Analysis of HC with Complementary Spectroscopic Methods
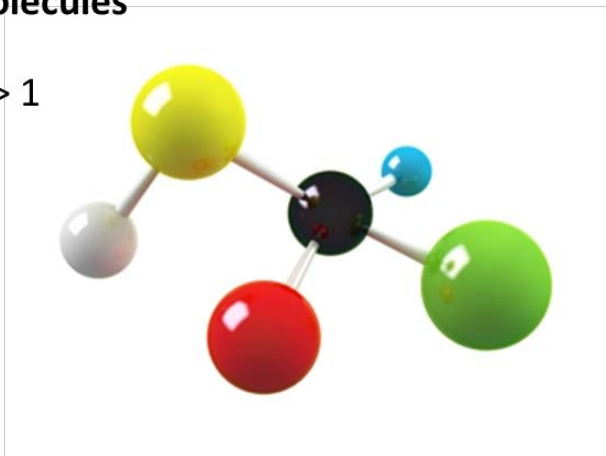
Dr. Johannes Hesper
Shimadzu Europe GmbH

Spectroscopic Methods

FTIR, UV-Vis, RF

molecules

N > 1

EDX, AAS, ICP-AES, ICP-MS

elements

N = 1

Spectroscopic Methods

Molecular

FTIR, UV-Vis-NIR, RF
- FAME in Bio-Diesel
- Soot in Oil
- Total petroleum hydrocarbons
- Oil in water
- Additives in Polymers
- Coumarin in Diesel
- Aged Polymers
- Etc.

Elemental

EDX, AAS, ICP-AES, ICP-MS
- Wear Metals in Oil
- Sulfur in Oil
- Lead, As in Gasoline
- Trace Elements in Petroleum naphtha, gasoline, Marine fuel, fuel oil, heavy oils
- Etc.

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FTIR

IRSpirit

Fatty Acid Methyl Ester in Bio-Diesel

Biodiesel fuel is produced through the conversion of fats and oils into fatty acid methyl esters (FAME) by the process of methyl esterification, in which glycerin is removed.

$$CH_2\text{-}COOR^1$$
$$|$$
$$CH\text{-}COOR^2 \quad + \quad 3CH_3OH \quad \xrightarrow{\text{Catalyst}} \quad R^1\text{-}COOCH_3 \qquad CH_2\text{-}OH$$
$$|$$
$$CH_2\text{-}COOR^3 \qquad\qquad\qquad\qquad\qquad R^2\text{-}COOCH_3 \quad + \quad CH\text{-}OH$$
$$R^3\text{-}COOCH_3 \qquad CH_2\text{-}OH$$

| Vegetable oil | Methanol | FAME | Glycerines |
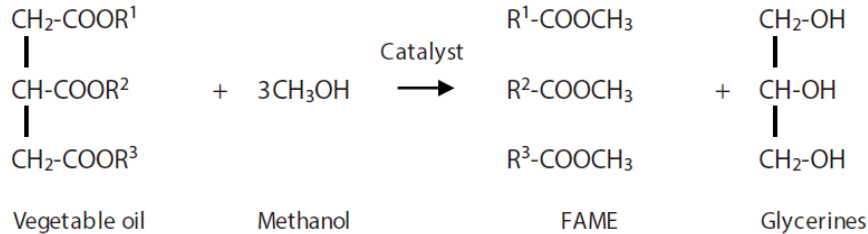
ATR = Attenuated total reflection
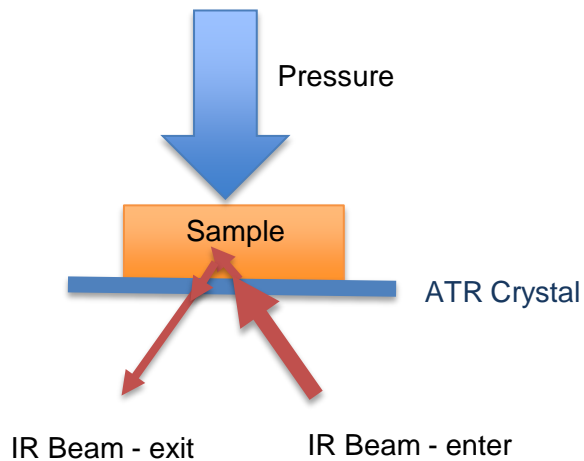
IRSpirit-T with QATR-S

ATR = Attenuated total reflection

● **Typical procedure**
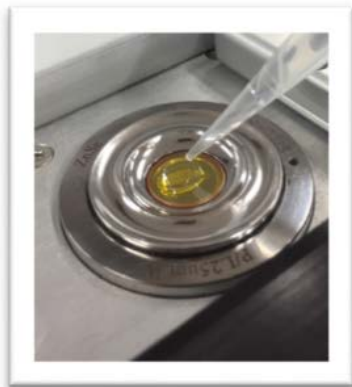
Drip liquid sample
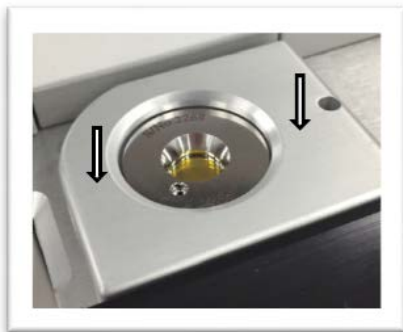
Cover with window from above

PearlTM Liquid FTIR ATR Accessory

ATR = Attenuated total reflection

- **ATR FTIR Spectra of FAME and Petroleum Diesel**
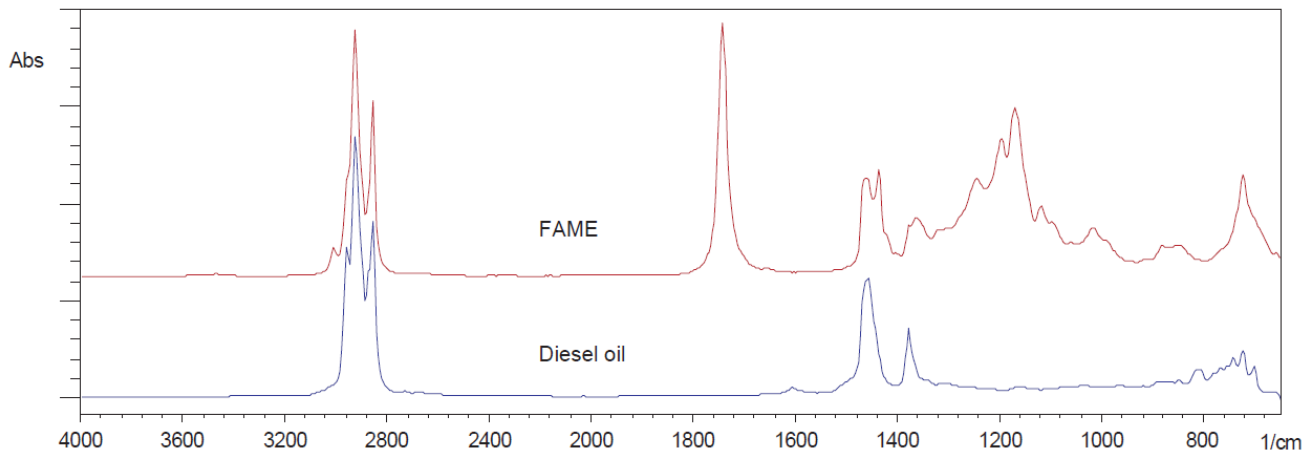
FAME Quantitation by ATR-FTIR

● Quantitation of FAME using the peak height @ 1,747.82 cm$_{-1}$
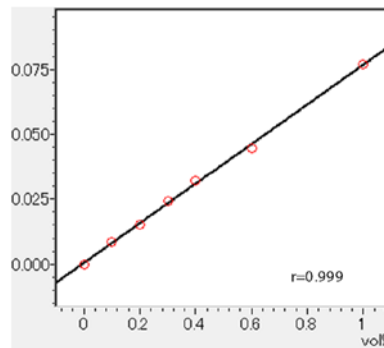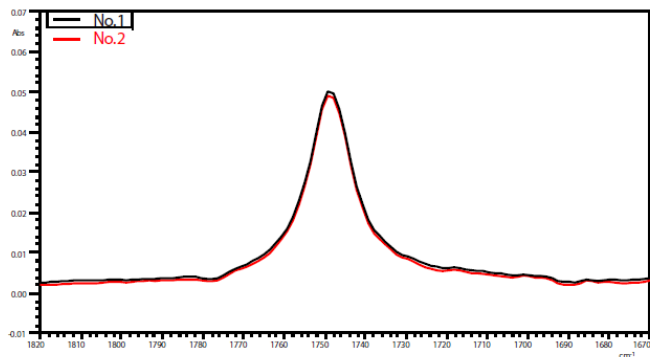
Peak of Carbonyl Group Used in Quantitation of FAME, 0.6 vol%

	Absorbance Abs	FAME concentration [vol%]
1st measurement	0.047	0.593
2nd measurement	0.046	0.590
Measurement error	0.001	0.003

FAME concentration [vol%]	Absorbance Abs
0.1	0.008
0.2	0.015
0.3	0.024
0.4	0.032
0.6	0.045
1.0	0.077

Lubricant and Additive Degradation

FTIR Degradation Analysis

Typical degradation by thermal + physical stress
- Water/Moisture
- Oxidation
- Nitration
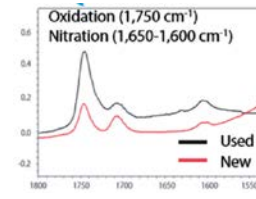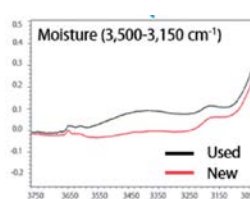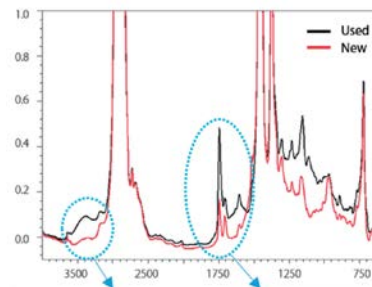
Specac Pearl™ Liquid Analyzer

10

2x Oil Samples

Sample A	Sample B
10W-60 gasoline engine lubricant Travel distance 3000 km Period of use: 3 months Used at high rotation range	0W-20 gasoline engine lubricant Travel distance 5000 km Period of use: 1 year Used at low rotation range

By analyzing lubricants at known wavelengths for O-H (water), C-O (oxidation), and C-N bonds, (nitration) among others, qualitative and quantitative assessment can be quickly performed on lubricant samples using the IRSpirit.

Sample A

Black = Used A
Red   = New A
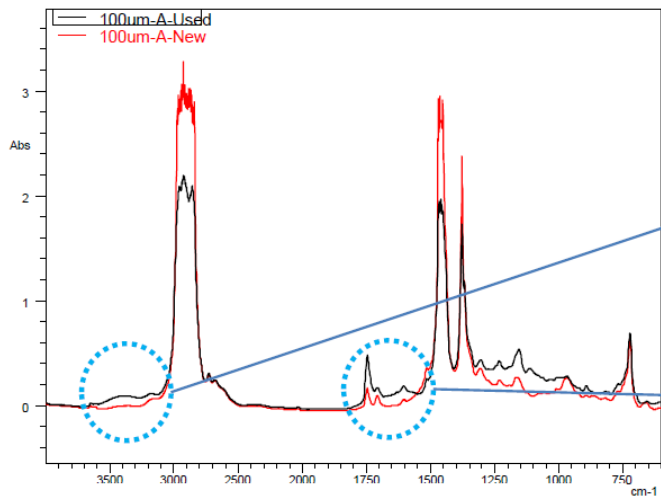
Water (Area 3500 to 3150 cm^{-1})
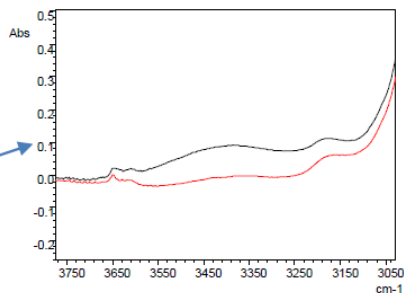
Oxidation (Around 1750 cm^{-1})
Nitration (Area 1650 to 1600 cm^{-1})
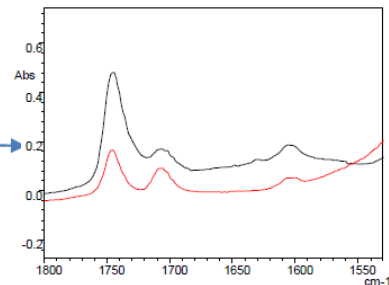
Sample A

10W-60 gasoline engine lubricant
Travel distance 3000 km
Period of use: 3 months
Used at high rotation range

Sample B

Anti-oxidants (Around 3650 cm^{-1})
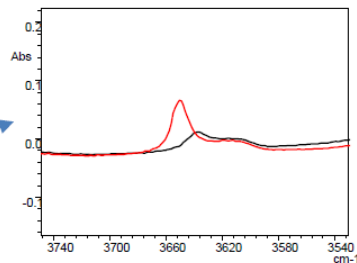
Nitration (Area 1650 to 1600 cm^{-1})
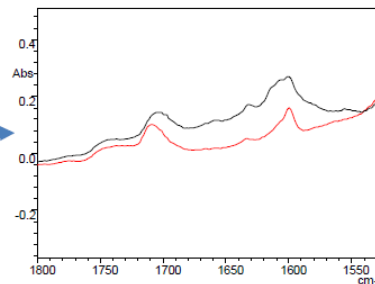
Sample B

0W-20 gasoline engine lubricant
Travel distance 5000 km
Period of use: 1 year
Used at low rotation range

Black = Used B
Red   = New B

Conclusion

Degradation Analysis
- Evaluations of lubricants by FTIR are simple and do not require Sample pretreatment. Efficient work is possible by using ATR technique.
- ATR = Cleaning is easy in comparison with conventional liquid cells.
- ATR = Optical path length with high accuracy, data with good reproducibility can be obtained in measurements based on ASTM E2412.

Soot in Engine Oil

Soot:
Incomplete combustion
of fuels results in the
production of soot,
carbonrich Particulates.

Soot Measurement
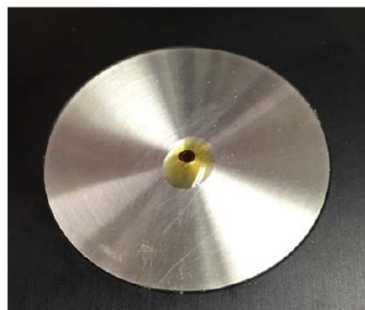
**Enlarged View of ATR Prism Plate
(with Drop of Engine Oil in Center)**
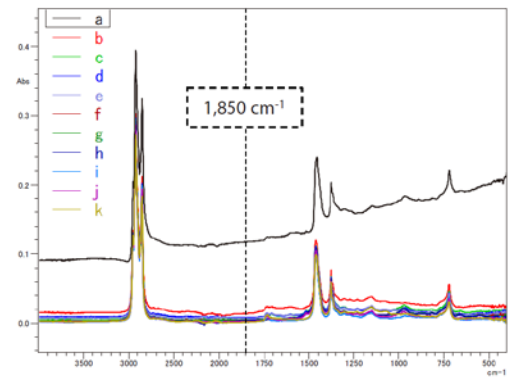
Sample	Soot content [mass%]
a	7.96
b	1.03
c	0.97
d	0.50
e	0.48
f	0.43
g	0.30
h	0.22
i	0.12
j	0.06
k	0.02

List of Stds for Calibration Curve

Soot Measurement at 1850 cm-1
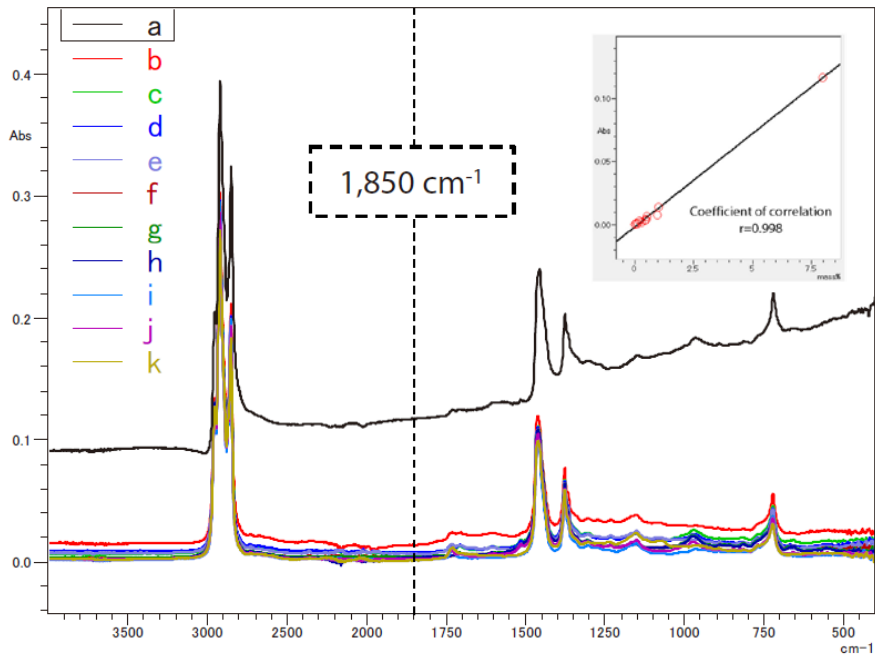
Sample	Soot content [mass%]
a	7.96
b	1.03
c	0.97
d	0.50
e	0.48
f	0.43
g	0.30
h	0.22
i	0.12
j	0.06
k	0.02

Maximum difference of variation: 0.0010 Abs
(CV value: 1.58%)
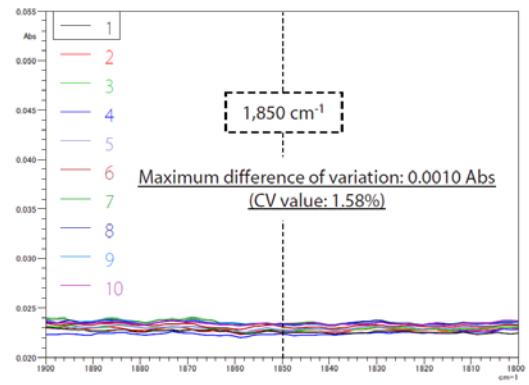
10x Infrared Spectrum for 0.20 Mass% Soot Content

Sample	Absorbance	Quantitation value [mass%]	Reference value [mass%]
X	0.008	0.65	0.60
Y	0.004	0.43	0.45
Z	0.001	0.18	0.02

FTIR for HPI

- The analysis of lubricants by FTIR does <u>not</u> require sample pretreatment, and the ATR technique makes it easy and quick for each analysis.

Spectroscopic Methods

FTIR, UV-Vis-NIR, RF

EDX, AAS, ICP-OES, ICP-MS

molecules

N > 1

elements

N = 1

Additive Elements and Wear Metals Analysis

EDX-7000P

- Elemental analyses for additives and wear metals in lubricating oils by ED-XRF

X-Ray Fluorescence
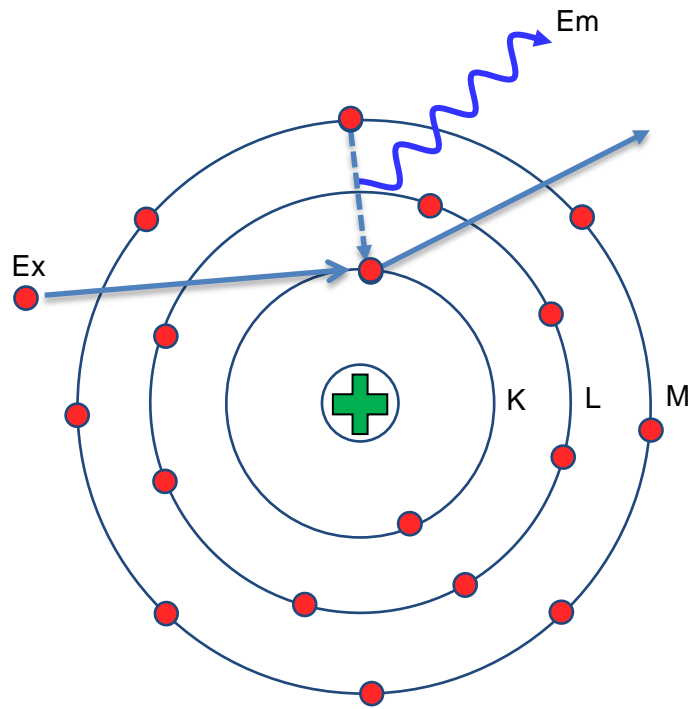
- **Characteristic emission**

- **Two detection principles**
  - Energy-dispersive → **EDX**
  - Wavelength-dispersive
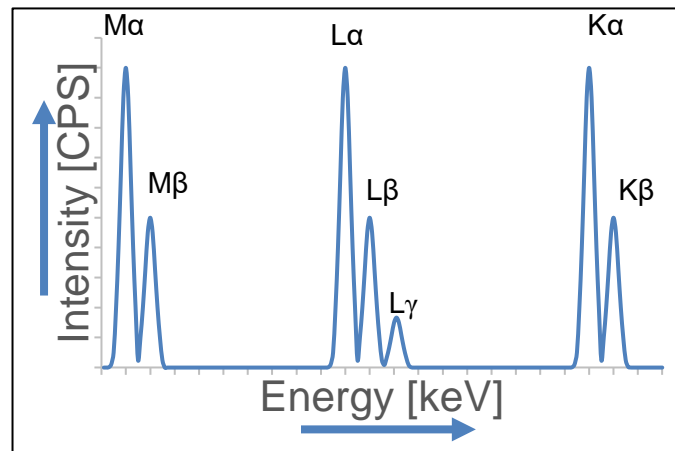
Quant. Analysis of Waste Oil by ED-XRF

- Waste oil can quickly and easily be analyzed by EDX.

- Analysed Elements: Ti, V, Cr, Ni, Cu, Zn, Ag, Cd, Sn, Sb, Ba, Pb

Approximately 8mL of waste oil sample
(each 10, 30, 50, 100, 300, 500 ppm)

Optical System EDX-7000P
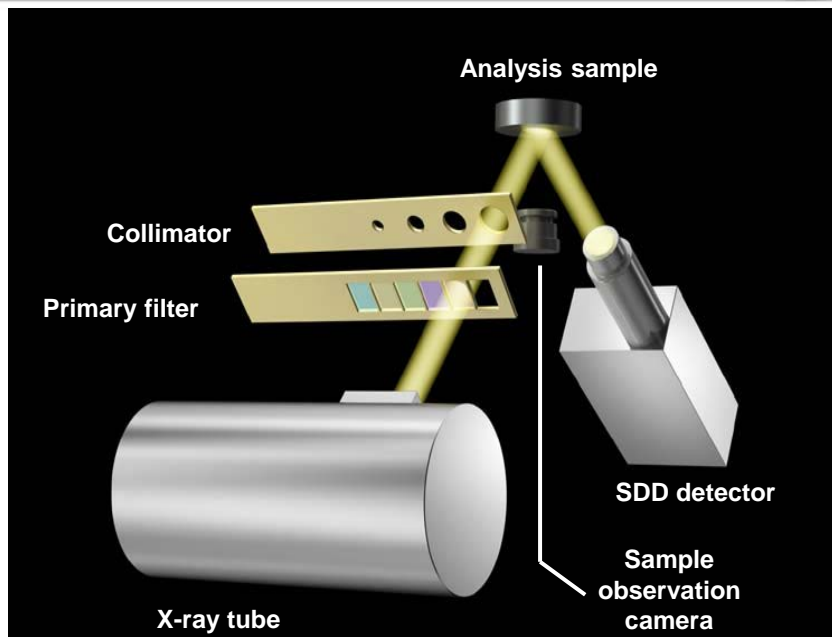
Analytical Conditions

Instrument	: EDX-7000		Collimator[mmφ]	: 10
Elements	: Ti, V, Cr, Ni, Cu, Zn, Ag, Cd, Sn, Sb, Ba, Pb		Primary Filter	: #1, #2, #4
Analytical Group	: Working Curve		Atmosphere	: Air
X-ray Tube	: Rh target		Detector	: SDD
Tube Voltage [kV]	: 15, 50		Integration Time[sec]	: 100, 300
Current [μA]	: Auto		Dead time [%]	: Max. 30

23

X-Ray Fluorescense Spectra
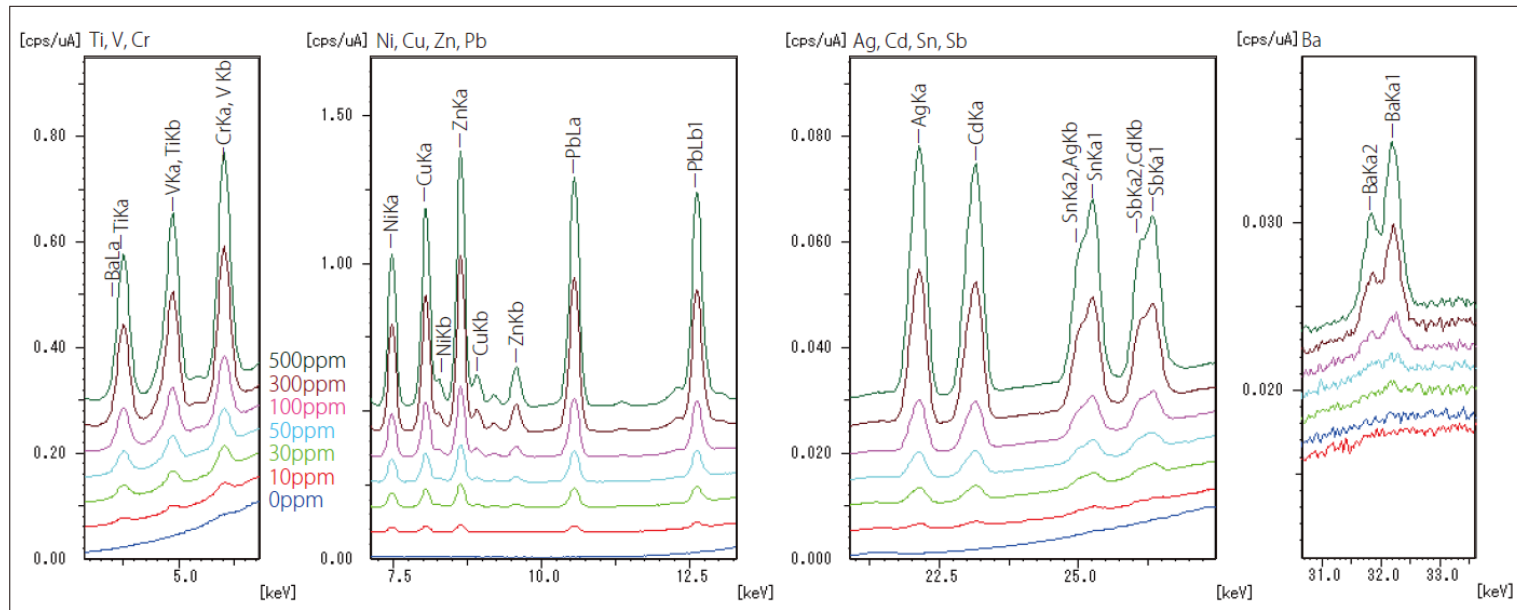
Oil Samples: 0, 10, 30, 50, 100, 300, 500 ppm

LLD 100 sec and 300 sec
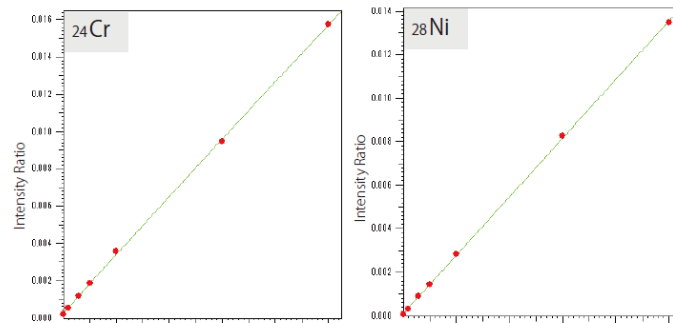
Table 1 Theoretical Lower Limits of Detection

Element	22Ti	23V	24Cr	28Ni	29Cu	30Zn	47Ag	48Cd	50Sn	51Sb	56Ba	82Pb
L.L.D. (300 sec)	1.2	1.3	1.2	0.4	0.3	0.3	0.7	0.9	1.9	2.8	9.9	0.3
L.L.D. (100 sec)	2.2	2.2	2.1	0.7	0.6	0.5	1.3	1.5	3.2	4.9	17.2	0.5

[ppm]

25
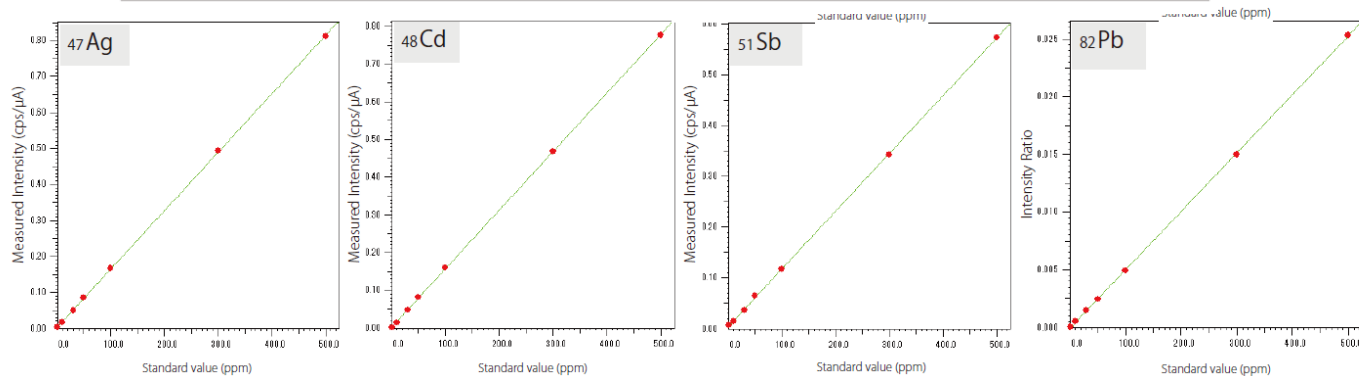
Plasma ICP
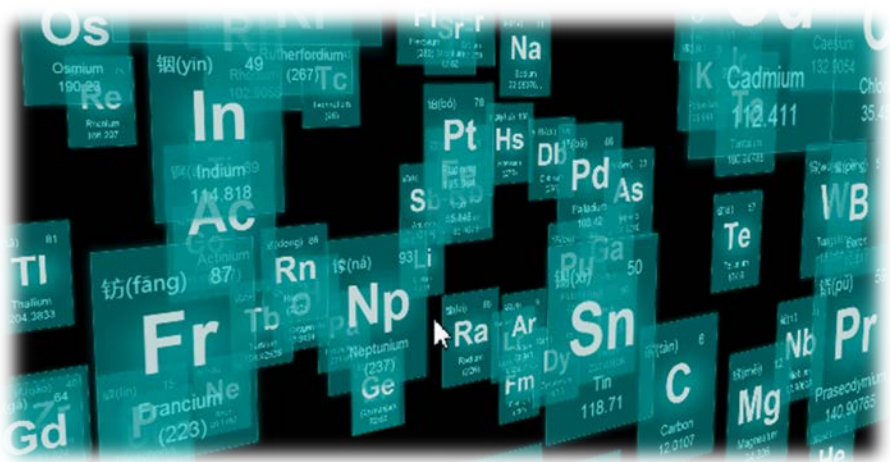
ICP-AES

ICPE-9820

Sample: <u>Used</u> automotive lubricants (Used for approximately 4000 km) and <u>new</u> lubricants were analyzed.

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Lubricating Oil

Additive Elements, Wear Metals, and Contaminants:

● Analysis of 22 x elements (Al, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, K, Si, Ag, Na, S, Sn, Ti, V, Zn) specified according to the ASTM standard D5185.

Instrument	: ICPE-9820
Radio Frequency Power	: 1.40 kW
Plasma Gas Flowrate	: 16.0 L/min
Auxiliary Gas Flowrate	: 1.40 L/min
Carrier Gas Flowrate	: 0.70 L/min
Sample Introduction	: Nebulizer, 10UES
Misting Chamber	: Organic solvent chamber
Plasma Torch	: Torch
Observation	: Radial (RD)

Some Spectral Profiles

- ## Spectral Profile Fe and P

Fe 259.940 nm

P 213.618 nm
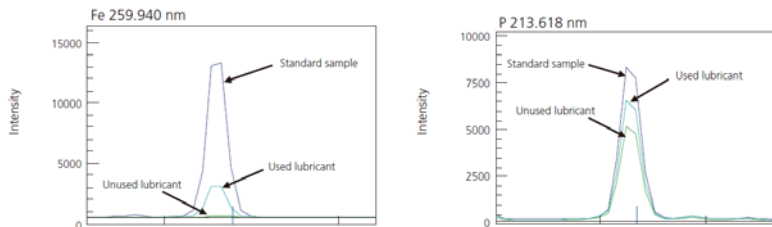
> ICPE-9820:
> dissolved elements in used lubricating oil can be stably analyzed without the introduction of oxygen.

- ## Calibration Curves of Fe, Mg and S

Fe 259.940 nm — r = 0.99999

Mg 285.213 nm — r = 0.99999

S 182.037 nm — r = 1.00000

30
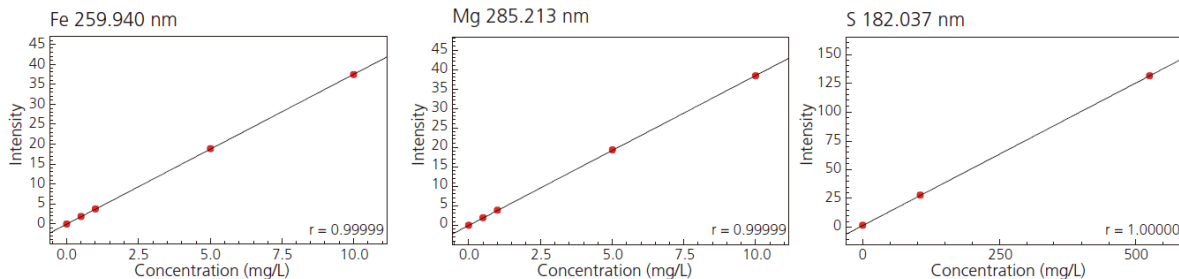
Analytical Result of Lubricant Oil

Element	Used lubricant (µg/g)	Used lubricant spike recovery rate (%)	Used lubricant dilution test (%)	Unused lubricant (µg/g)	Detection limit (µg/g)
Ag	<	100	-	<	0.02
Al	10	101	-	6.51	0.3
B	65.9	-	98	121	-
Ba	0.123	101	-	<	0.02
Ca	3970	-	98	2250	-
Cr	1.03	101	-	<	0.01
Cu	0.65	100	-	<	0.02
Fe	10.8	101	-	0.43	0.01
K	22.1	99	-	<	0.6
Mg	10.4	100	-	5.48	0.02
Mn	0.618	101	-	0.139	0.002
Mo	184	-	98	183	-
Na	2.5	100	-	<	0.4
Ni	<	102	-	<	0.05
P	756	-	99	731	-
Pb	<	100	-	<	0.5
S	3980	-	100	3810	-
Si	8.96	103	-	5.07	0.03
Sn	<	100	-	<	0.5
Ti	<	100	-	<	0.01
V	<	103	-	<	0.02
Zn	872	-	97	882	-

Result ICPE-9800

- Excellent results near 100 % were obtained in the dilution test for the high-concentration elements and the spike-and-recovery test for the low-concentration elements, both with respect to the used lubricants.

- Using the ICPE-9820, dissolved elements in used lubricants can be analyzed stably <u>without</u> the introduction of oxygen.

Conclusion

- Analysis of lubricant can be obtained by using FTIR and ICP-AES.
- Data conforming to different ASTM Standards can be easily obtained by combining compact IRSpirit and ATR technique.
- Using the ICPE-9820, dissolved elements in lubricants can be analyzed stably without the introduction of oxygen, by low Ar-consumption.

Evaluation item/Measurement object		Instrument	ASTM
Degradation	Oxidation	FTIR	E2412
	Nitration		
	Sulfonation		
Contamination	Moisture	FTIR	E2412
	Soot		
	Gasoline	GC	D3525 D7593
		FTIR	E2412
	Diesel	GC	D3524 D7593
		FTIR	E2412
	Coolant (B, Na, K)	ICP-AES	D5185
		FTIR	E2412
	Antifreeze (Na)	ICP-AES	D5185
	Dust (Si)		
	Sealant (Si)		
Wear	Metal (Al, Fe, Cu, Cr, Ni, Zn, etc.)	ICP-AES	D5185
Additives	Antioxidant (Zn, Cu, B)	ICP-AES	D4951
		FTIR	E2412
	Anti-wear agent (B, Cu, K, S, Zn, etc.)	ICP-AES	D4951
		FTIR	E2412
	Surfactant (Ba, Mg, Ca, etc.)	ICP-AES	D4951
	Corrosion inhibitor (Ba, Zn)		
	Anti-rust agent (K, Ba)		
	Lubricant (Mo)		

Shimadzu Europa GmbH

Thank You!

Have a nice 30 Min. Lunch Break ☺