

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

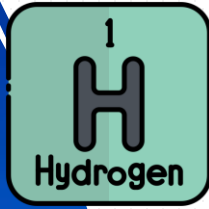
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Trace Element Analysis (TEA) Sci Spec Team



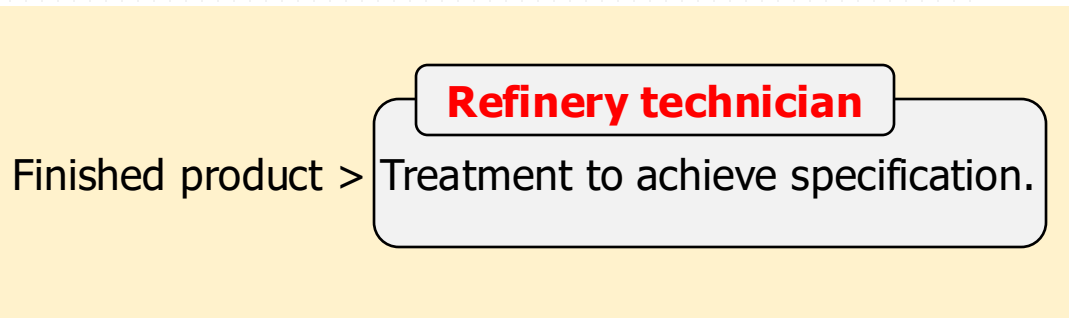
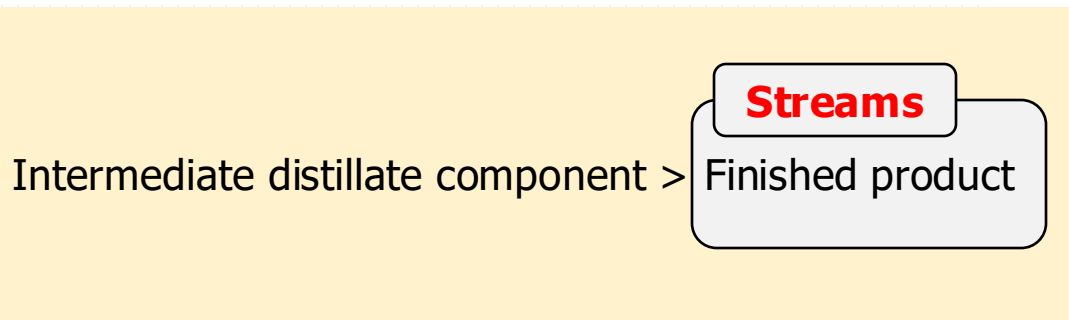
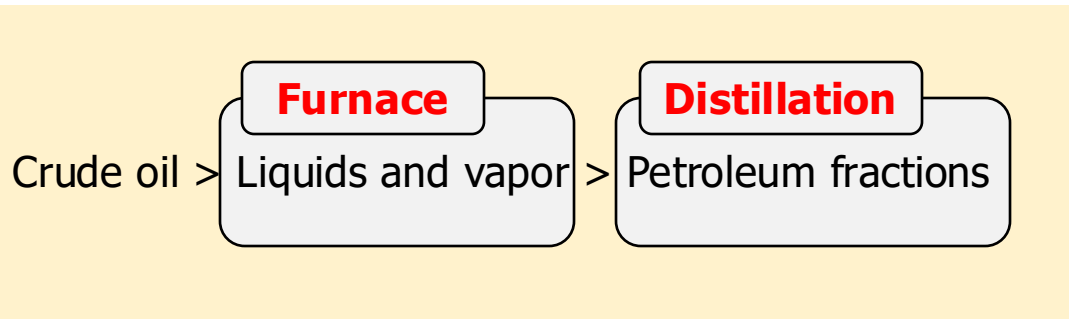


What's Petroleum

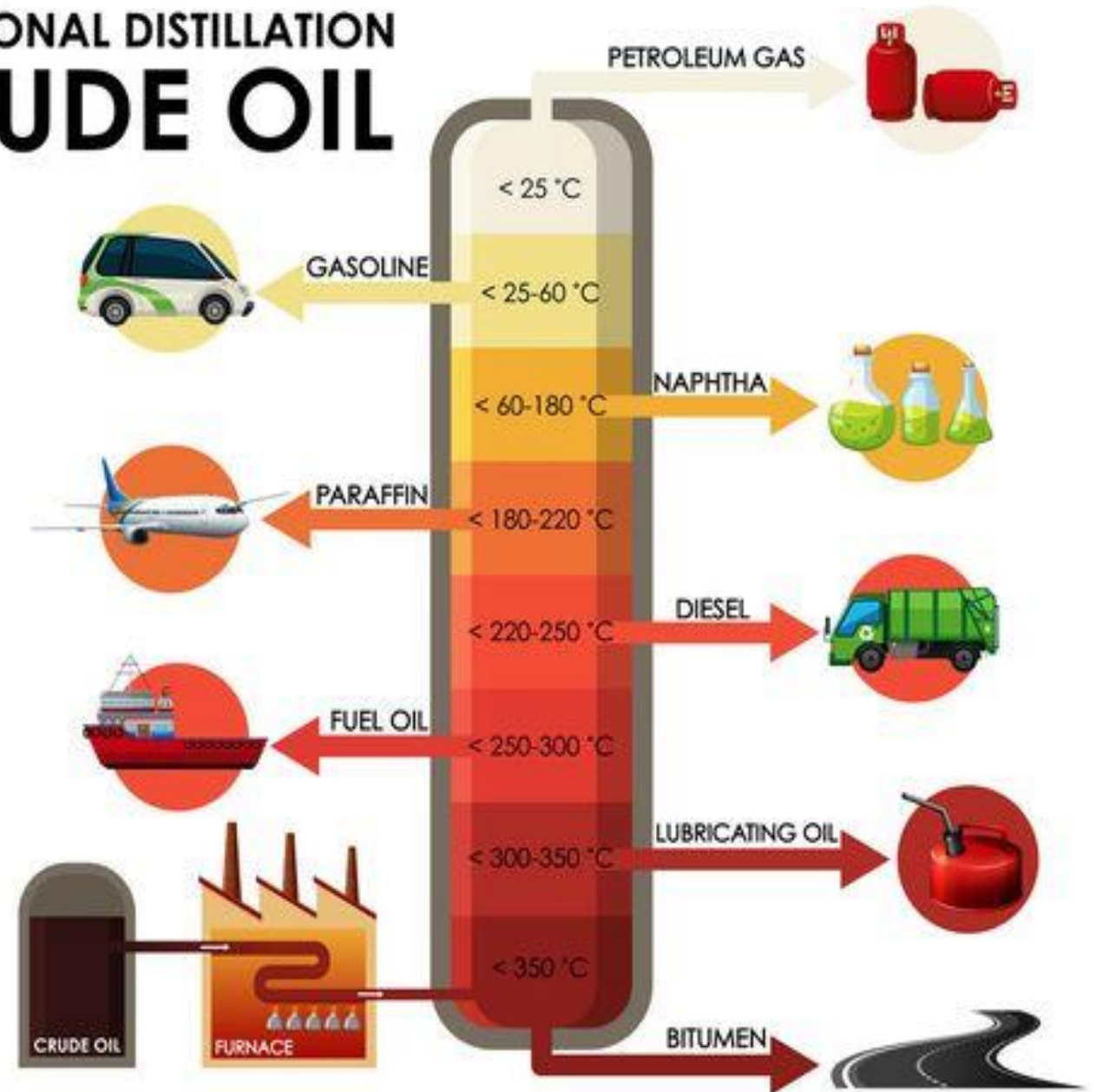


Basic steps for crude oils refinery

- Separation
- Conversion
- Treatment



FRACTIONAL DISTILLATION CRUDE OIL



Why should we test the Oil and Petroleum products?



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

This method is used to determine the concentration of various elements in the crude oils... by using inductively coupled plasma atomic emission spectrometry (ICP-AES).

1. Scope 1.1 This test method covers the determination of several elements (including iron, nickel, sulfur, and vanadium) occurring in crude oils.

1.2 For analysis of any element using wavelengths below 190 nm, a vacuum or inert gas optical path is required.

1.3 Analytic for elements such as arsenic, selenium, or sulfur in whole crude oil may be difficult by this test method due to the presence of their volatile compounds in these real samples.

1.4 Because of the particulate present in crude oil samples, if they do not dissolve in the organic solvent used or if they do not separate in the sediment, low chemical values may result, particularly for iron and sulfur. This can also occur if the elements are associated with water which can show up in the extracts which diluted with solvent.

1.5 An alternative in such cases is using Test Method D6790, Procedure B, which involves wet digestion of the sample, and iron, or Test Method D5953, Procedure A, which also uses wet acid digestion and detection via inductively coupled plasma atomic emission spectrometry.

1.6 From ASTM Interlaboratory Checkbook Program (ICP) on crude oils data available to date, it is not clear that organic solvent dilution techniques would necessarily give lower results than those obtained using acid decomposition techniques.

1.7 It is also possible that, particularly in the case of sulfur, low results may be obtained regardless of whether organic dilution or acid decomposition is utilized. Since sulfur is

¹This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants, Subcommittee D02.02 on Fuel Oils, and Subcommittee D02.02.01 on Fuel Oils.

A Summary of Changes section appears at the end of this standard.

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

This method is used to determine the concentration of various elements in used lubricating oils... by using inductively coupled plasma atomic emission spectrometry (ICP-AES).

1. Scope 1.1 This test method covers the determination of several elements (including iron, nickel, sulfur, and vanadium) occurring in used lubricating oils.

1.2 For analysis of any element using wavelengths below 190 nm, a vacuum or inert gas optical path is required.

1.3 Analytic for elements such as arsenic, selenium, or sulfur in whole crude oil may be difficult by this test method due to the presence of their volatile compounds in these real samples.

1.4 Because of the particulate present in used lubricating oils, if they do not dissolve in the organic solvent used or if they do not separate in the sediment, low chemical values may result, particularly for iron and sulfur. This can also occur if the elements are associated with water which can show up in the extracts which diluted with solvent.

1.5 An alternative in such cases is using Test Method D6790, Procedure B, which involves wet digestion of the sample, and iron, or Test Method D5953, Procedure A, which also uses wet acid digestion and detection via inductively coupled plasma atomic emission spectrometry.

1.6 From ASTM Interlaboratory Checkbook Program (ICP) on crude oils data available to date, it is not clear that organic solvent dilution techniques would necessarily give lower results than those obtained using acid decomposition techniques.

1.7 It is also possible that, particularly in the case of sulfur, low results may be obtained regardless of whether organic dilution or acid decomposition is utilized. Since sulfur is

¹This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants, Subcommittee D02.02 on Fuel Oils, and Subcommittee D02.02.01 on Fuel Oils.

A Summary of Changes section appears at the end of this standard.

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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), selenium (Se), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr), in organic matrices such as crude petroleum, asphalt, 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 analyses 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	Ni	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				

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 Spectrometry (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 D711, "Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)."

References

ASTM Specification D1919, "Reagent Water," www.astm.org

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

This method is used to determine the concentration of various trace elements in middle distillate fuels... by using inductively coupled plasma atomic emission spectrometry (ICP-AES).

1. Scope 1.1 This test method covers the determination of selected elements in middle distillate fuels by inductively coupled plasma atomic emission spectrometry (ICP-AES). The specific elements are listed in Table 1. The concentration range of this test method is approximately 0.1 to 1000 µg/g (ppm).

1.2 This test method may be used for concentrations outside this range; however, the precision statements may not be applicable. Middle distillate fuels used in this test method have all distillate fractions contained within the boiling range of 149°C to 390°C. This includes, but is not limited to, diesel fuel and aviation turbine fuels.

1.3 This test method is not intended to analyze insoluble particulates. However, very small particulate matter (smaller than a micron) will not be carried into the plasma and will be included in the quantitative analysis.

1.4 The values stated in SI units are to be regarded as standard. The values stated in inch pounds are not to be regarded as standard. No other units of measurement are included in this standard.

1.5 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific warning statements are given in 6.1, 8.2, and 8.4.

1.6 This test method uses available metals for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size dependent, and low results are obtained for particles larger than a few micrometers.

1.7 Elements present at concentrations above the upper limit of the calibration curve can be determined with additional appropriate dilutions and with no degradation of precision.

1.8 For elements other than calcium, sulfur, and zinc, the low limits listed in Table 2 and Table 3 were estimated by ten times the repeatability standard deviation. For calcium, sulfur, and zinc, the low limits listed in Table 3 were estimated by ten times the repeatability standard deviation. For calcium, sulfur, and zinc, the low limits listed in Table 3 were estimated by ten times the repeatability standard deviation.

¹This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants, Subcommittee D02.02 on Fuel Oils, and Subcommittee D02.02.01 on Fuel Oils.

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

This method is used to determine the concentration of various elements in distillate products... by using inductively coupled plasma mass spectrometry (ICP-MS).

1. Scope 1.1 This test method describes the procedure for the determination of trace elements in light and middle distillate petroleum products using inductively coupled plasma mass spectrometry (ICP-MS).

1.2 This test method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS) with knowledge of interpretation of spectra, isotopes, polymers, and matrix interferences, as well as the procedures for the determination of these elements.

1.3 The table in 4.1 lists elements for which the test method applies along with recommended ranges. Actual working detection limits are sample dependent and, as the sample matrix varies, these detection limits may vary.

1.4 The concentration range of this test method is typically from 10 to 1000 µg/g (ppm) to 1000 µg/g (ppm); however, the precision and bias statement in this section is the smaller concentration range based on test samples analyzed in the U.S., as in the table in Section 15. This test method may not be used for concentrations outside this range; however, the precision statements may not be applicable.

1.5 Elements present at concentrations above the upper limit of the calibration curve can be determined with additional appropriate dilutions and with no degradation of precision.

1.6 For elements other than calcium, sulfur, and zinc, the low limits listed in Table 2 and Table 3 were estimated by ten times the repeatability standard deviation. For calcium, sulfur, and zinc, the low limits listed in Table 3 were estimated by ten times the repeatability standard deviation.

1.7 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific warning statements are given in 8.2, 8.4, and Section 15.

1.8 This international standard was developed in accordance with the International Organization of Standardization (ISO) and is consistent with the International Organization of Standardization (ISO) and is consistent with the International Organization of Standardization (ISO) and is consistent with the International Organization of Standardization (ISO).

¹This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants, Subcommittee D02.02 on Fuel Oils, and Subcommittee D02.02.01 on Fuel Oils.

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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), selenium (Se), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn) in organic matrices such as crude petroleum, asphalt, 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 - Atomic Emission Spectrometry (ICP-OES). The lower limits of quantitation for the above elements, except palladium, are listed in Table 1; see Note 1.

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

Al	0.05	Li	0.03	Pb	0.04
Ca	0.08	Mg	0.04	Pt	0.01
Co	0.02	Mn	0.01	Sr	0.10
Cr	0.04	Mo	0.01	Sr	0.01
Cu	0.01	Na	0.04	Ti	0.03
Fe	0.05	Ni	0.03	V	0.01
P	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 Spectrometry (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."

References

ASTM Method D1919, "Specification for Reagent Water," www.astm.org
ASTM Method 391, "Trace Metals in Petroleum Products or Organics by AAS," www.astm.org
UOP Method 407, "Trace Metals in Organics by Dry Ashing - ICP-OES," www.astm.org

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Trace Metals in Organics by ICP-OES

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, asphalt, 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 analyses during digestion.

Table 1 Lower Limits of Quantitation, mg/kg (mass-ppm)
Al 0.02, As 0.01, Ca 0.03, Cd 0.01, Co 0.01, Cr 0.01, Cu 0.01, Fe 0.02, Ga 0.01, K 0.03, Li 0.01, Mg 0.02, Mn 0.01, Mo 0.01, Ni 0.01, Na 0.06, P 0.02, Pb 0.01, Pt 0.01, Sr 0.01, Sn 0.01, Ti 0.03, V 0.01, Zn 0.01, Zr 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 Spectrometry (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

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Trace Metals in Organics by ICP-OES

UOP Method 389-10

Scope

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

Table 1 Lower Limits of Quantitation, mg/kg (mass-ppm)
Al 0.05, Ca 0.08, Co 0.02, Cr 0.04, Cu 0.01, Fe 0.09, K 0.05, Li 0.03, Mg 0.04, Mn 0.01, Mo 0.01, Na 0.04, Ni 0.03, P 0.11, Pb 0.04, Pt 0.01, Sn 0.10, Sr 0.01, Ti 0.03, V 0.01, 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 Spectrometry (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."

References

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

UOP Method 391, "Trace Metals in Petroleum Products or Organics by AAS," www.astm.org

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

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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)

Erzugnisse aus pflanzlichen und tierischen Fetten und Ölen - Fett säure-methylester (FAME) - Bestimmung von Ca, K, Mg und Na durch optische Emissionsspektalanalyse mit induktiv gekoppeltem Plasma (ICP OES)

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Comité Européen de Normalisation
Europäisches Komitee für Normung

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

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BSI BS EN 15944 : 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 d'émission spectrométrique à couplage inductif par plasma (ICP-OES)

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

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IP IP 59271

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).

Table with 2 columns: Element, Range mg/kg
Vanadium 1-6
Nickel 1-6
Zinc 20-900
Lead 150-0
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/L to 50 ng/L 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 standard. 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.



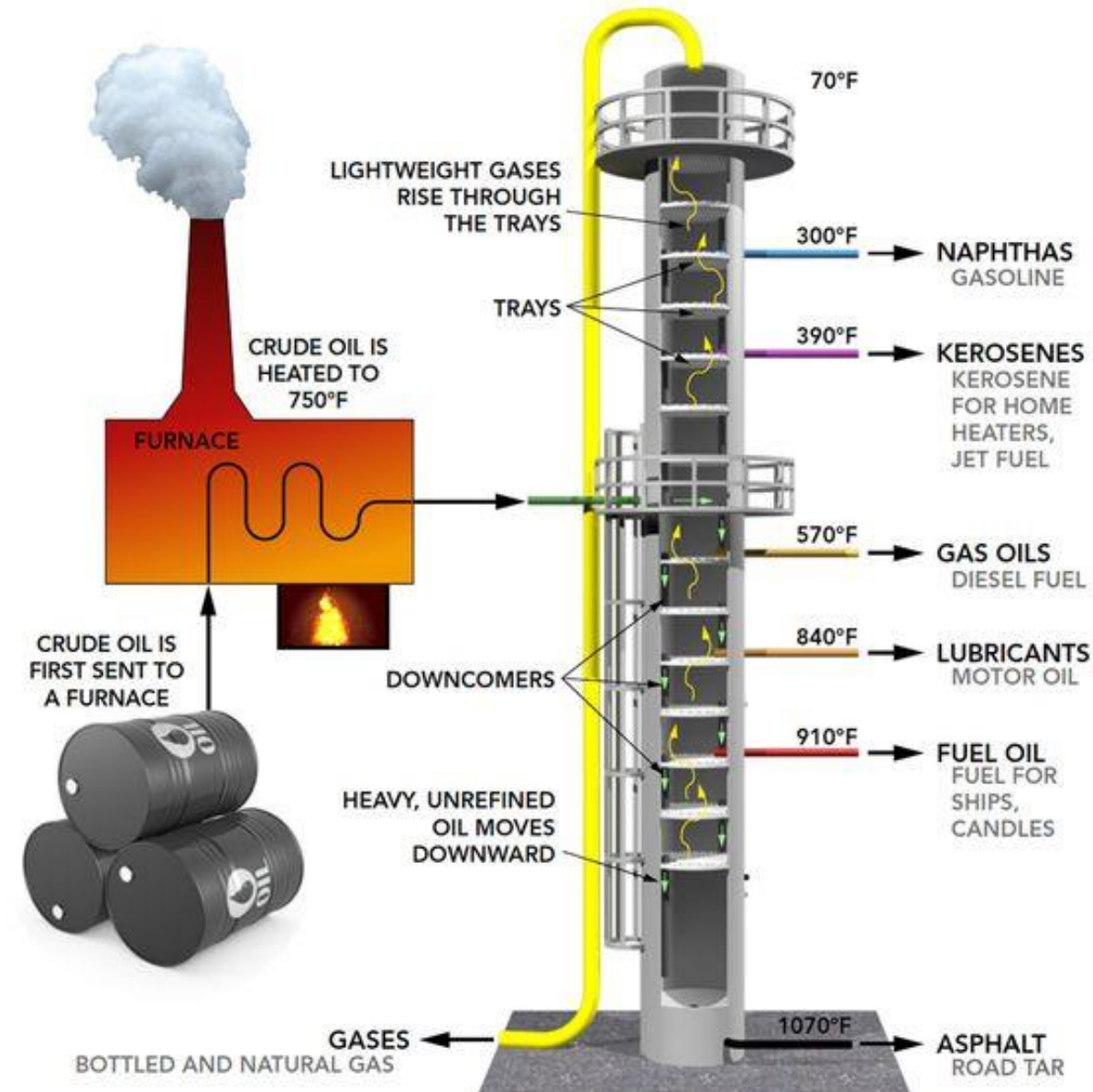
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What's the importance of quality **crude oil**?

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

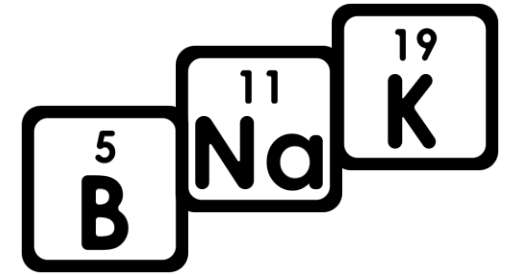
To achieve the specification of the lubricating product determine!!





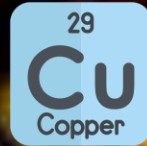
Why should we analyze **used Lubricating oils**?

ASTM D5185



ASTM D7111

Turbine Fuels
Diesel Fuels
Naval Fuels



<https://www.welkinchemi.com/content/16114/scale>

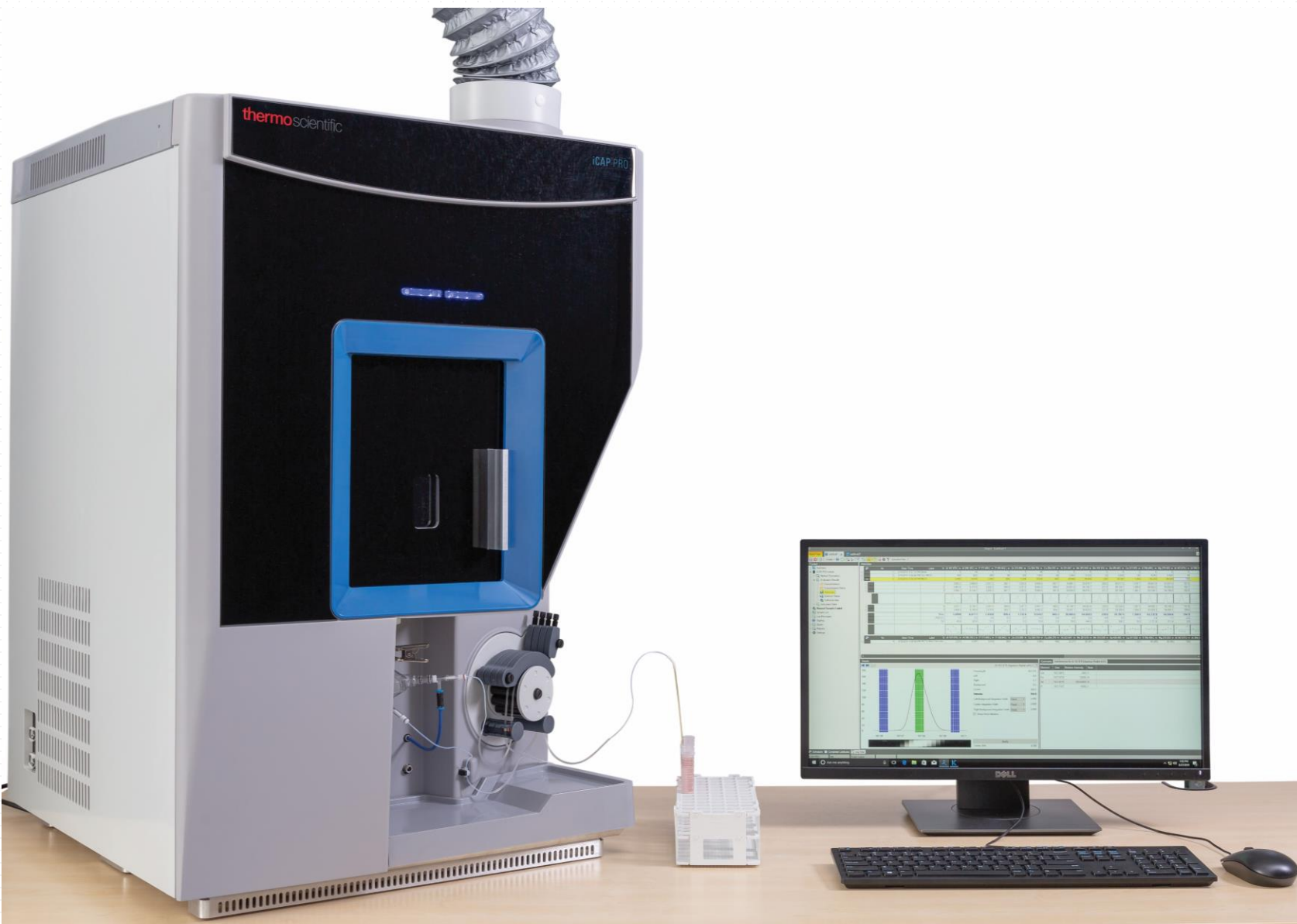
The impact of contamination in **Middle Distillation fuels?**

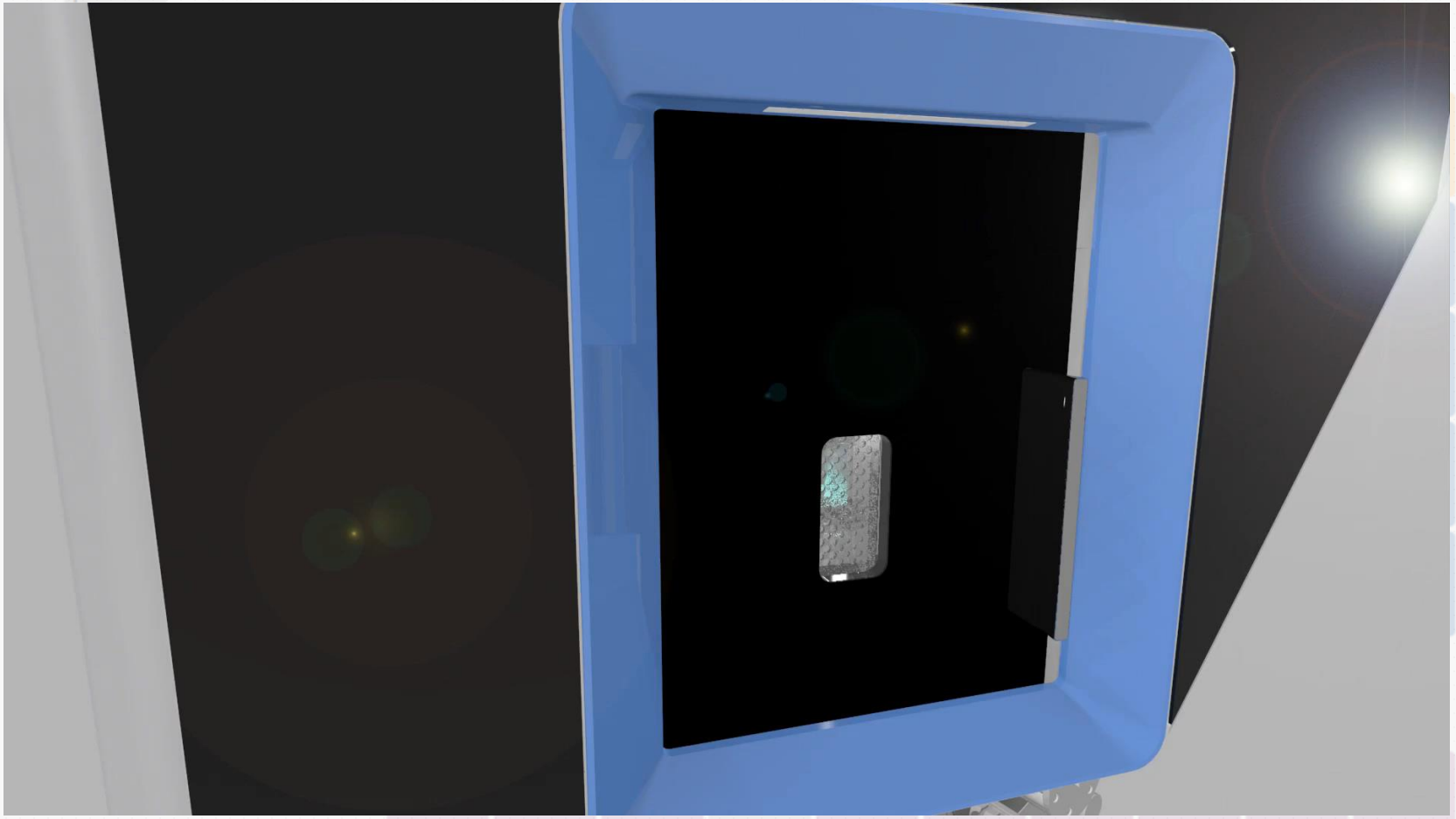
What is the effect of the contaminant in **light and middle distillate fuels**

ASTM D8110

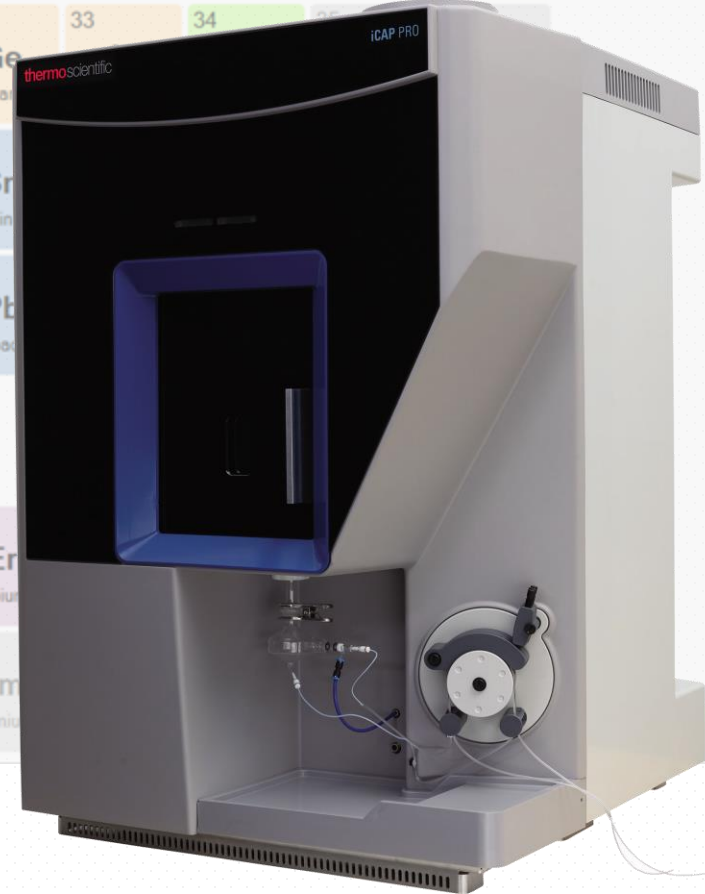
- Petroleum condensate and naphtha are derived products from crude oils.
- Petroleum condensate and naphtha are important raw materials for the petrochemical industry. It use in production of ethylene, propene, benzene, toluene, and xylenes.
- Naphtha is a colorless liquid that comprises a mixture of 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.







2	He																				
	Helium																				
6	C	7	N	8	O	9	F	10	Ne												
	Carbon		Nitrogen		Oxygen		Fluorine		Neon												
14	Si	15	P	16	S	17	Cl	18	Ar												
	Silicon		Phosphorus		Sulfur		Chlorine		Argon												
32	Ge	33	As	34	Se	35	Br	36	Kr												
	Germanium		Arsenic		Selenium		Bromine		Krypton												
50	Sn	51	Sb	52	Te	53	I	54	Xe												
	Tin		Antimony		Tellurium		Iodine		Xenon												
82	Pb	83	Bi	84	Po	85	At	86	Rn												
	Lead		Bismuth		Polonium		Astatine		Radon												
68	Er	69	Tm	70	Yb	71	Lu	72	Hf												
	Erbium		Thulium		Ytterbium		Lutetium		Hafnium												
90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm
	Thorium		Protactinium		Uranium		Neptunium		Plutonium		Americium		Curium		Berkelium		Californium		Einsteinium		Fermium





Analytes

1 H Hydrogen	2 He Helium
3 Li Lithium	4 Be Beryllium
5 B Boron	6 C Carbon
7 N Nitrogen	8 O Oxygen
9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium
13 Al Aluminium	14 Si Silicon
15 P Phosphorus	16 S Sulfur
17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium
21 Sc Scandium	22 Ti Titanium
23 V Vanadium	24 Cr Chromium
25 Mn Manganese	26 Fe Iron
27 Co Cobalt	28 Ni Nickel
29 Cu Copper	30 Zn Zinc
31 Ga Gallium	32 Ge Germanium
33 As Arsenic	34 Se Selenium
35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium
39 Y Yttrium	40 Zr Zirconium
41 Nb Niobium	42 Mo Molybdenum
43 Tc Technetium	44 Ru Ruthenium
45 Rh Rhodium	46 Pd Palladium
47 Ag Silver	48 Cd Cadmium
49 In Indium	50 Sn Tin
51 Sb Antimony	52 Te Tellurium
53 I Iodine	54 Xe Xenon
55 Cs Caesium	56 Ba Barium
57 La Lanthanum	58 Ce Cerium
59 Pr Praseodymium	60 Nd Neodymium
61 Pm Promethium	62 Sm Samarium
63 Eu Europium	64 Gd Gadolinium
65 Tb Terbium	66 Dy Dysprosium
67 Ho Holmium	68 Er Erbium
69 Tm Thulium	70 Yb Ytterbium
71 Lu Lutetium	72 Hf Hafnium
73 Ta Tantalum	74 W Tungsten
75 Re Rhenium	76 Os Osmium
77 Ir Iridium	78 Pt Platinum
79 Au Gold	80 Hg Mercury
81 Tl Thallium	82 Pb Lead
83 Bi Bismuth	84 Po Polonium
85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium
89 Ac Actinium	90 Th Thorium
91 Pa Protactinium	92 U Uranium
93 Np Neptunium	94 Pu Plutonium
95 Am Americium	96 Cm Curium
97 Bk Berkelium	98 Cf Californium
99 Es Einsteinium	100 Fm Fermium
101 Md Mendelevium	102 No Nobelium
103 Lr Lawrencium	

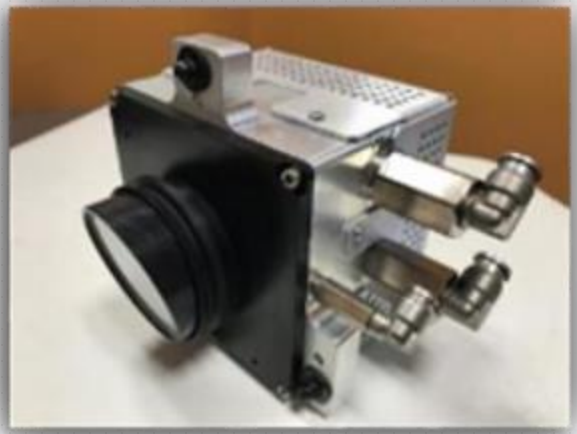
Analyte

Be (313.042)	Intensity	40000000
	Excitation	II
Be (234.861)	Intensity	25000000
	Excitation	I
Be (313.107)	Intensity	15000000
	Excitation	II
Be (265.045)	Intensity	900000
	Excitation	I
Be (249.473)	Intensity	800000
	Excitation	I
Be (332.134)	Intensity	250000
	Excitation	I

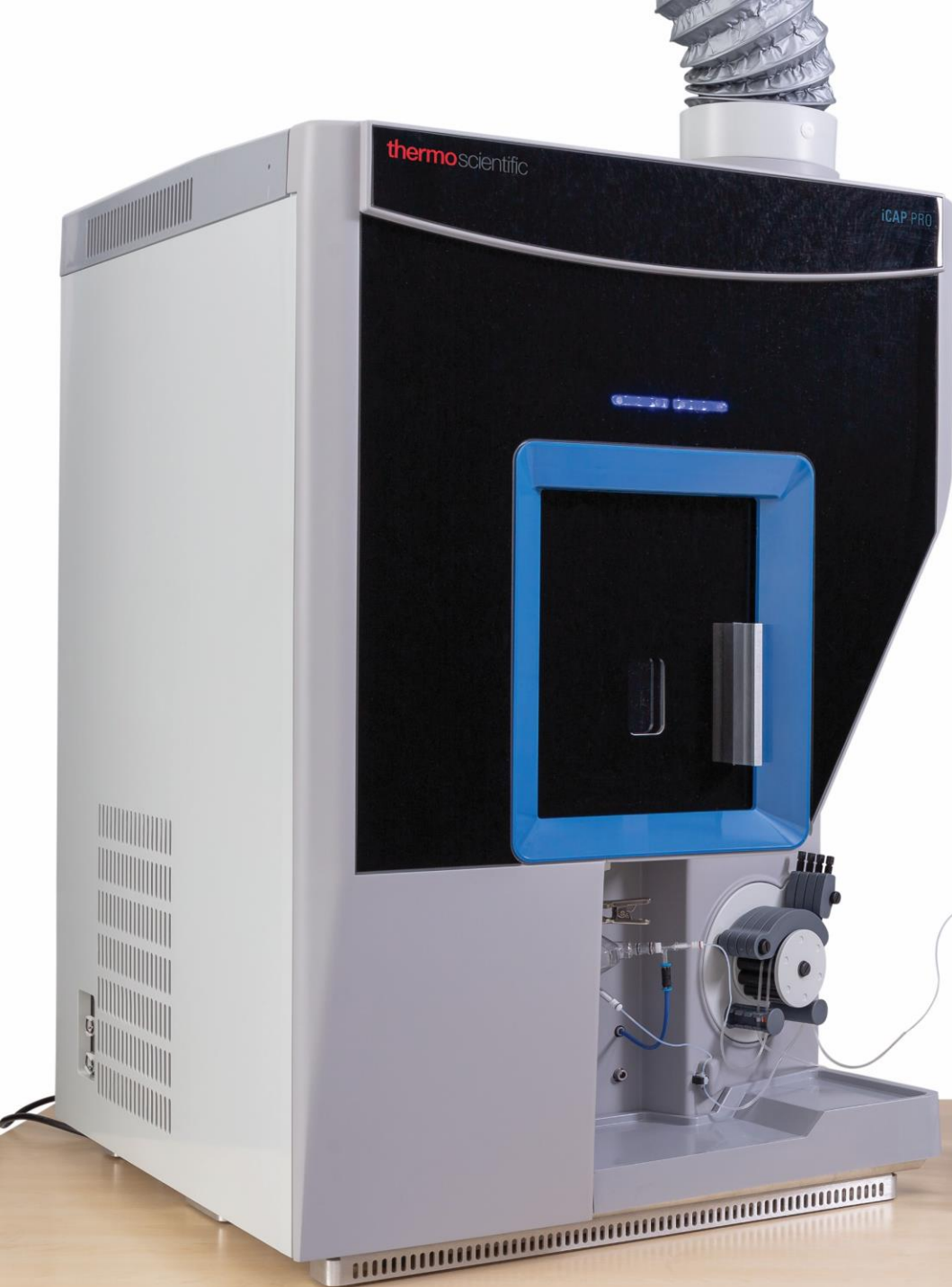
Interferences

Analyte	Line	Relative intensity	State
Th	312.997	5000	II
Ag	313.002	818	I
V	313.027	450000	II
Ce	313.033	11429	II
Be	313.042	40000000	II
Ta	313.058	51154	I
Eu	313.073	10000	II
Ho	313.077	25000	II
Rh	313.079	931	I
Nb	313.079	900000	II
Gd	313.081	8966	II
Ti	313.081	70000	II

Interfering Lines



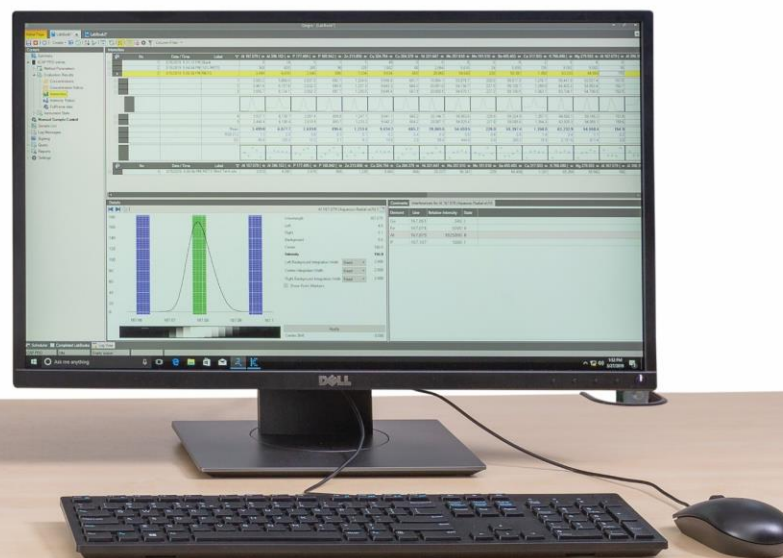
CID Detector



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

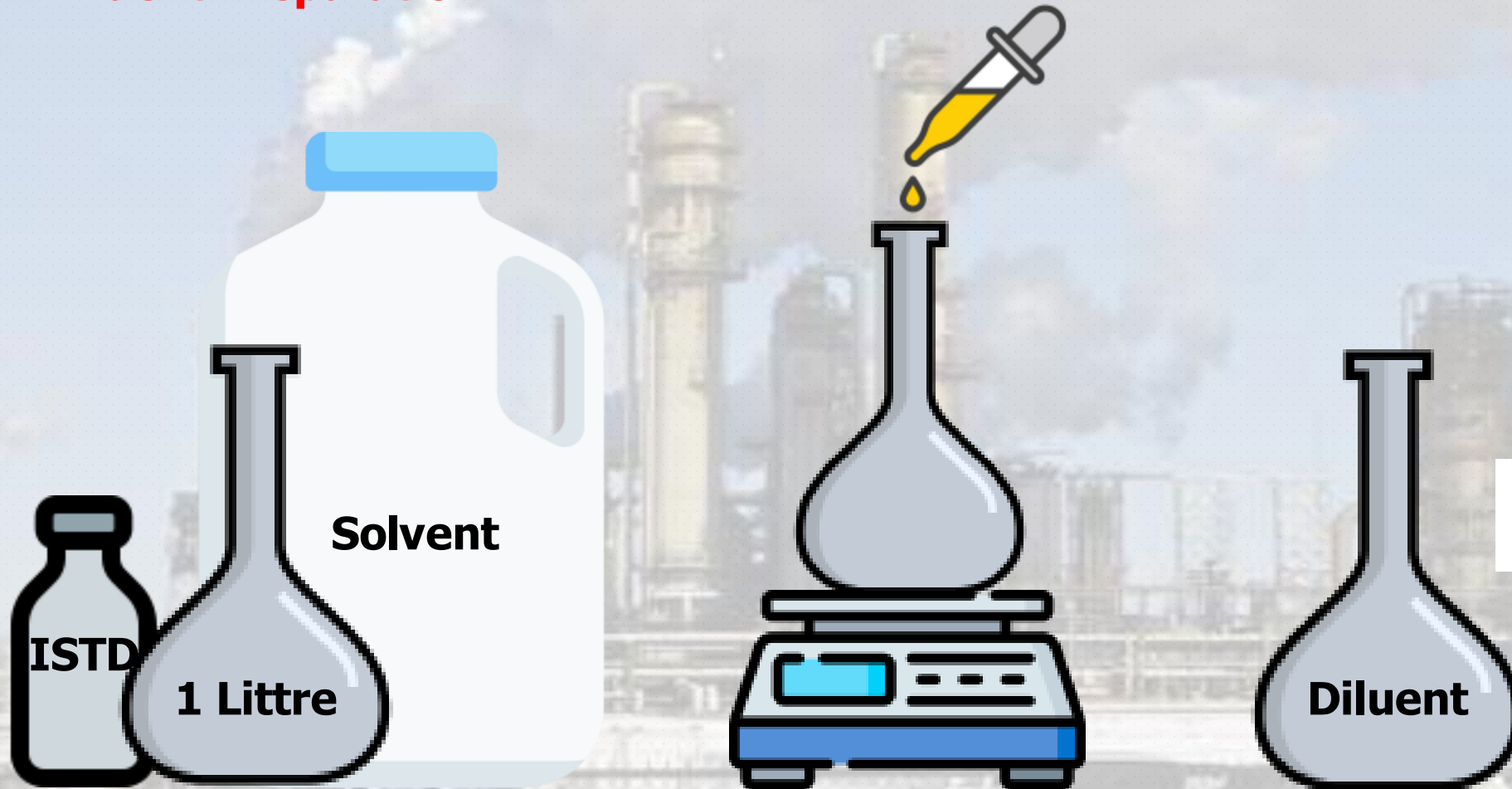
ASTM D7691-23

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



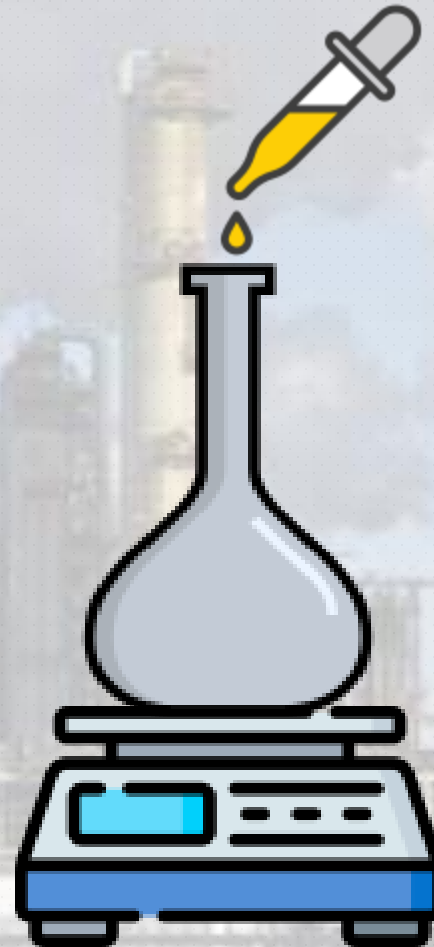
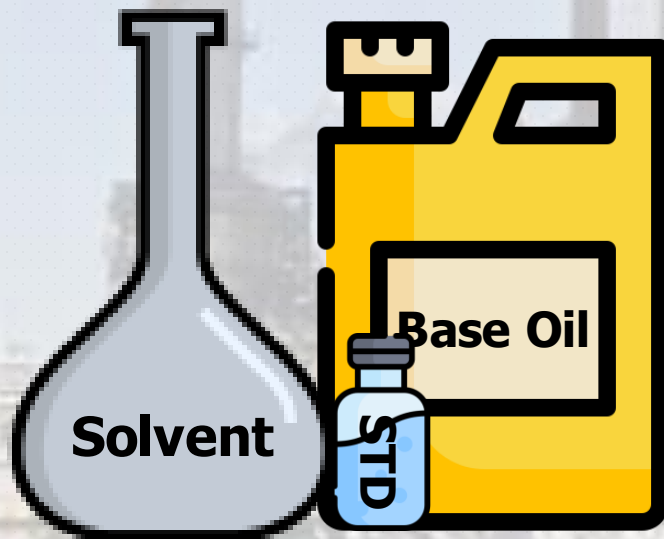
Internal Standard concentration
is about 10 – 20 mg/kg

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

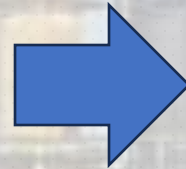
*** It is not required when the sample is at a low pour point.***



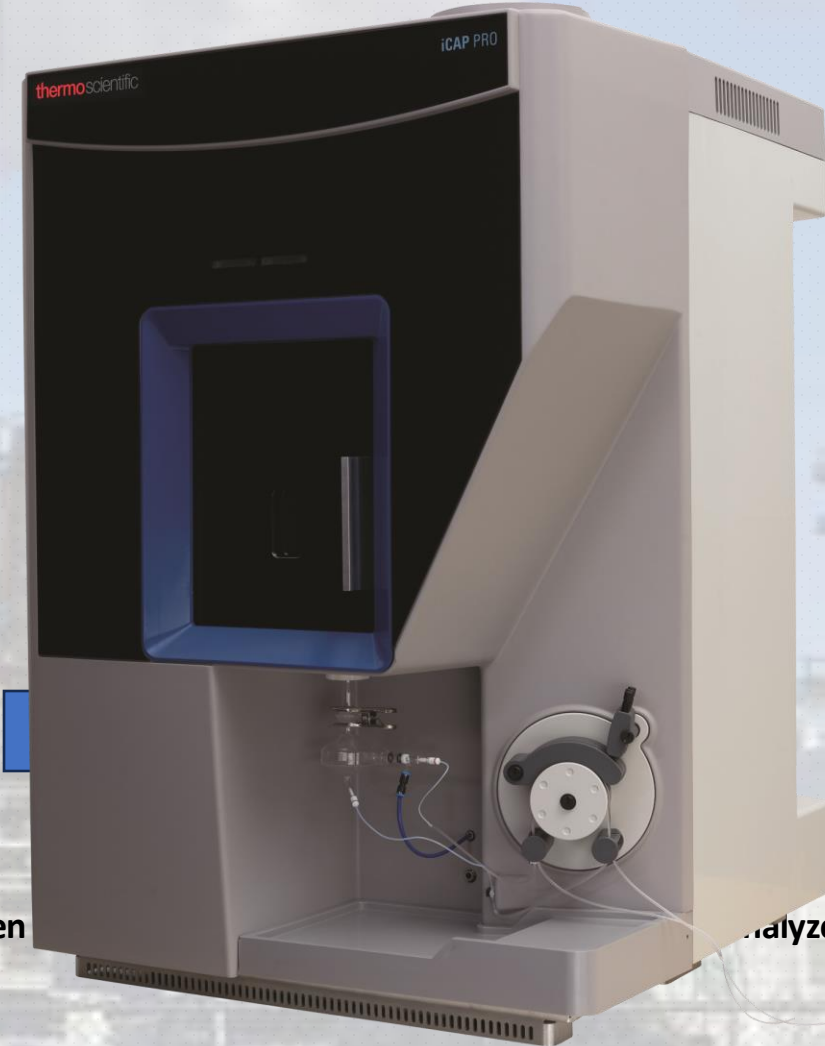
Heat the specimen at 50 – 60 °C



50 – 60 °C



Mix to homogenize the specimen



Analyze

ASTM D7691

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

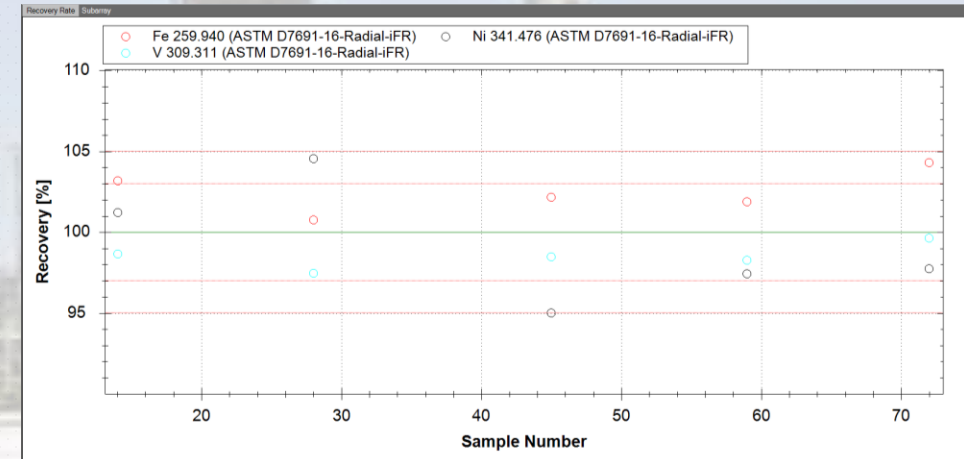
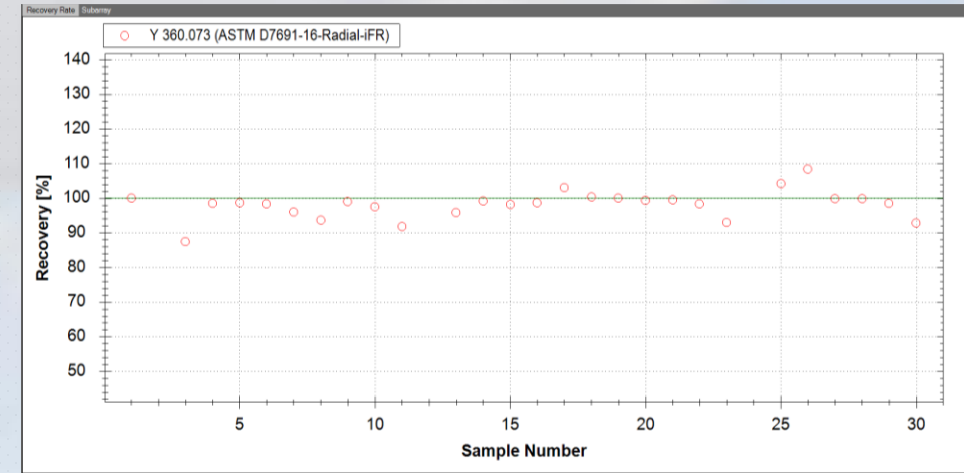
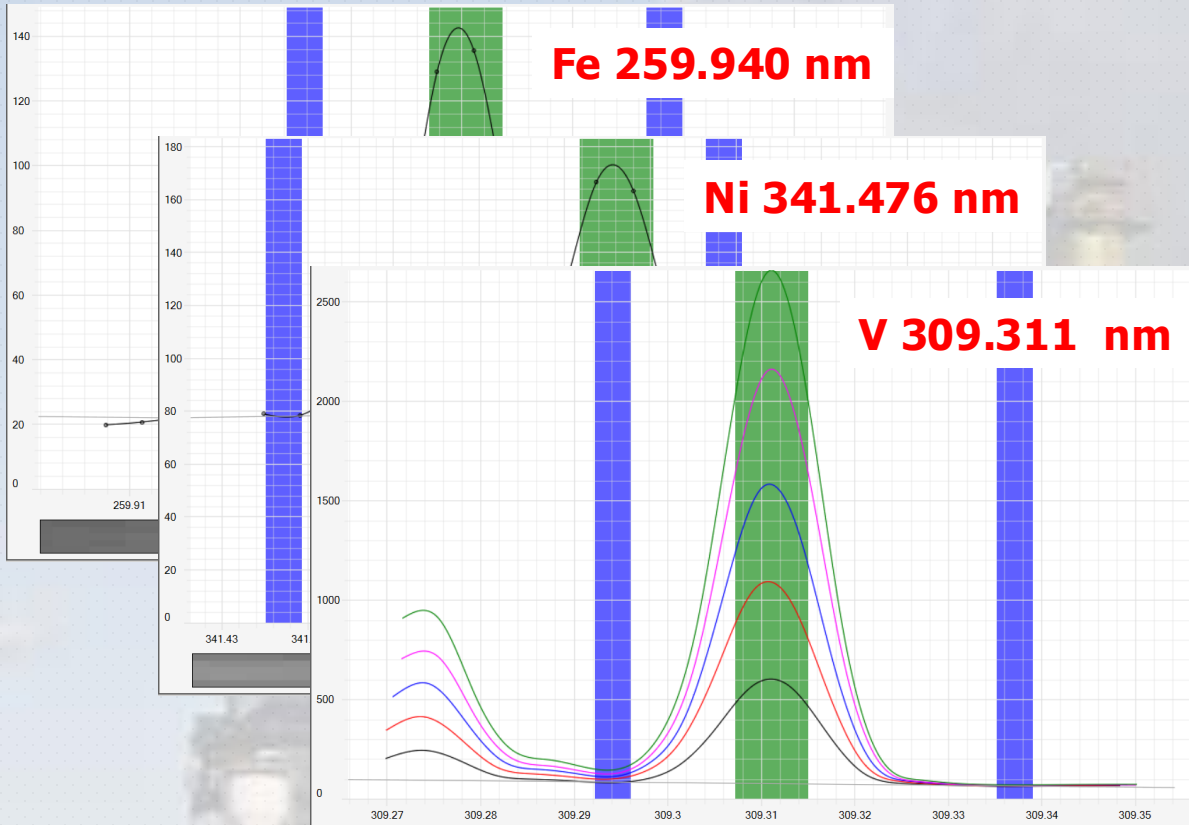


Operating and Method parameter

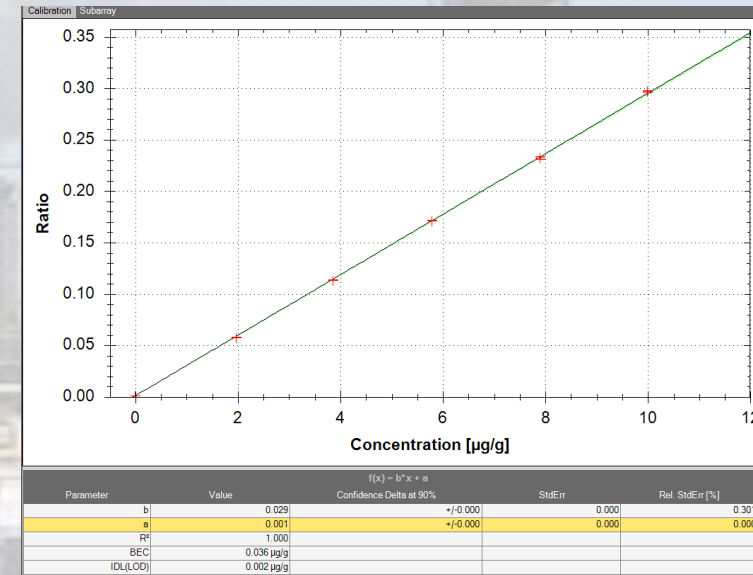
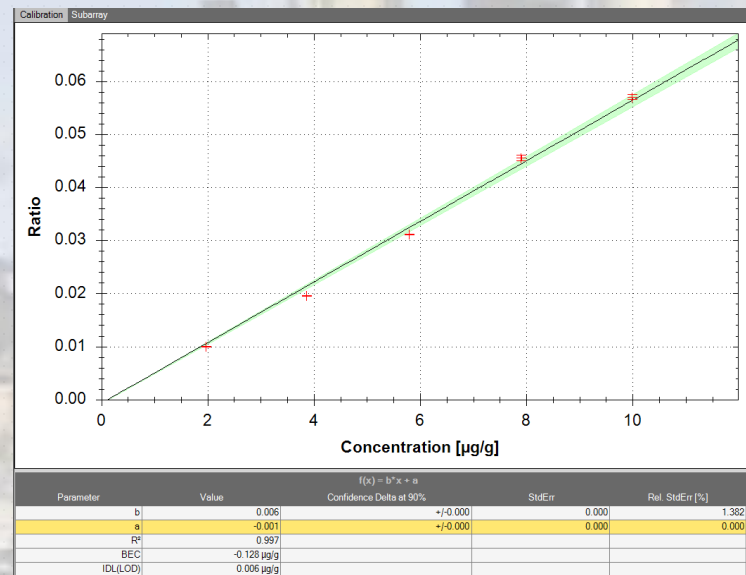
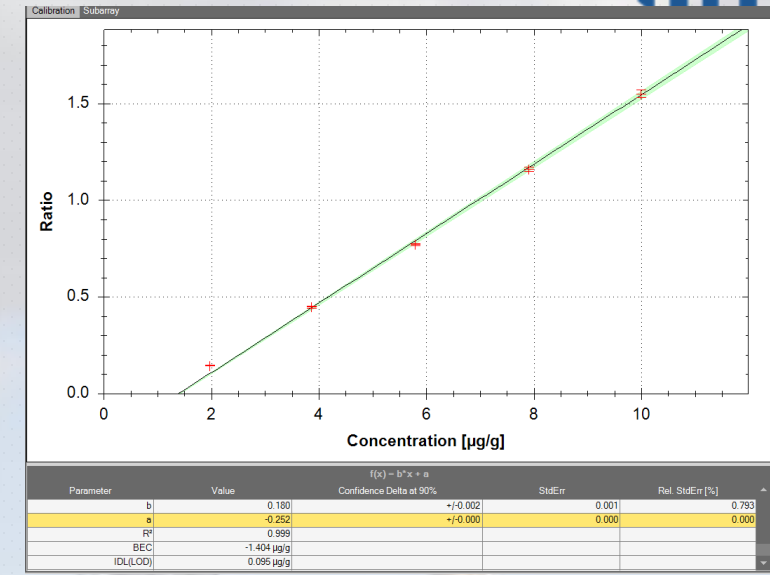
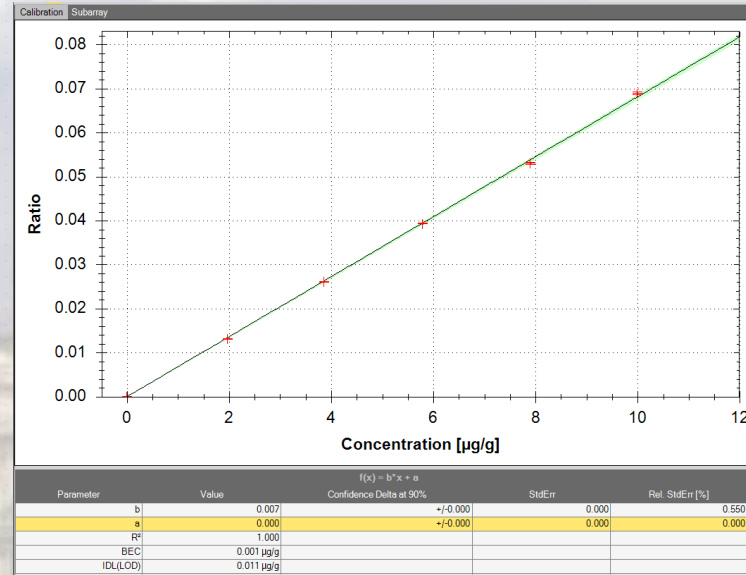
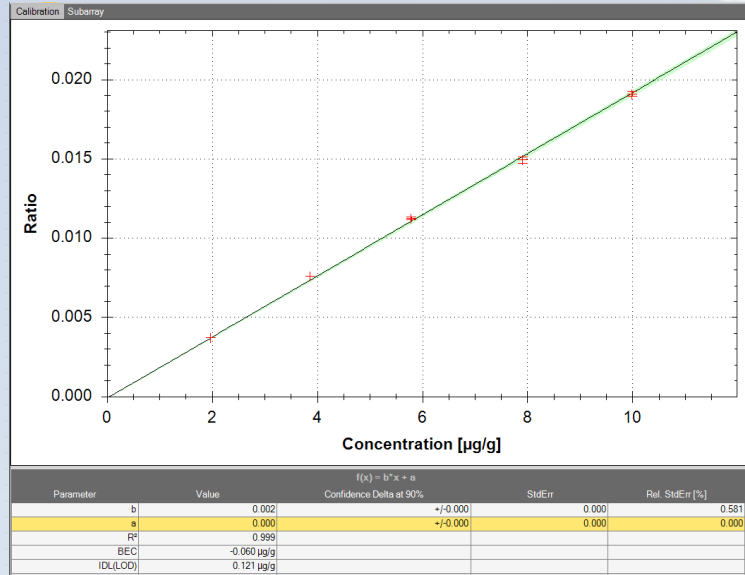
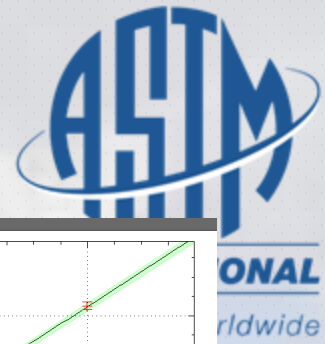
Torch	Quartz torch
Nebulizer	V-groove nebulizer
Spray chamber	Organic Spray chamber
Injector	Quartz 1.0 mm ID
Sample tube	Viton pump tube 0.54 mm ID (Orange/White)
Drain tubing	Viton pump tube 1.02 mm ID (White/White)
Plasma RF power	1350 w
Coolant gas flow	14.5 L/min
Auxiliary gas flow	2.0 L/min
Nebulizer 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)
Al	0.006	0.021
Ca	0.071	0.237
Fe	0.007	0.025
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. Reurick, 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

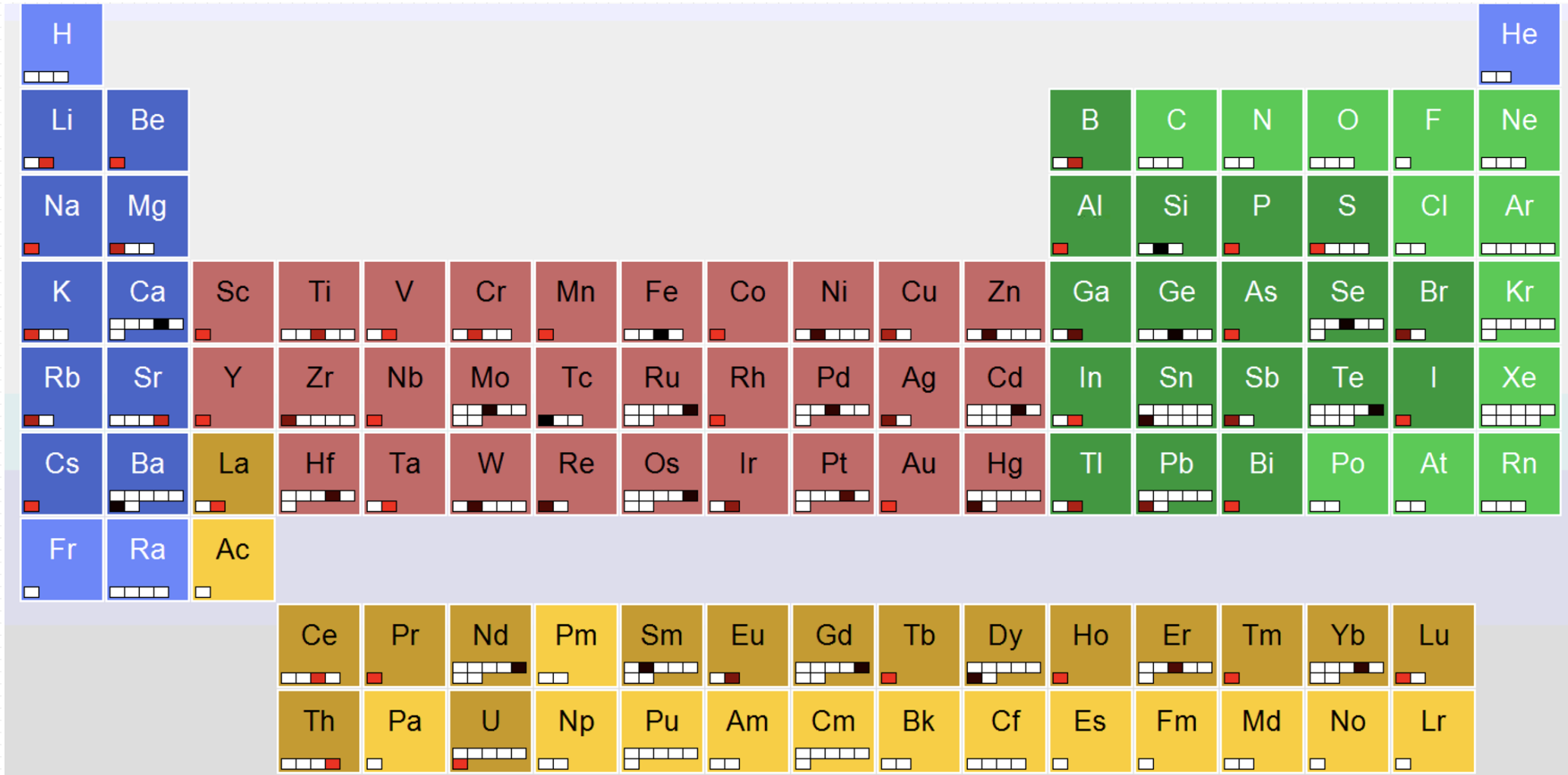


Multi-Element Analysis of Distillate Products by iCAP RQplus

ASTM D8110-17

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

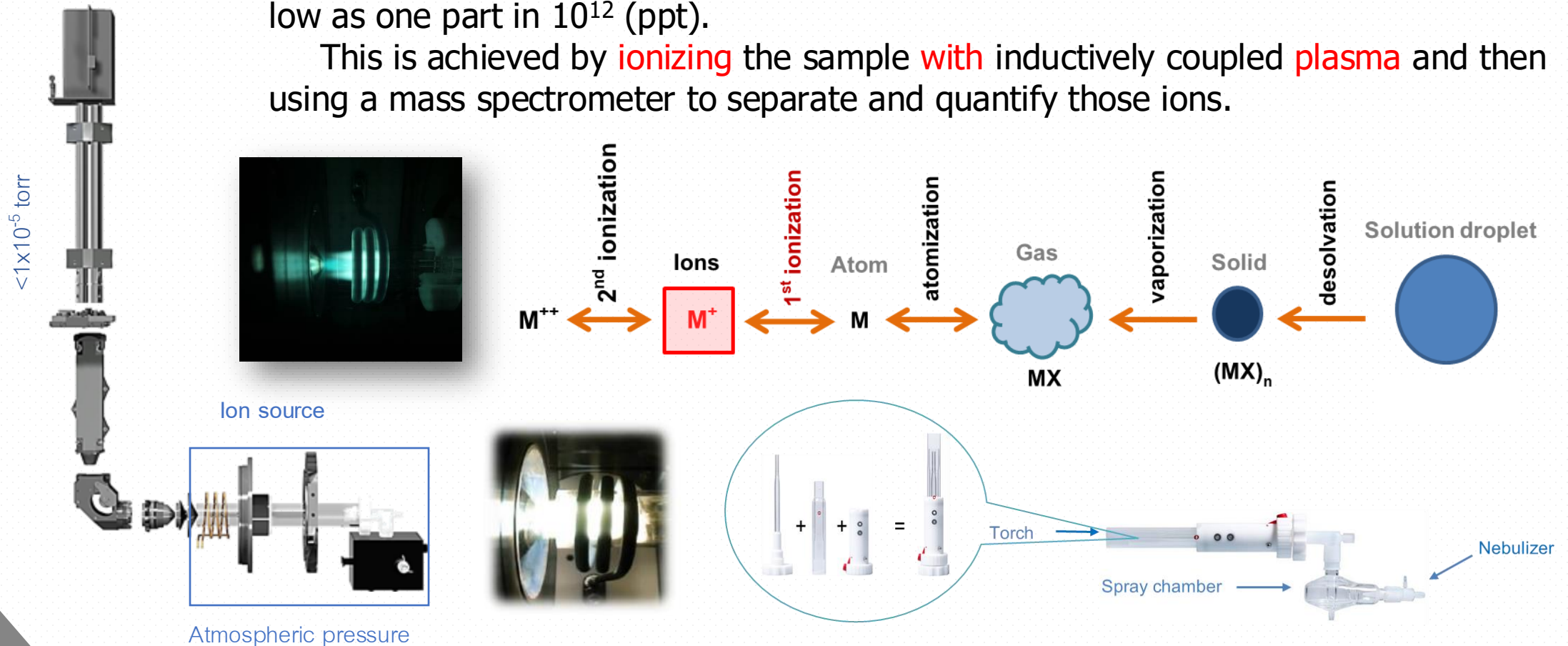
Element coverage of ICP-MS



Ion generation in ICP-MS

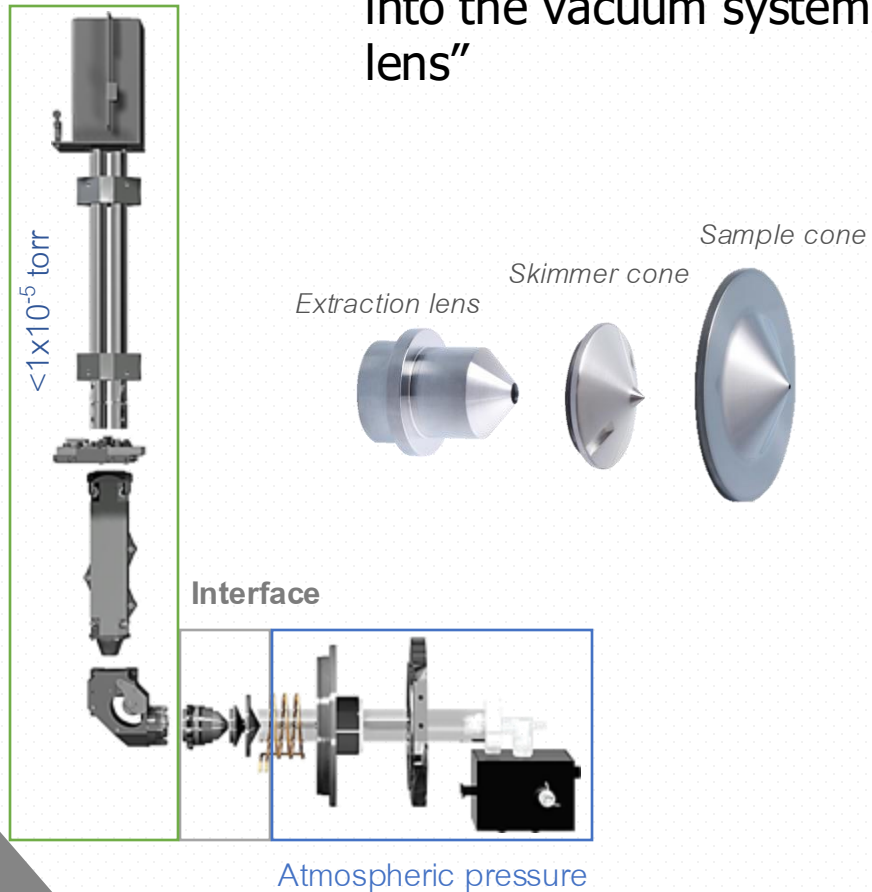
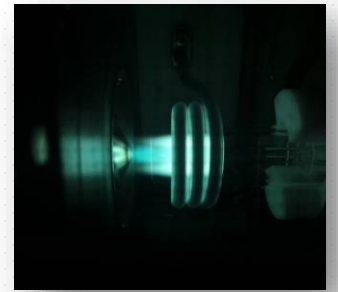
Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry which can detect metals and several non-metals at concentrations as low as one part in 10^{12} (ppt).

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

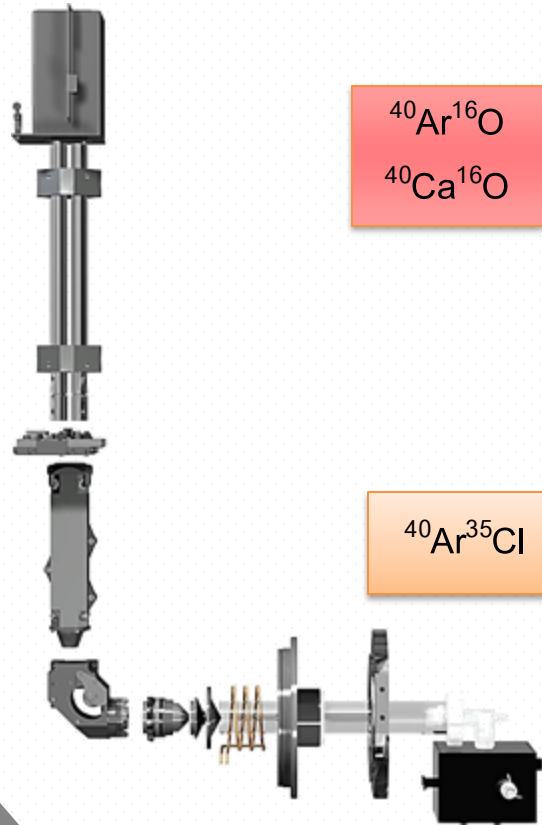


How to extract the ions into MS ?

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"

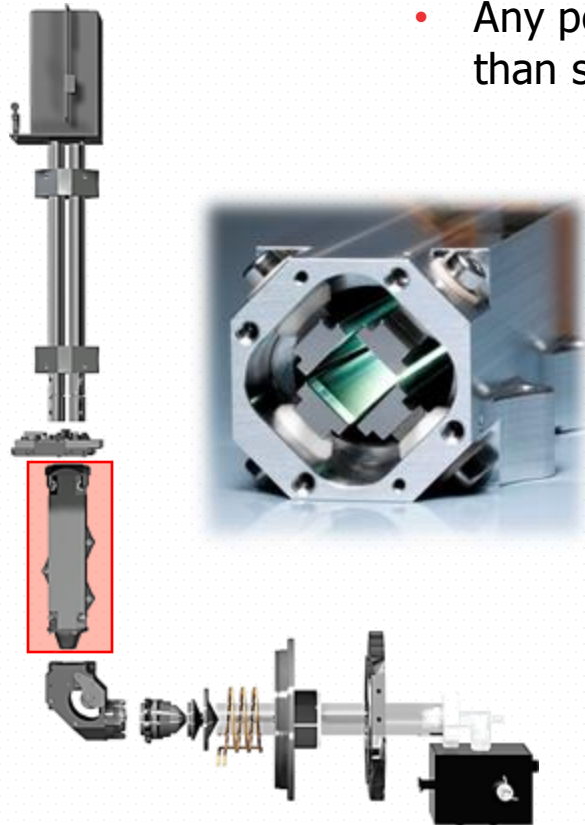


Polyatomic interference

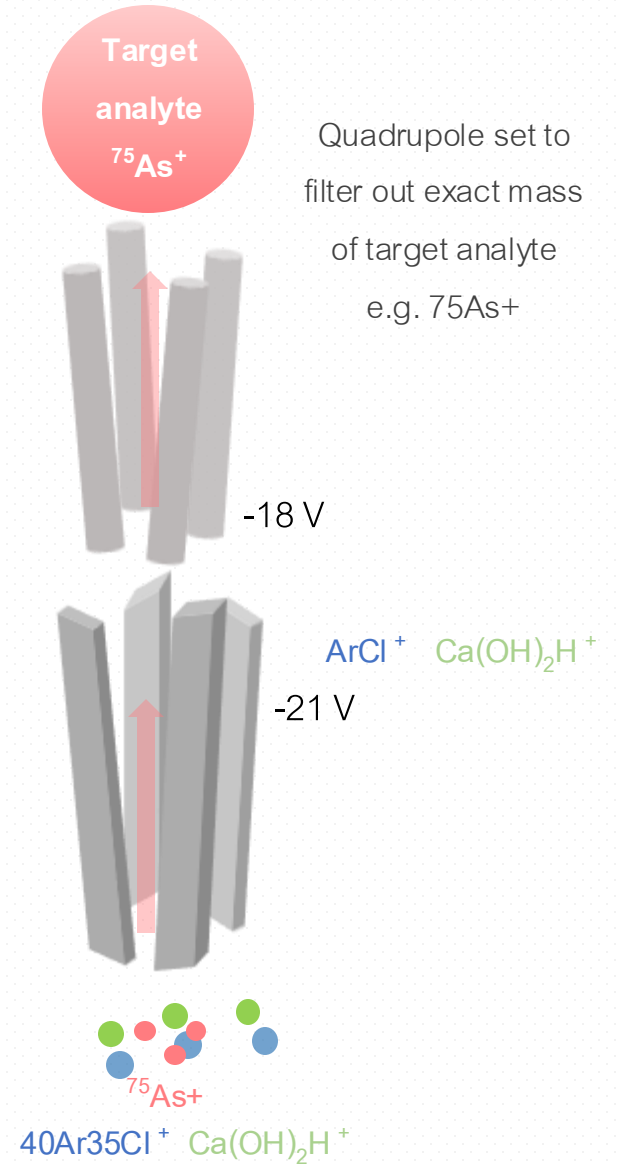
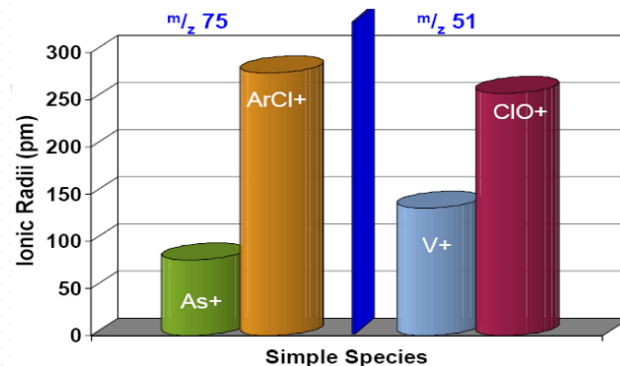


ANALYTE	POTENTIAL INTERFERENT	PRECURSORS
⁴⁵ Sc	¹³ C ¹⁶ O ₂ , ¹² C ¹⁶ O ₂ H, ⁴⁴ CaH, ³² S ¹² CH, ³² S ¹³ C, ³³ S ¹² C	H, C, O, S, Ca
⁴⁷ Ti	³¹ P ¹⁶ O, ⁴⁶ CaH, ³⁵ Cl ¹² C, ³² S ¹⁴ NH, ³³ S ¹⁴ N	H, C, N, O, P, S, Cl, Ca
⁴⁹ Ti	³¹ P ¹⁸ O, ⁴⁸ CaH, ³⁵ Cl ¹⁴ N, ³⁷ Cl ¹² C, ³² S ¹⁶ OH, ³³ S ¹⁶ O	H, C, N, O, P, 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 O ₂ , 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 O ₂ H, ³² S ₂ H, 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 ₂ H, ³⁴ S ₂ H, 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 ₂ H	H, S, Cl, Ca, Ae
⁷⁷ Se	⁴⁰ Ar ³⁷ Cl, ⁴⁰ Ca ³⁷ Cl	Cl, Ca, Ar
⁷⁸ Se	⁴⁰ Ar ³⁸ Ar	Ar
⁸⁰ Se	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

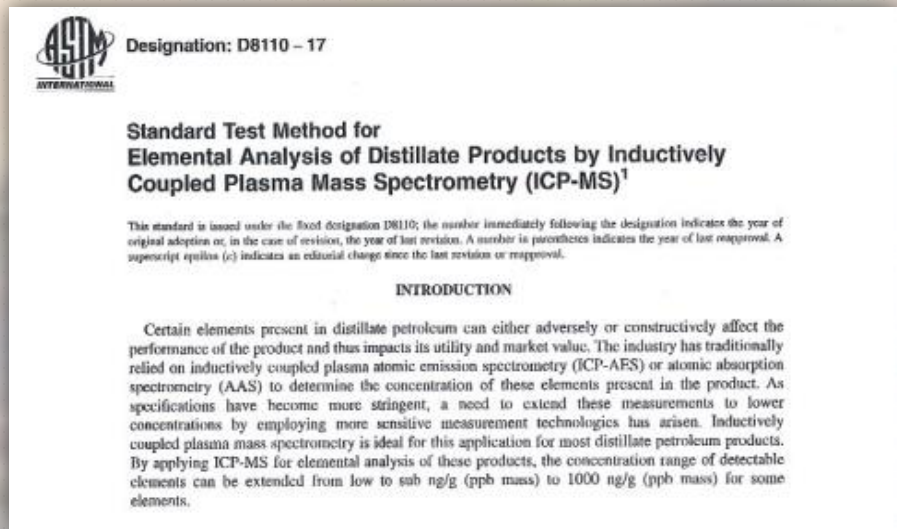
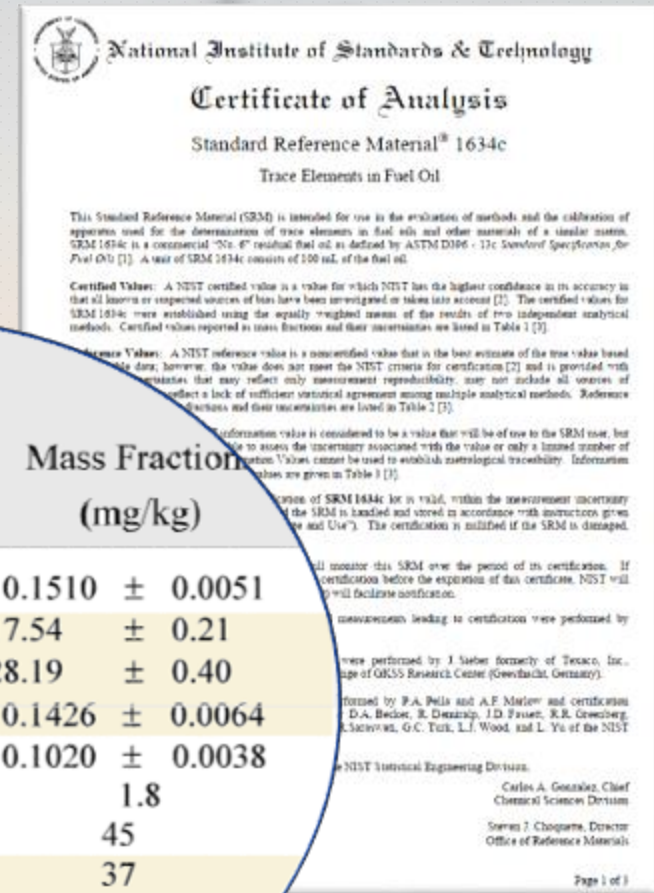
This method was developed using the Thermo Scientific™ iCAP™ RQ ICP-MS .

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)

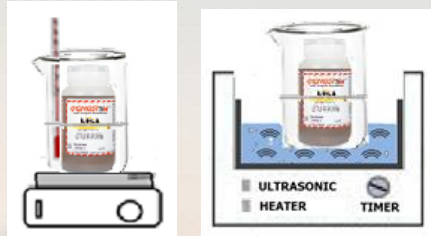


Element	Mass Fraction (mg/kg)
Cobalt	0.1510 ± 0.0051
Nickel	17.54 ± 0.21
Vanadium	28.19 ± 0.40
Arsenic	0.1426 ± 0.0064
Selenium	0.1020 ± 0.0038
Barium	1.8
Chlorine	45
Sodium	37
	(%)
Sulfur	2

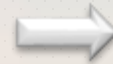
Sample Preparation Procedures



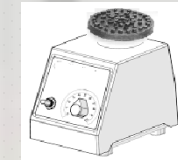
Measured density of Standards and Sample.



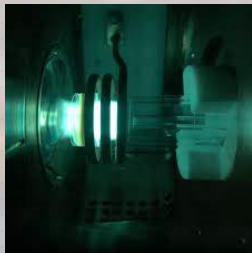
Before diluting, it's homogenized by sonication.
For very viscous oils, the sample can be pre-heated to 60 °C, 15 min.



Weighing the appropriate amount.



Vortex mixer to homogenized



ICP-MS model iCAP RQ
Thermo Scientific

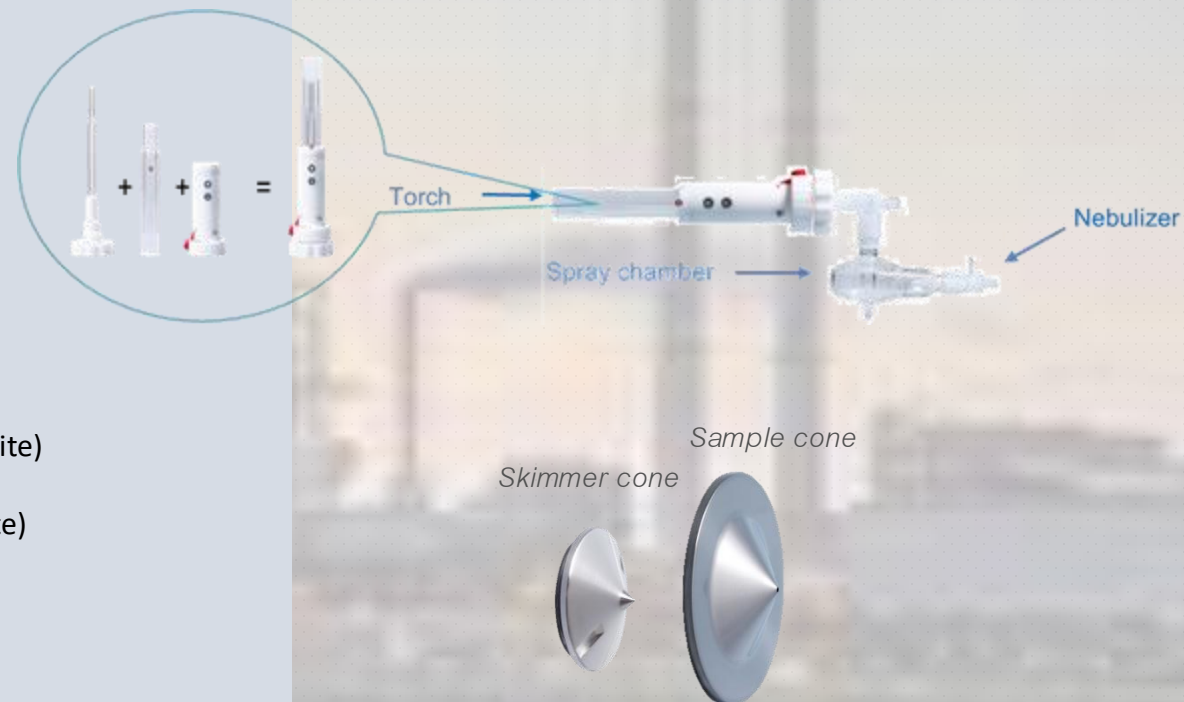


Sample Preparation

- 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 μ L/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

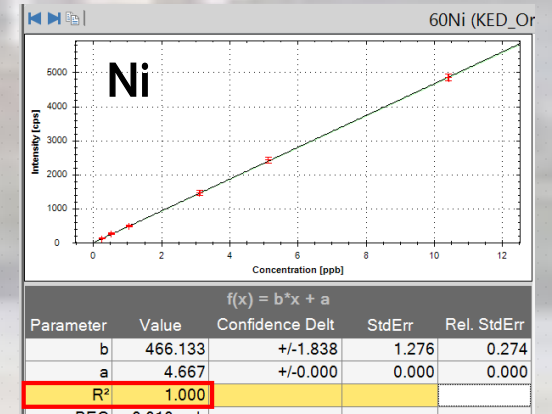
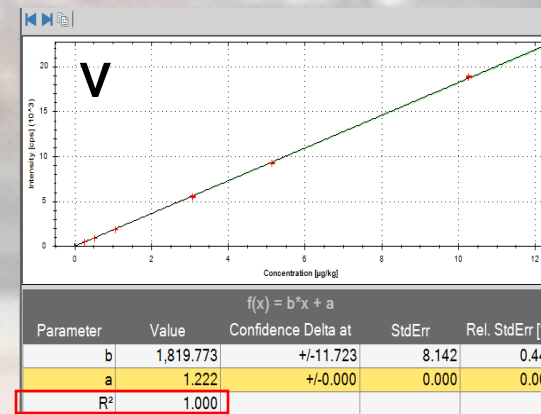
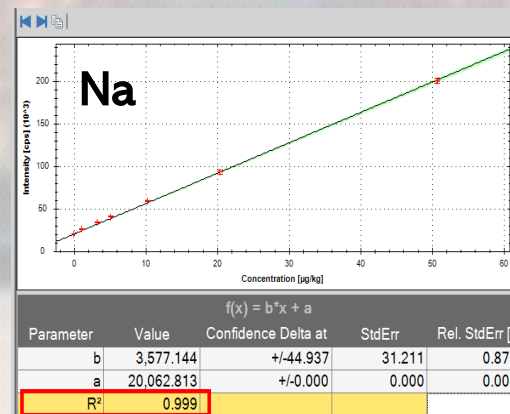
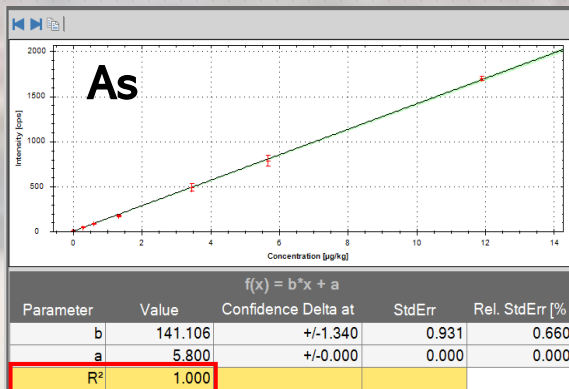
Analyte	Mode	Mass (m/z)	LOD (ug/kg)
As	KED	75	0.1
Ca	KED	48	0.36
Cu	KED	63	0.05
Fe	KED	54	0.26
Na	STD	23	3.83
Ni	KED	60	0.06
Pb	KED	208	0.24
Si	KED	28	36.81
V	KED	51	0.55

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 %



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).