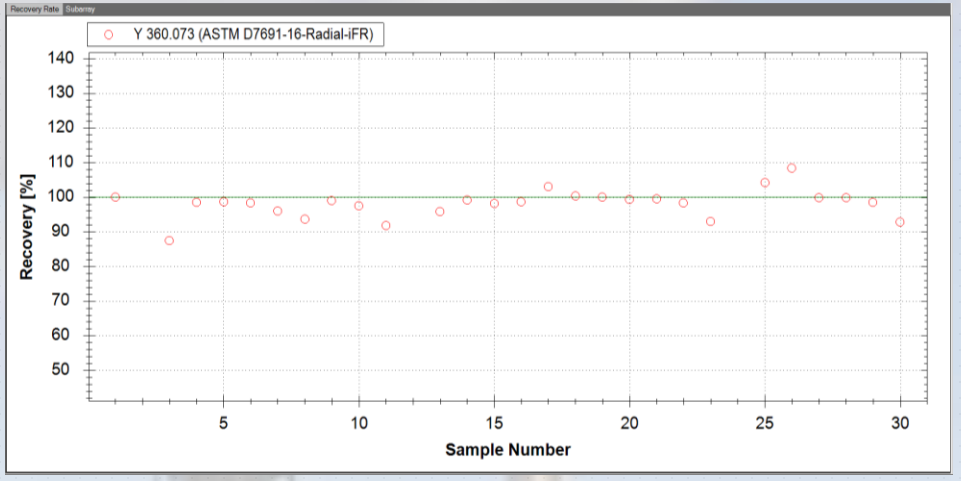
Operating and Method parameter

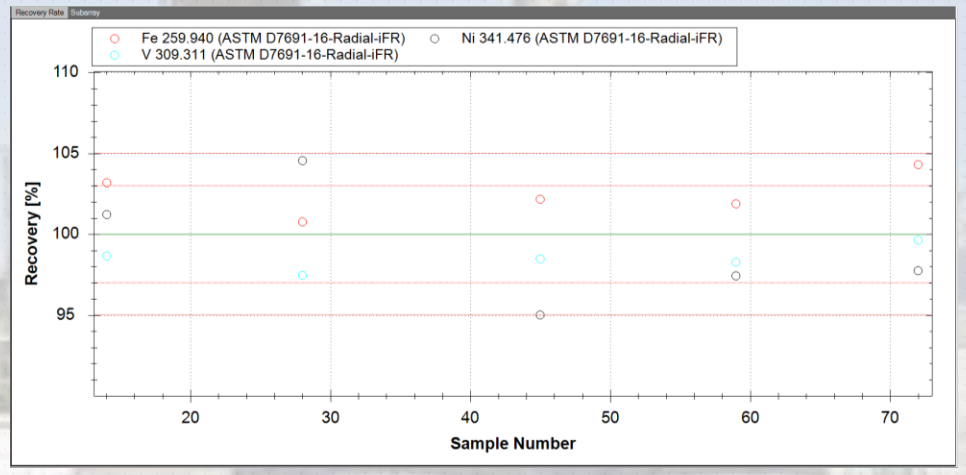
Torch	Quartz torch
Nebulizer	V-groove nebulizer
Spray chamber	Organic Spray chamber
Injector	Quartz 1.0 mm ID
Sample tube	Viton pump tube 0.54 mm ID (Orange/White)
Drain tubing	Viton pump tube 1.02 mm ID (White/White)
Plasma RF power	1350 w
Coolant gas flow	14.5 L/min
Auxiliary gas flow	2.0 L/min
Nebulizer gas flow	0.65 L/min
Radial Viewing Height	10 mm



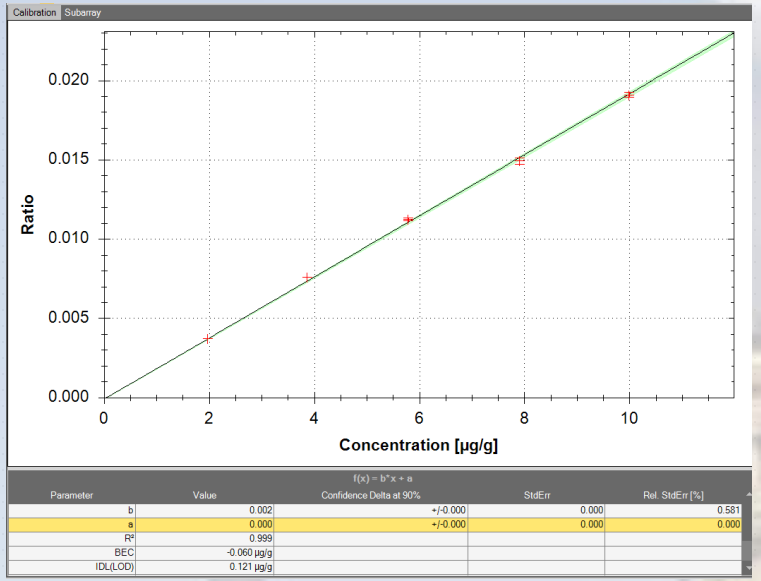
ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

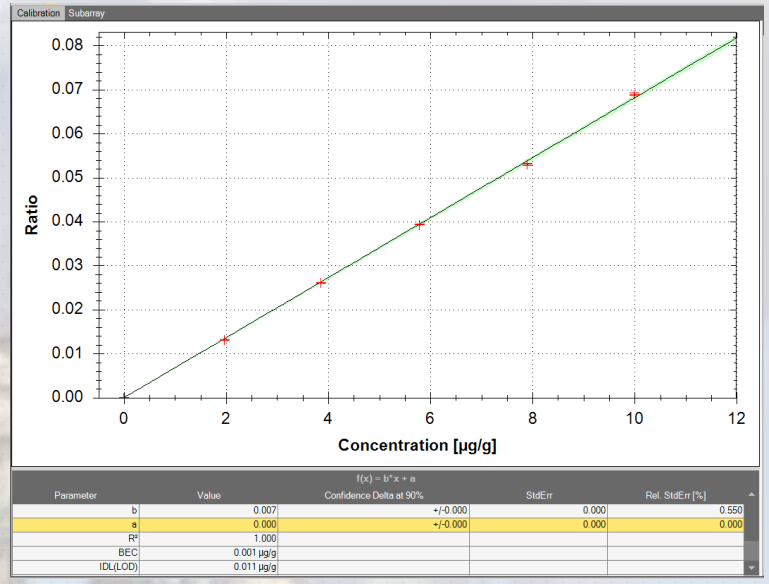


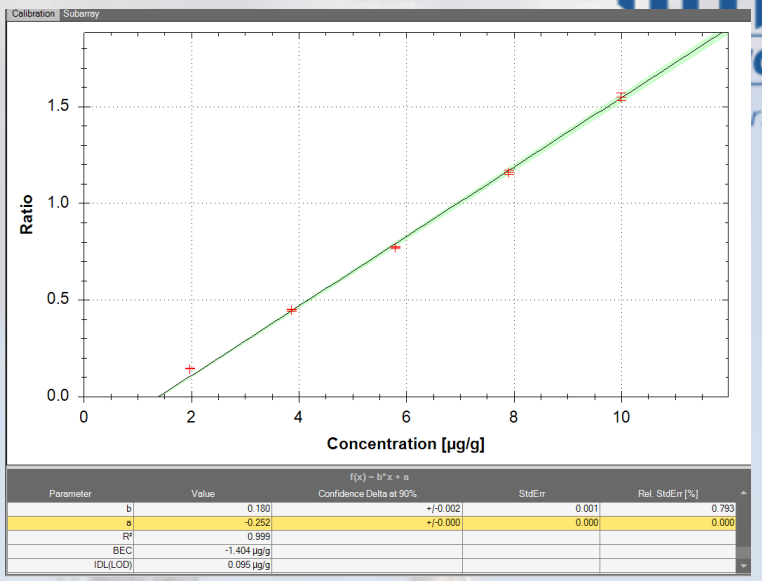


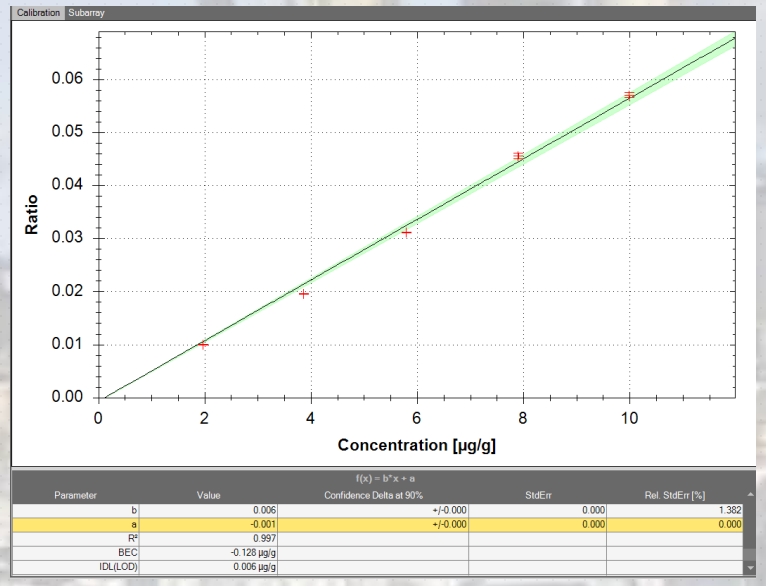


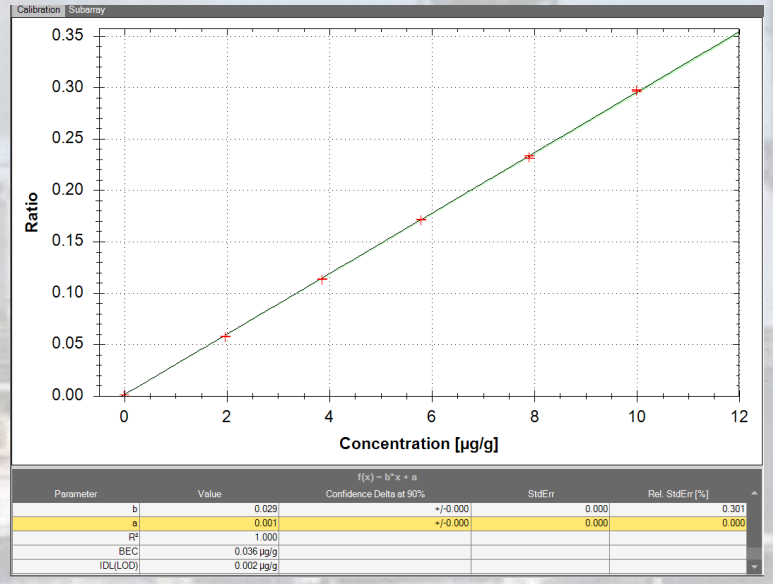
ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry











ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

Analyte	Wavelength (nm)	Viewing mode	LOD (mg/kg)	LOQ (mg/kg)
Al	396.152	Radial	0.006	0.021
Ca	315.887	Radial	0.071	0.237
Fe	259.940	Radial	0.007	0.025
Na	588.995	Radial	0.152	0.506
Ni	341.476	Radial	0.023	0.078
Si	288.158	Radial	0.028	0.093
V	309.311	Radial	0.007	0.022

LOD = 3SD of sample blank

(Repeat 3 times, 10 vial)

ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

Analyte	LOD (mg/kg)	LOQ (mg/kg)
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Na	0.152	0.506
Ni	0.023	0.078
Si	0.028	0.093
V	0.007	0.022

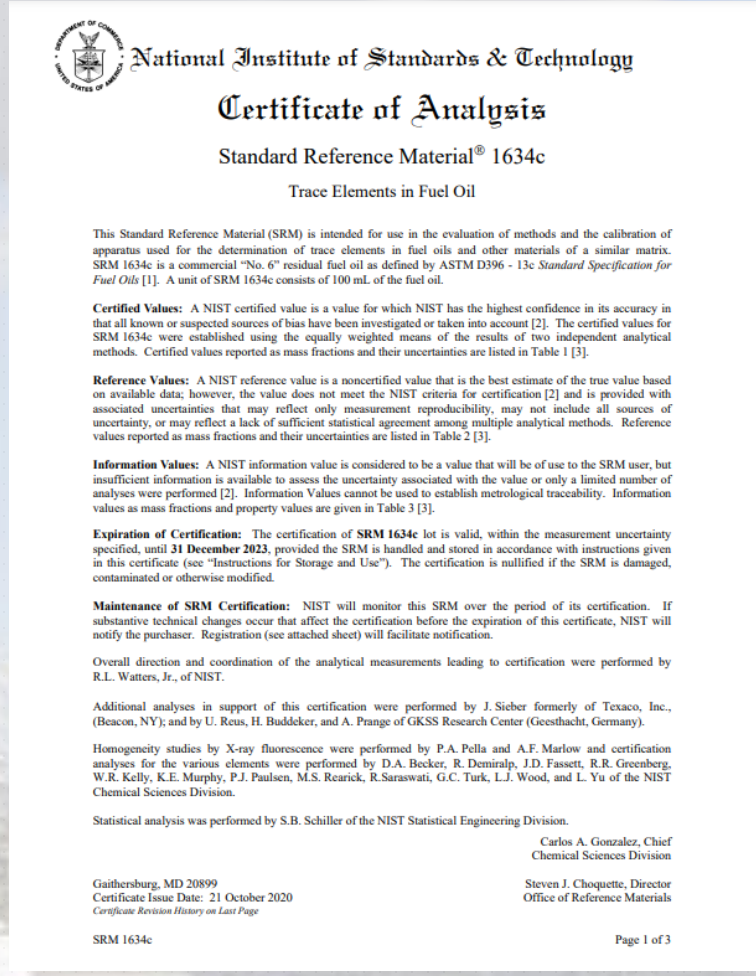
Element	mg/kg
Aluminum	1
Barium	0.2
Boron	1
Calcium	0.1
Chromium	0.1
Copper	0.1
Lead	1.4
Magnesium	1
Manganese	0.1
Molybdenum	0.2
Phosphorous	1
Potassium	0.5
Silicon	4
Zinc	0.5

ASTM D7691
Multi-Element Analysis of Crude Oils using Inductively Coupled Plasma Atomic Emission Spectrometry

Table 1. Certified Values

Element	Mass Fractions (mg/kg)	Methods of Analysis
Cobalt	0.1510 ± 0.0051	ICP-MS, INAA
Nickel	17.54 ± 0.21	ID-ICPMS, LEI
Vanadium	28.19 ± 0.40	ICP-AES, INAA

Analyte	Wavelength (nm)	Viewing mode	SRM 1634c (mg/kg)	Measured by ICP-OES	Recovery Percent
Ni	341.476	Radial	17.33 - 17.75	17.40	99.2
V	309.311	Radial	27.79 - 28.59	28.07	99.6



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1634c

Trace Elements in Fuel Oil

This Standard Reference Material (SRM) is intended for use in the evaluation of methods and the calibration of apparatus used for the determination of trace elements in fuel oils and other materials of a similar matrix. SRM 1634c is a commercial "No. 6" residual fuel oil as defined by ASTM D396 - 13c *Standard Specification for Fuel Oils* [1]. A unit of SRM 1634c consists of 100 mL of the fuel oil.

Certified Values: A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [2]. The certified values for SRM 1634c were established using the equally weighted means of the results of two independent analytical methods. Certified values reported as mass fractions and their uncertainties are listed in Table 1 [3].

Reference Values: A NIST reference value is a noncertified value that is the best estimate of the true value based on available data; however, the value does not meet the NIST criteria for certification [2] and is provided with associated uncertainties that may reflect only measurement reproducibility, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods. Reference values reported as mass fractions and their uncertainties are listed in Table 2 [3].

Information Values: A NIST information value is considered to be a value that will be of use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed [2]. Information Values cannot be used to establish metrological traceability. Information values as mass fractions and property values are given in Table 3 [3].

Expiration of Certification: The certification of **SRM 1634c** lot is valid, within the measurement uncertainty specified, until **31 December 2023**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Storage and Use"). The certification is nullified if the SRM is damaged, contaminated or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Overall direction and coordination of the analytical measurements leading to certification were performed by R.L. Watters, Jr., of NIST.

Additional analyses in support of this certification were performed by J. Sieber formerly of Texaco, Inc., (Beacon, NY); and by U. Reus, H. Buddeker, and A. Prange of GKSS Research Center (Geesthacht, Germany).

Homogeneity studies by X-ray fluorescence were performed by P.A. Pella and A.F. Marlow and certification analyses for the various elements were performed by D.A. Becker, R. Demiralp, J.D. Fassett, R.R. Greenberg, W.R. Kelly, K.E. Murphy, P.J. Paulsen, M.S. Rearick, R.Saraswati, G.C. Turk, L.J. Wood, and L. Yu of the NIST Chemical Sciences Division.

Statistical analysis was performed by S.B. Schiller of the NIST Statistical Engineering Division.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 21 October 2020
Certificate Revision History on Last Page

Steven J. Choquette, Director
Office of Reference Materials

SRM 1634c

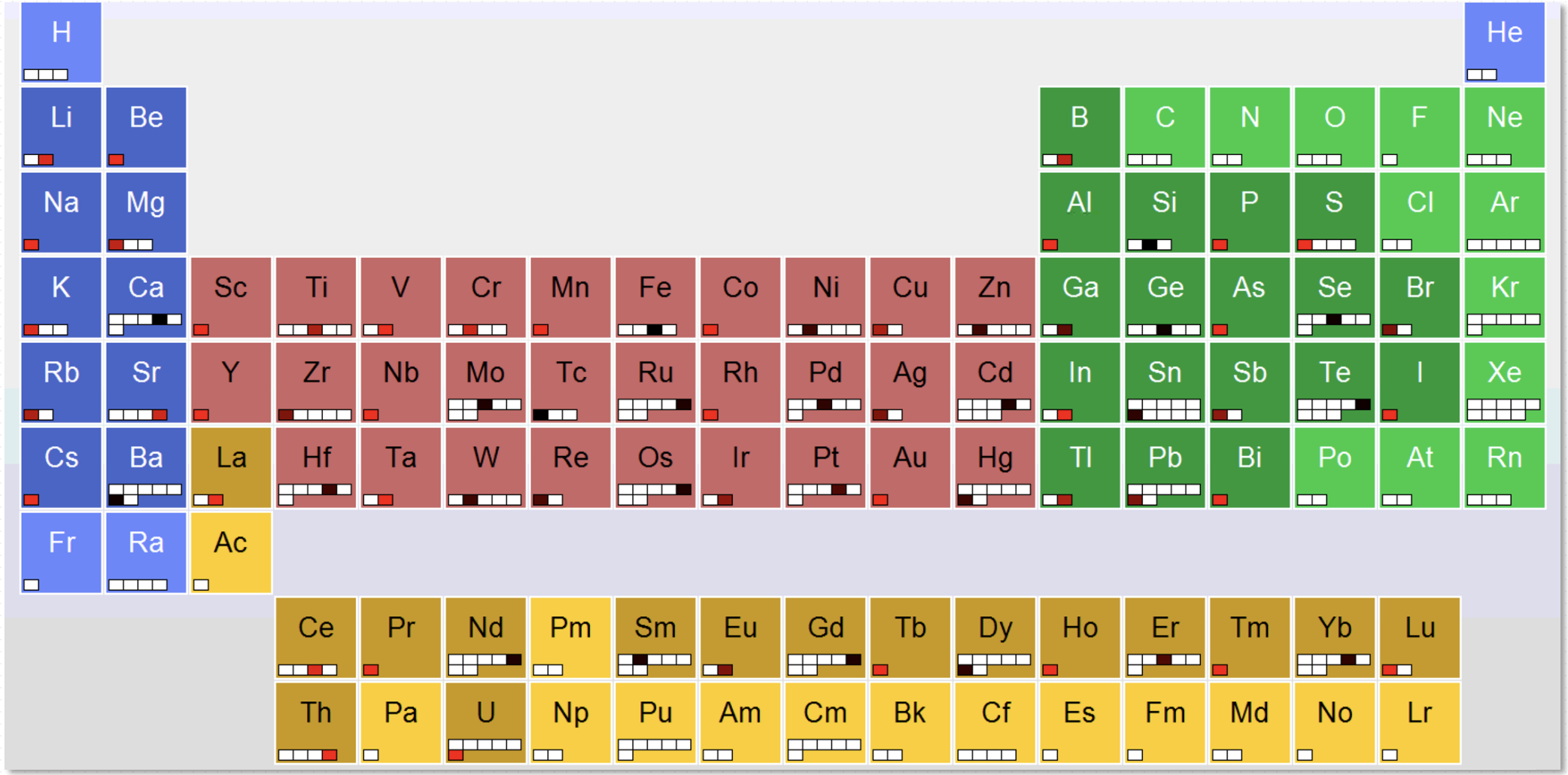
Page 1 of 3

Multi-Element Analysis of Distillate Products by iCAP RQplus

ASTM D8110-17

This analysis includes Aluminum, Arsenic, Calcium, Copper, Iron, Lead, Magnesium, Nickel, Potassium, Sodium, Vanadium

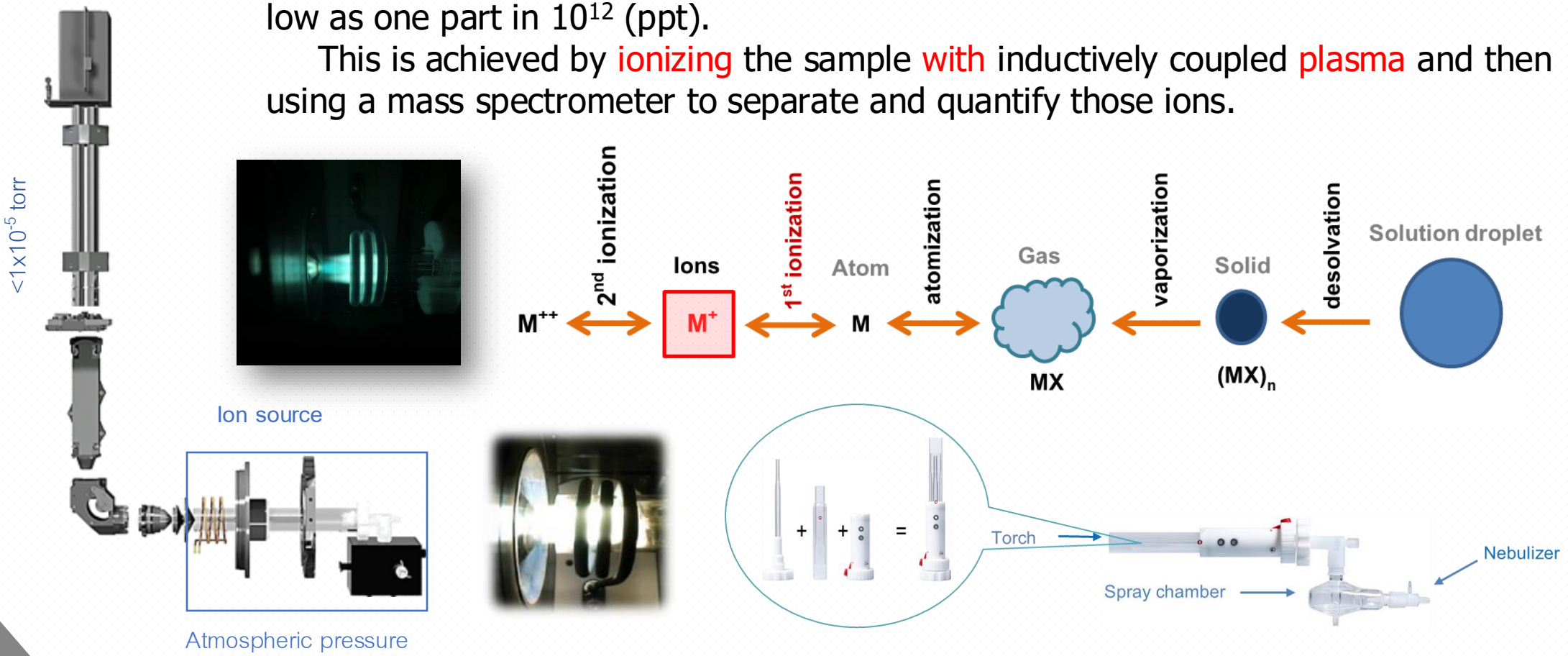
Element coverage of ICP-MS



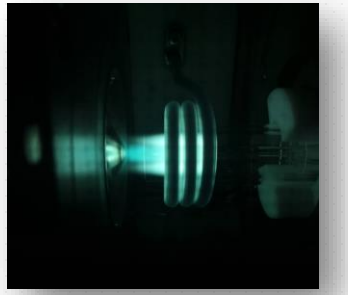
Ion generation in ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry which can detect metals and several non-metals at concentrations as low as one part in 10^{12} (ppt).

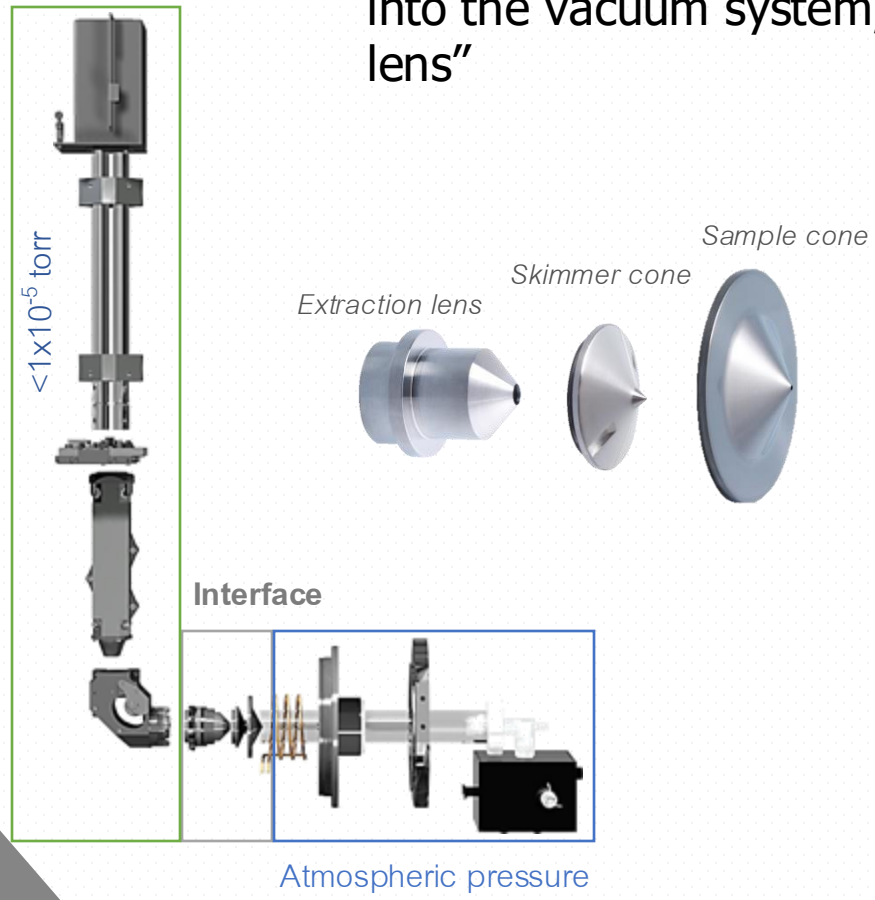
This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.



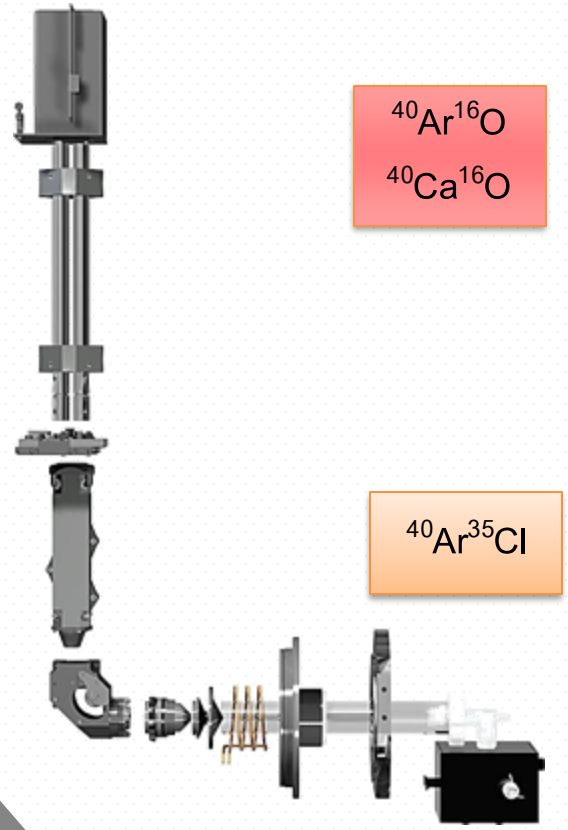
How to extract the ions into MS ?



The positively charged ions that are produced in the plasma are extracted into the vacuum system, via a pair of interface "cones" and the "extraction lens"

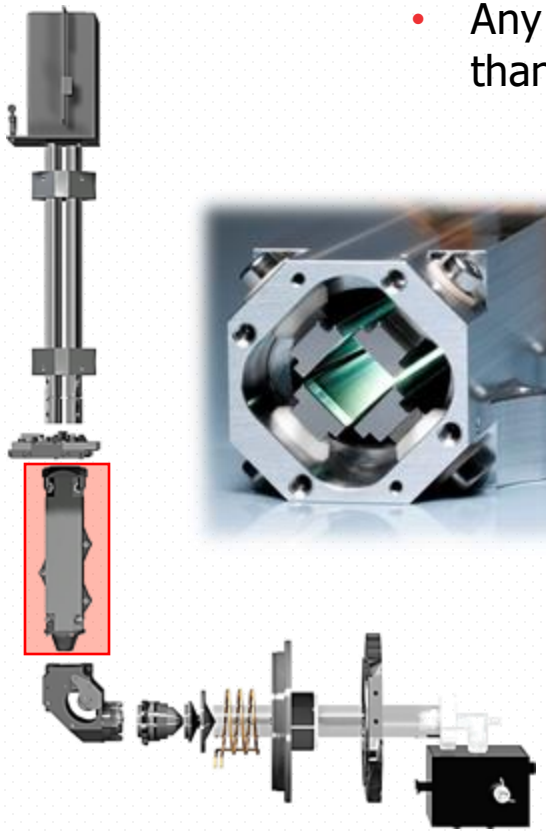


Polyatomic interference

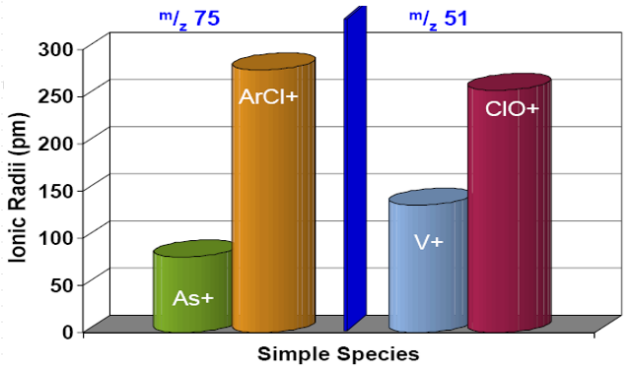


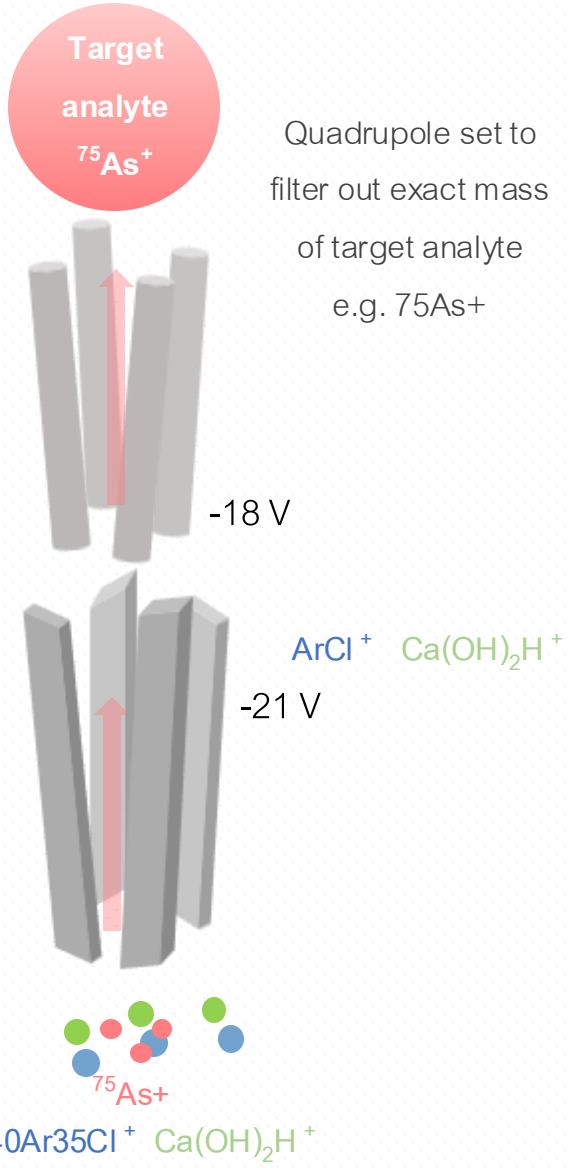
ANALYTE	POTENTIAL INTERFERENT	PRECURSORS
^{45}Sc	$^{13}C^{16}O_2$, $^{12}C^{16}O_2H$, ^{44}CaH, $^{32}S^{12}CH$, $^{32}S^{13}C$, $^{33}S^{12}C$	H, C, O,S, Ca
^{47}Ti	$^{31}P^{16}O$, ^{46}CaH, $^{35}Cl^{12}C$, $^{32}S^{14}NH$, $^{33}S^{14}N$	H, C, N, O, P, S, Cl, Ca
^{49}Ti	$^{31}P^{18}O$, ^{48}CaH, $^{35}Cl^{14}N$, $^{37}Cl^{12}C$, $^{32}S^{16}OH$, $^{33}S^{16}O$	H, C, N, O, P, S, Cl, Ca
^{50}Ti	$^{34}S^{16}O$, $^{32}S^{18}O$, $^{35}Cl^{14}NH$, $^{37}Cl^{12}CH$	H, C, N, O, S, Cl
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$	H, O, N, S, Cl
^{52}Cr	$^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{16}OH$, $^{37}Cl^{14}NH$, $^{34}S^{18}O$	H, C, O, N, S, Cl, Ar
^{55}Mn	$^{37}Cl^{18}O$, $^{23}Na^{32}S$, $^{23}Na^{31}PH$	H, O, Na, P, S, Cl, Ar
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	O, Ar, Ca
^{57}Fe	$^{40}Ar^{16}OH$, $^{40}Ca^{16}OH$	H, O, Ar, Ca
^{58}Ni	$^{40}Ar^{18}O$, $^{40}Ca^{18}O$, $^{23}Na^{35}Cl$	O, Na, Cl, Ar, Ca
^{59}Co	$^{40}Ar^{18}OH$, $^{43}Ca^{16}O$, $^{23}Na^{35}ClH$	H, O, Na, Cl, Ar, Ca
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$	O, Na, Cl, Ca
^{61}Ni	$^{44}Ca^{16}OH$, $^{38}Ar^{23}Na$, $^{23}Na^{37}ClH$	H, O, Na, Cl, Ca
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{12}C^{14}N^{37}Cl$, $^{31}P^{32}S$, $^{31}P^{16}O_2$	C, N, O, Na, P, S, Cl
^{64}Zn	$^{32}S^{16}O2$, $^{32}S_2$, $^{36}Ar^{12}C^{16}O$, $^{38}Ar^{12}C^{14}N$, $^{48}Ca^{16}O$	C, N, O, S, Ar, Ca
^{65}Cu	$^{32}S^{16}O2H$, $^{32}S_2H$, $^{14}N^{16}O^{35}Cl$, $^{48}Ca^{16}OH$	H, N, O, S, Cl, Ca
^{66}Zn	$^{34}S^{16}O$, $^{32}S^{34}S$, ^{33}S, ^{48}C, ^{18}O	O, C, S
^{69}Ga	$^{32}S^{18}O_2H$, $^{34}S_2H$, $^{37}Cl^{16}O_2$	H, O, S, Cl
^{70}Zn	$^{34}S^{18}O_2$, $^{35}Cl_2$	O, S, Cl
^{75}As	$^{40}Ar^{34}SH$, $^{40}Ar^{35}Cl$, $^{40}Ca\ ^{35}Cl$, $^{37}Cl_2H$	H, S, Cl, Ca, Ae
77Se	$^{40}Ar\ ^{37}Cl$, $^{40}Ca\ ^{37}Cl$	Cl, Ca, Ar
78Se	$^{40}Ar^{38}Ar$	Ar
80Se	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$, $^{32}S_2{}^{16}O$, $^{32}S^{16}O_3$	O, S, Ar, Ca

KED – Kinetic Energy Discrimination



- Any polyatomic species will have larger-cross section than single ions
- The larger poly-atomics will collide with the cell gas a greater number of times than the smaller analyte ions and lose energy
- Low energy ions cannot enter the mass analyzer





Impurities in Distillate Products using ICP-MS

This method was developed using the Thermo Scientific™ iCAP™ RQ ICP-MS .

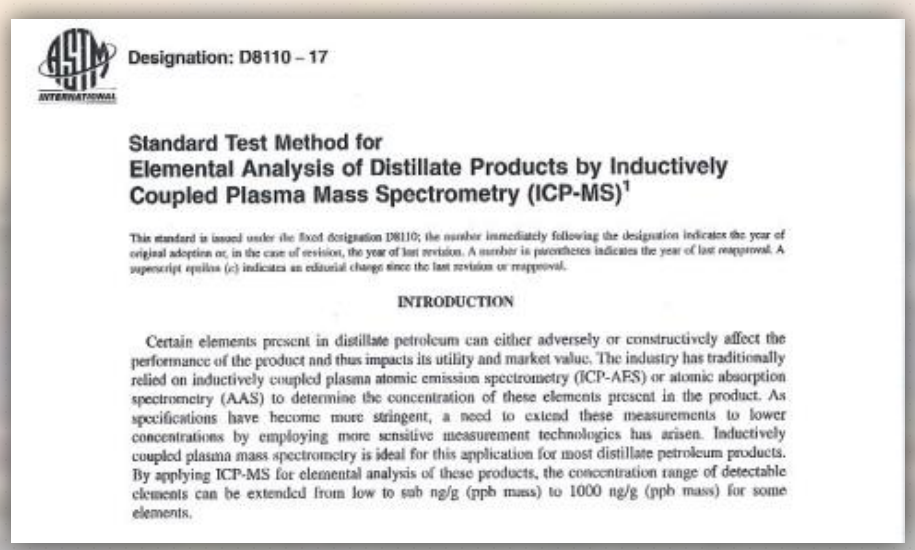
Direct Determination of Trace Metal Impurities in Condensate residue and Naphtha using ICP-MS

- Light Naphtha , Heavy Naphtha
  - As , Pb , Cu , Na , Fe , Ni , V , Ca

- Condensate residue
  - Si and As

Standard Method and Standard Reference Material (ASTM D 8110 – 17 & SRM 1634c)

Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)



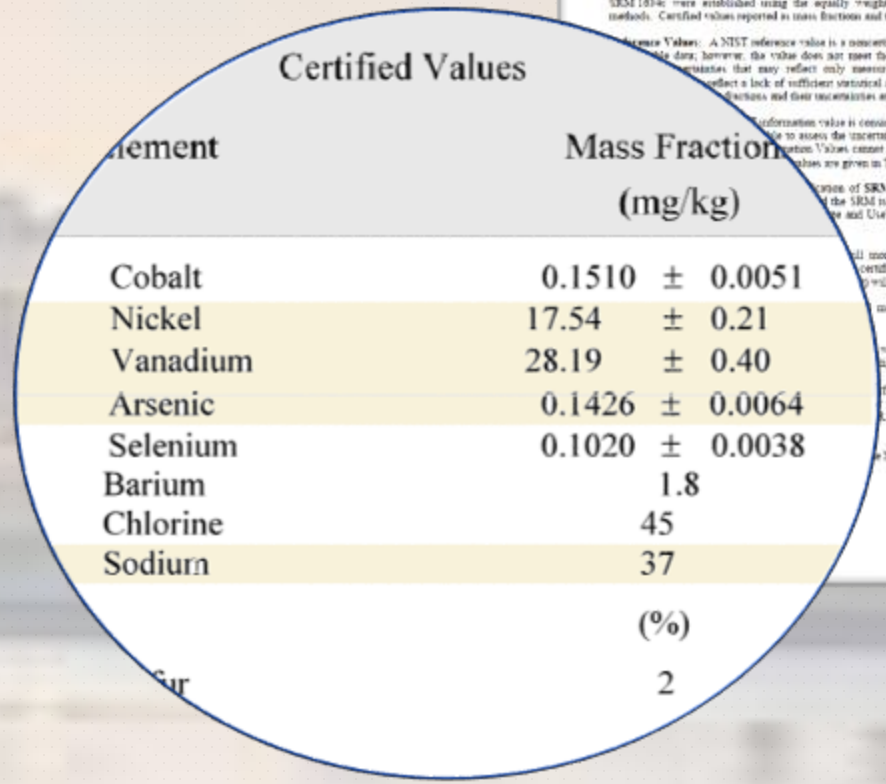
Designation: D8110 – 17

Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[1]

This standard is issued under the fixed designation D8110; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

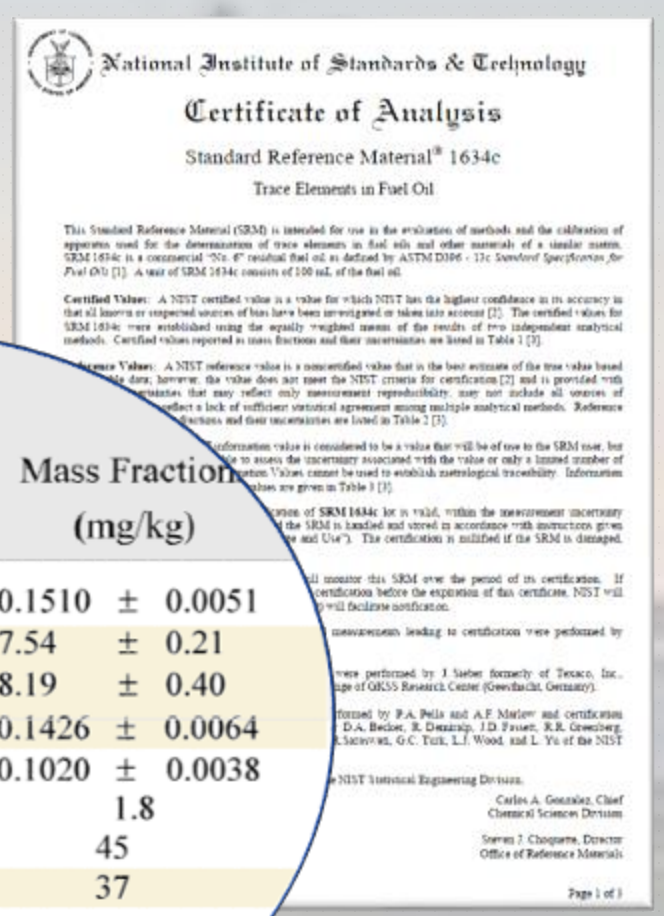
INTRODUCTION

Certain elements present in distillate petroleum can either adversely or constructively affect the performance of the product and thus impacts its utility and market value. The industry has traditionally relied on inductively coupled plasma atomic emission spectrometry (ICP-AES) or atomic absorption spectrometry (AAS) to determine the concentration of these elements present in the product. As specifications have become more stringent, a need to extend these measurements to lower concentrations by employing more sensitive measurement technologies has arisen. Inductively coupled plasma mass spectrometry is ideal for this application for most distillate petroleum products. By applying ICP-MS for elemental analysis of these products, the concentration range of detectable elements can be extended from low to sub ng/g (ppb mass) to 1000 ng/g (ppb mass) for some elements.



Certified Values

...lement	Mass Fraction (mg/kg)
Cobalt	0.1510 ± 0.0051
Nickel	17.54 ± 0.21
Vanadium	28.19 ± 0.40
Arsenic	0.1426 ± 0.0064
Selenium	0.1020 ± 0.0038
Barium	1.8
Chlorine	45
Sodium	37
	(%)
...fur	2



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1634c

Trace Elements in Fuel Oil

This Standard Reference Material (SRM) is intended for use in the evaluation of methods and the calibration of apparatus used for the determination of trace elements in fuel oils and other materials of a similar matrix. SRM 1634c is a commercial "No. 6" residual fuel oil as defined by ASTM D396 - 12c *Standard Specifications for Fuel Oils* [1]. A unit of SRM 1634c consists of 100 mL of the fuel oil.

Certified Values: A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [2]. The certified values for SRM 1634c were established using the equally weighted means of the results of two independent analytical methods. Certified values reported as mass fractions and their uncertainties are listed in Table 1 [3].

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...information value is considered to be a value that will be of use to the SRM user, but ...le to assess the uncertainty associated with the value or only a limited number of ...rtainty Values cannot be used to establish metrological traceability. Information ...alues are given in Table 3 [3].

...ration of SRM 1634c for is valid, within the measurement uncertainty ...f the SRM is handled and stored in accordance with instructions given ...ns and Use"). The certification is nullified if the SRM is damaged.

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...e NIST Statistical Engineering Division.

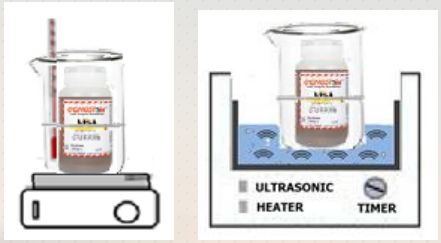
Carlos A. Gonzalez, Chief
Chemical Sciences Division

Steven J. Choquette, Director
Office of Reference Materials

Page 1 of 3

Sample Preparation Procedures

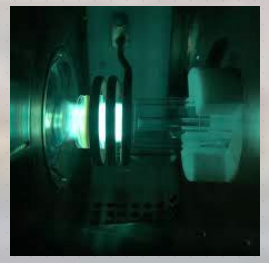
Measured density of Standards and Sample.



Before diluting, it's homogenized by sonication.
For very viscous oils, the sample can be pre-heated to 60 °C, 15 min.

Weighing the appropriate amount.

Vortex mixer to homogenized



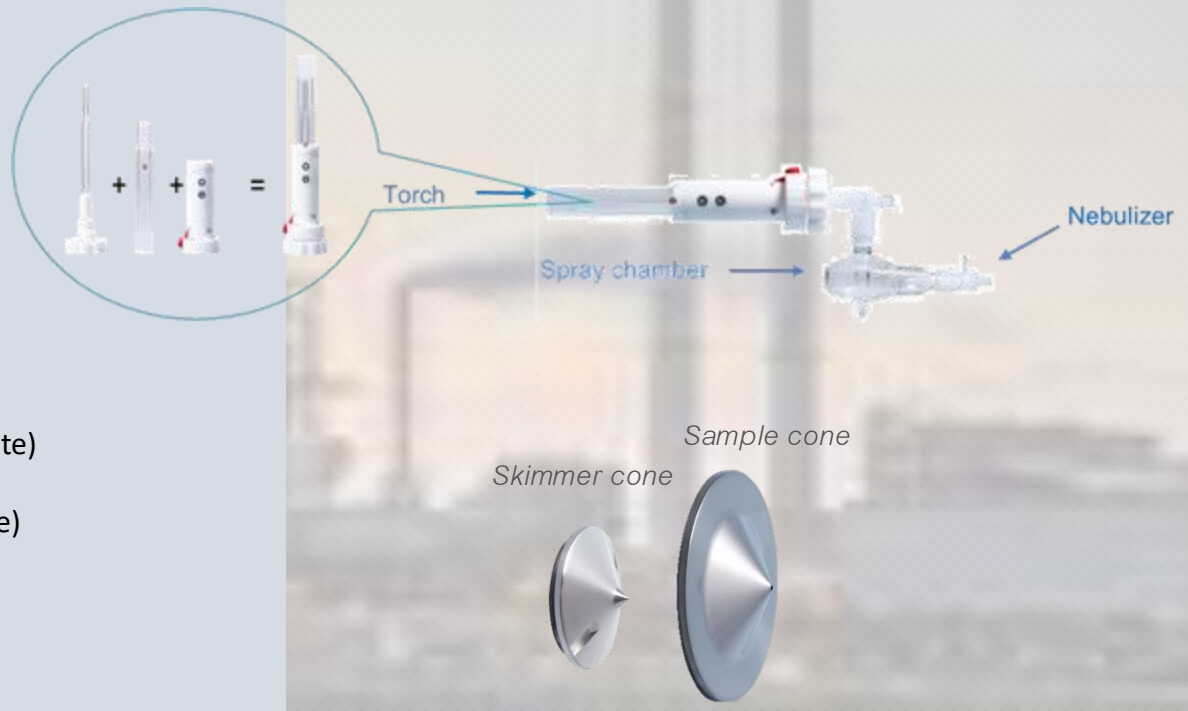
ICP-MS model iCAP RQ Thermo Scientific

Sample Preparation

- Standard / sample / oil-based was diluted (by weight) in o-xylene , p-xylene or premisolv
- For all samples and standards to ensure that differences in viscosity were minimized such as the final solution (std and sample) contained 10% oil (by weight)
- Add internal Standard into standards and samples, mix to homogenized.

Operating parameters of iCAP RQplus ICP-MS

Torch	Quartz torch organics
Torch	Quartz torch organics
Nebulizer	Micro Flow PFA-50 (Self Aspirating Teflon) (45-65 µL/min)
Spray chamber	Cyclonic Quartz
Injector	Quartz 1.0 mm ID
Interface	Pt Sample cone Pt Skimmer cone
Sample tube	Solvent Flex pump tube 0.51 mm ID (Orange/White)
Drain tubing	Solvent Flex pump tube 1.02 mm ID (White/White)
Plasma RF power	1550 w
Coolant gas flow	14 L/min
Auxiliary gas flow	0.8 L/min
Nebulizer gas flow	0.5 L/min



Measurement mode and limit of detection information

Analyte	Mode	Mass (m/z)	LOD (ug/kg)
As	KED	75	0.1
Ca	KED	48	0.36
Cu	KED	63	0.05
Fe	KED	54	0.26
Na	STD	23	3.83
Ni	KED	60	0.06
Pb	KED	208	0.24
Si	KED	28	36.81
V	KED	51	0.55

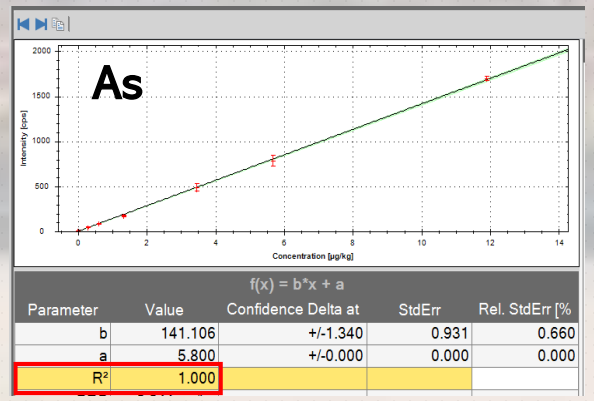
LOD = 3SD of sample blank

(Repeat 3 times, 10 vial)

%Recovery of SRM 1634c Trace Elements in Fuel Oil

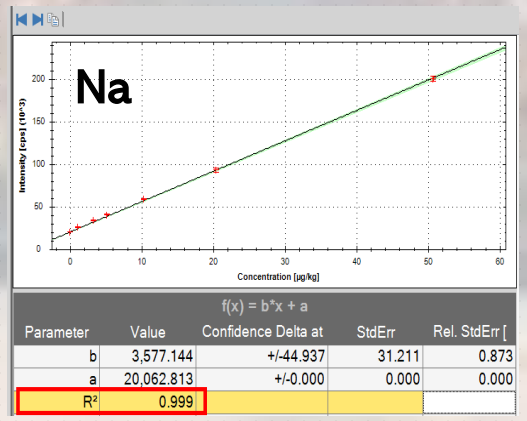
Analyte	Mass (m/z)	SRM 1634c (mg/kg)	Measure by ICP-MS Conc. (mg/kg)	%Recovery
As	75	0.1362 - 0.1490	0.14	98.60
Na	23	37.0	36.98	99.94
V	51	27.79 – 28.59	28.55	101.06
Ni	60	17.33 – 17.75	17.33	98.80

%Recovery 95 – 105 %



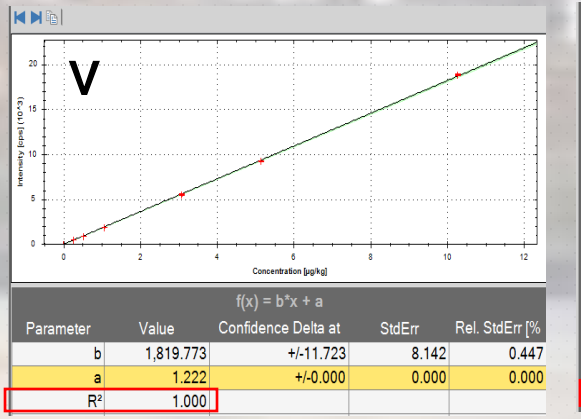
f(x) = b*x + a

Parameter	Value	Confidence Delta at	StdErr	Rel. StdErr [%
b	141.106	+/-1.340	0.931	0.660
a	5.800	+/-0.000	0.000	0.000
R^2	1.000			



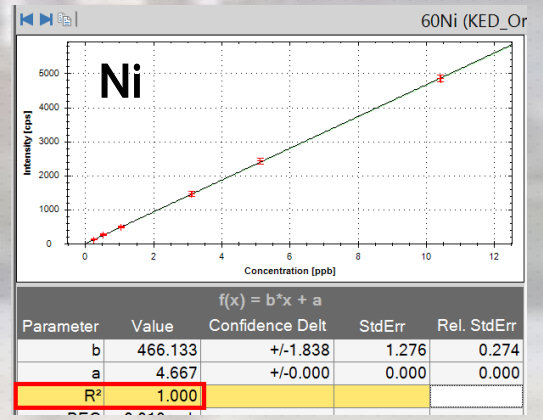
f(x) = b*x + a

Parameter	Value	Confidence Delta at	StdErr	Rel. StdErr [
b	3,577.144	+/-44.937	31.211	0.873
a	20,062.813	+/-0.000	0.000	0.000
R^2	0.999			



f(x) = b*x + a

Parameter	Value	Confidence Delta at	StdErr	Rel. StdErr [%
b	1,819.773	+/-11.723	8.142	0.447
a	1.222	+/-0.000	0.000	0.000
R^2	1.000			



f(x) = b*x + a

Parameter	Value	Confidence Delt	StdErr	Rel. StdErr
b	466.133	+/-1.838	1.276	0.274
a	4.667	+/-0.000	0.000	0.000
R^2	1.000			

SUMMARY

The iCAP PRO Series and iCAP RQplus is capable to analyze Petroleum products samples in accordance with the ASTM D7691 and ASTM D8110 requirements respectively. The developed method allows to achieve excellent detection limits.

The precision for unknown samples was verified according to the ASTM D7691 and ASTM D8110 with recovery measurements of a spike and triplicated sample analyses.

The accuracy of method have been presented by triplicate analysis of SRM1634c (Trace Elements in Fuel Oil).