VALUTAZIONE DELLA STABILITÀ OSSIDATIVA DI OLI VEGETALI E BIODIESEL TRAMITE SPETTROSCOPIA RAMAN E FTIR

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- DENSITY AND CONCENTRATION MEASUREMENT
- VISCOMETRY
- POLARIMETRY AND REFRACTOMETRY
- DETERMINATION OF PETROLEUM PROPERTIES
- RHEOMETRY
- PARTICLE, PORE, AND SURFACE CHARACTERIZATION
- MECHANICAL SURFACE CHARACTERIZATION
- ANALYTICAL AND SYNTHETIC CHEMISTRY
- X-RAY STRUCTURE ANALYSIS
- FTIR AND RAMAN SPECTROSCOPY
- PROCESS INSTRUMENTATION
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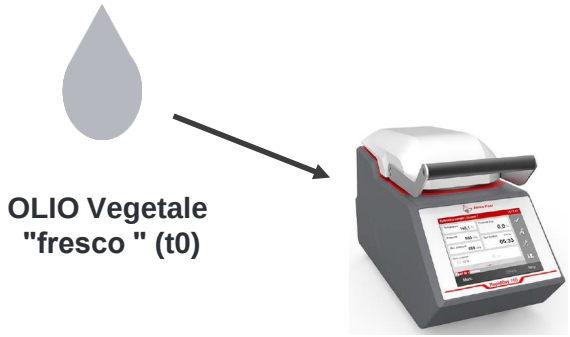
I

II

Application Report

Analisi Stabilità Ossidativa e Analisi Qualitativa Pre/Post Ossidazione



"Formazione residuo solido ad alte T "

Analisi Spettroscopica

Application Report

Analisi Stabilità Ossidativa e Analisi Qualitativa Pre/Post Ossidazione

OLIO Vegetale "fresco " (t0)

Rapidoxy 100

Ossidazione (controllata, cinetica rapida)

120 °C | 150 °C | 180 °C

OLIO Vegetale Ossidato (?)

Analisi Spettroscopica

Cora 5001

Application Report

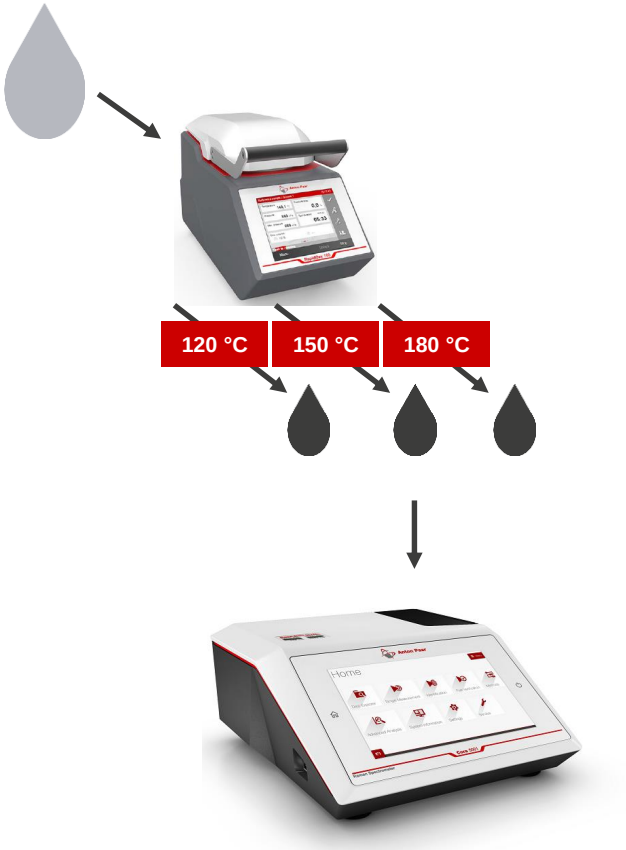
Analisi Stabilità Ossidativa e Analisi Qualitativa Pre/Post Ossidazione

Campioni esaminati:

- Olio atb(OVA) 17081
- Olio atb(OVA) 22150

Analisi effettuate sui due campioni in 4 condizioni:

- T0: pre ossidazione
- T1: post ossidazione con RapidOxy a 120 °C
- T2: post ossidazione con RapidOxy a 150 °C
- T3: post ossidazione con RapidOxy a 180 °C



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Rapidoxy 100

STABILITÀ OSSIDATIVA

Analisi Stabilità Ossidativa

Rapidoxy100

- **Accelerated aging of sample**

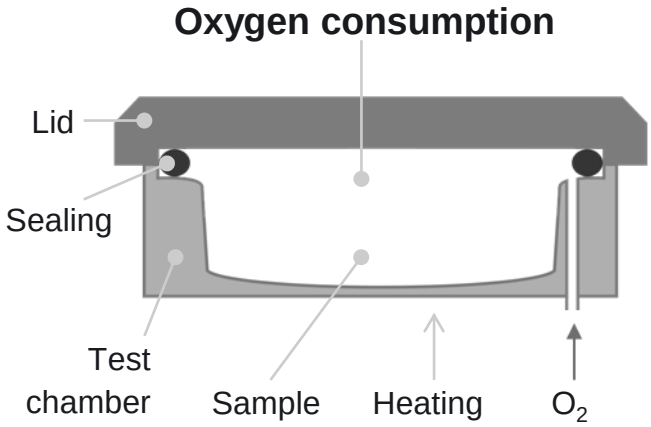
Sample is set under pressure with pure oxygen and heated to initiate a fast oxidation process

- **Monitoring the oxygen uptake**

The temperature is kept strictly constant during measurement and the pressure is continuously traced => due to oxygen consumption the pressure drops accordingly

- **According to ASTM D8206**

RSSOT (RAPID SMALL SCALE OXIDATION TEST), determining the oxidation stability of lubricating greases



Analisi Stabilità Ossidativa

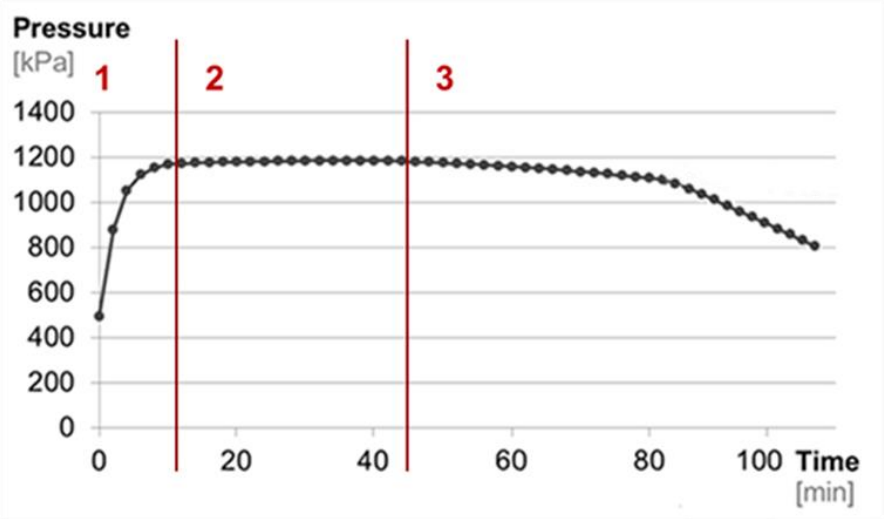
Rapidoxy100

Measurement starts with heating of the test chamber: Very fast process, less than 300 s to reach target temperature

1 Pressure rises due to heating

2 When a stable equilibrium gas/liquid phase is reached the pressure is constant (typically maximum pressure of the measurement)

3 As soon as oxygen is consumed by the sample the pressure drops accordingly



Standard measurement: Induction Period (IP)
Time elapsed between starting the heating procedure of the test chamber and a 10 % pressure drop from the maximum pressure

The longer the IP (the slower the pressure drop), the slower is the oxygen uptake, the more oxidative stable is the sample

Analisi Stabilità Ossidativa

Rapidoxy100

Variazione di peso post ossidazione:

Sample	17081				22150			
	t0	t1	t2	t3	t0	t1	t2	t3
Massa [g]	5,002	5	5	4,9767	5	5	4,972	4,9929
Massa Post Oxy [g]		4,992	6,6121	5,0257		5,026	5,0144	5,0409
Tempo Oxy (10%) [min]		111,75	29,37	15,93		126,7	40,3	22,97

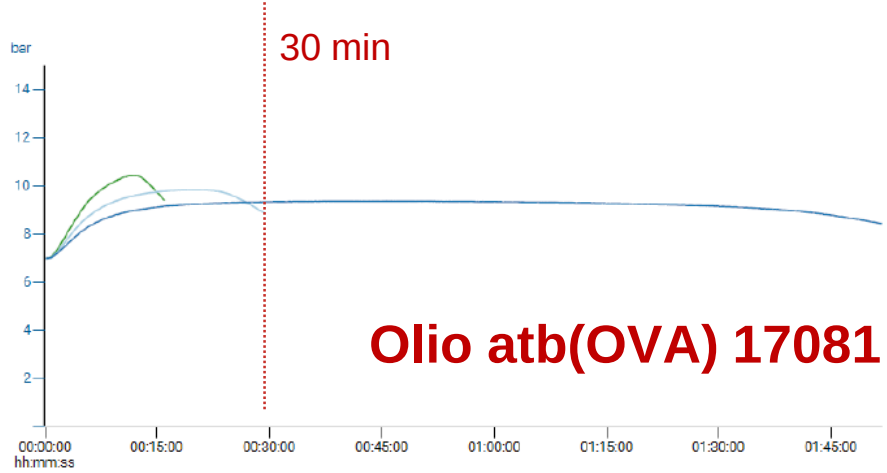
Campioni analizzati:

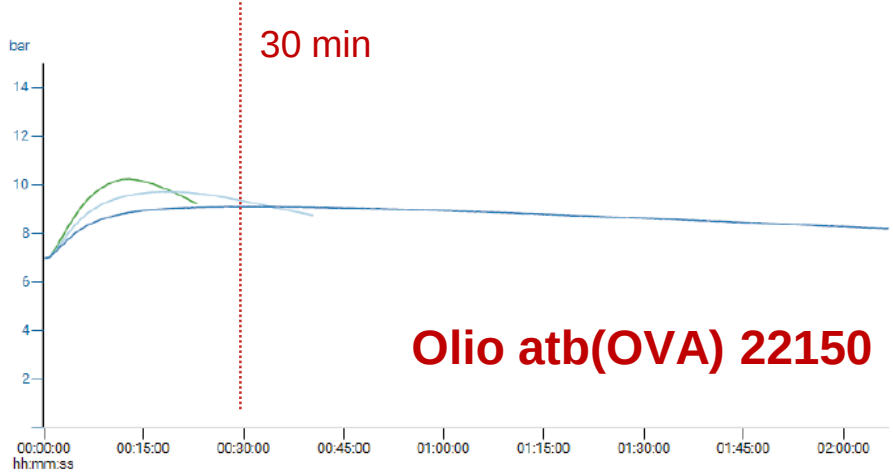
- Olio atb(OVA) 17081
- Olio atb(OVA) 22150

In tutti i campioni trattati con Rapidoxy a T più elevata, viene rilevato un aumento di peso

Analisi Stabilità Ossidativa

Rapidoxy100





Olio vegetale atb OVA

Device serial number	60064905
Status	OK
Pressure drop result	10,0 % at 01:51:45 hh:mm:ss
Average temperature	120,0 °C

Olio vegetale atb OVA_150°C

Device serial number	60064905
Status	OK
Pressure drop result	10,0 % at 00:29:22 hh:mm:ss
Average temperature	150,1 °C

Olio vegetale atb OVA_180°C

Device serial number	60064905
Status	OK
Pressure drop result	10,0 % at 00:15:56 hh:mm:ss
Average temperature	180,2 °C

Olio vegetale atb OVA_2

Device serial number	60064905
Status	OK
Pressure drop result	10,0 % at 02:06:42 hh:mm:ss
Average temperature	120,0 °C

Olio vegetale atb OVA_150°C 22150

Device serial number	60064905
Status	OK
Pressure drop result	10,0 % at 00:40:18 hh:mm:ss
Average temperature	150,1 °C

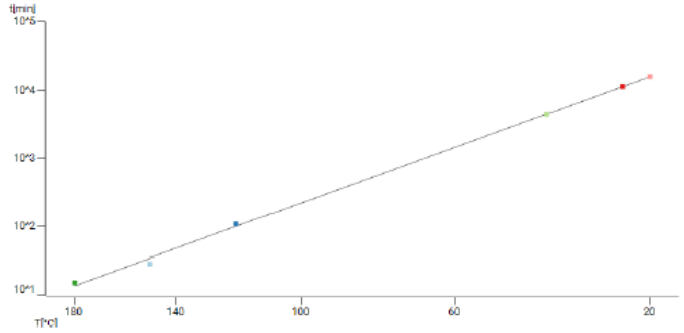
Olio vegetale atb OVA_180°C 22150_2

Device serial number	60064905
Status	OK
Pressure drop result	10,0 % at 00:22:58 hh:mm:ss
Average temperature	180,2 °C

Analisi Stabilità Ossidativa – Shelf-life

Rapidoxy100

Shelf-life estimation of fats and oils (pressure drop)



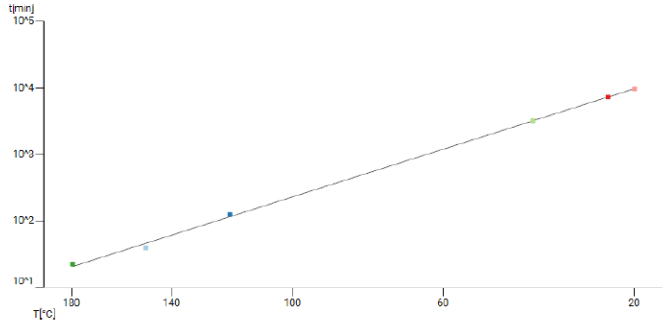
Expected shelf-life at 40,0 °C	3 day(s) and 2 hour(s)
Expected shelf-life at 25,0 °C	7 day(s) and 20 hour(s)
Expected shelf-life at 20,0 °C	10 day(s) and 22 hour(s)

Olio atb(OVA) 17081

Regression line equation	ln(t[min]) = 5800,00 K / T - 10,00 ln(t[min]) = 48000,00 Jmol⁻¹ / (8,31446 Jmol⁻¹K⁻¹ * T) - 10,00
Activation energy:	48000,00 Jmol⁻¹
R²	0,97

Olio vegetale atb OVA	
Device serial number	60064905
Status	OK
Duration to pressure drop:	10,0 % at 01:51:45 hh:mm:ss
Average temperature	120,0 °C
Olio vegetale atb OVA_150°C	
Device serial number	60064905
Status	OK
Duration to pressure drop:	10,0 % at 00:29:22 hh:mm:ss
Average temperature	150,1 °C
Olio vegetale atb OVA_180°C	
Device serial number	60064905
Status	OK
Duration to pressure drop:	10,0 % at 00:15:56 hh:mm:ss
Average temperature	180,2 °C

Shelf-life estimation of fats and oils (pressure drop)



Expected shelf-life at 40,0 °C	2 day(s) and 5 hour(s)
Expected shelf-life at 25,0 °C	5 day(s) and 1 hour(s)
Expected shelf-life at 20,0 °C	6 day(s) and 19 hour(s)

Olio atb(OVA) 22150

Regression line equation	ln(t[min]) = 5100,00 K / T - 8,20 ln(t[min]) = 42000,00 Jmol⁻¹ / (8,31446 Jmol⁻¹K⁻¹ * T) - 8,20
Activation energy:	42000,00 Jmol⁻¹
R²	0,98

Olio vegetale atb OVA_2	
Device serial number	60064905
Status	OK
Duration to pressure drop:	10,0 % at 02:06:42 hh:mm:ss
Average temperature	120,0 °C
Olio vegetale atb OVA_150°C 22150	
Device serial number	60064905
Status	OK
Duration to pressure drop:	10,0 % at 00:40:18 hh:mm:ss
Average temperature	150,1 °C
Olio vegetale atb OVA_180°C 22150_2	
Device serial number	60064905
Status	OK
Duration to pressure drop:	10,0 % at 00:22:58 hh:mm:ss
Average temperature	180,2 °C

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Cora 5001

SPETTROSCOPIA RAMAN

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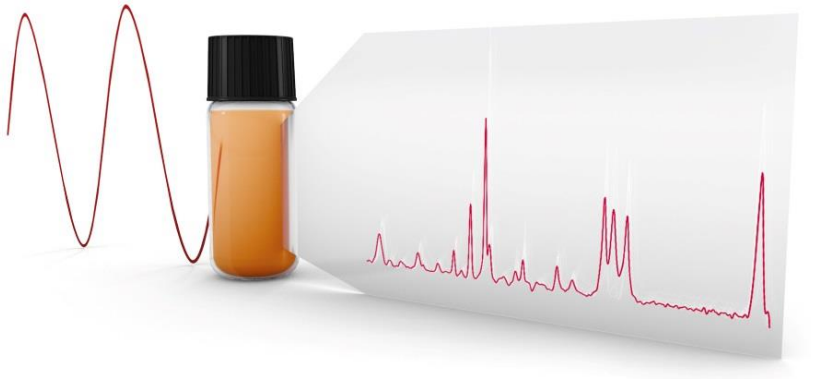
Spettroscopia Raman

Cora 5001



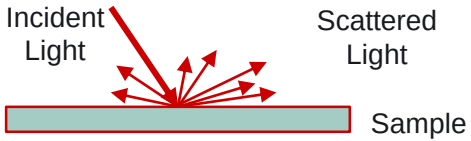
Inelastic light scattering observed by **C.V. Raman**
in 1928 (Nobel prize 1930)

➔ When light interacts with a molecule, some of the light changes wavelength

- Raman is a spectroscopic technique using excitation of a sample to provide a **chemical fingerprint** by which molecules and substances can be identified
- This technique is mainly used for **qualitative and quantitative** chemical identification

Spettroscopia Raman

Inelastic light scattering

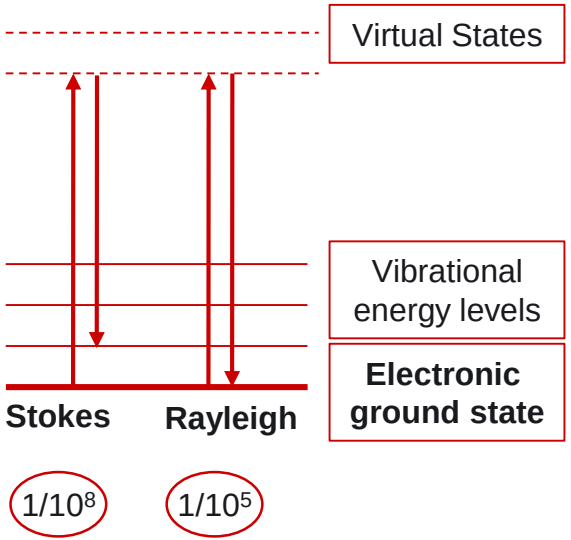


Rayleigh: elastic scattering, no energy transfer, emission of photon of equal energy (only change of direction)

Stokes: inelastic scattering, energy of incoming light is shifted to longer wavelength (color change), energy transferred to molecular vibration

→ Raman shift

→ Probability $1/10^8$ - weak signal



The Raman effect: inelastic light scattering

Spettroscopia Raman

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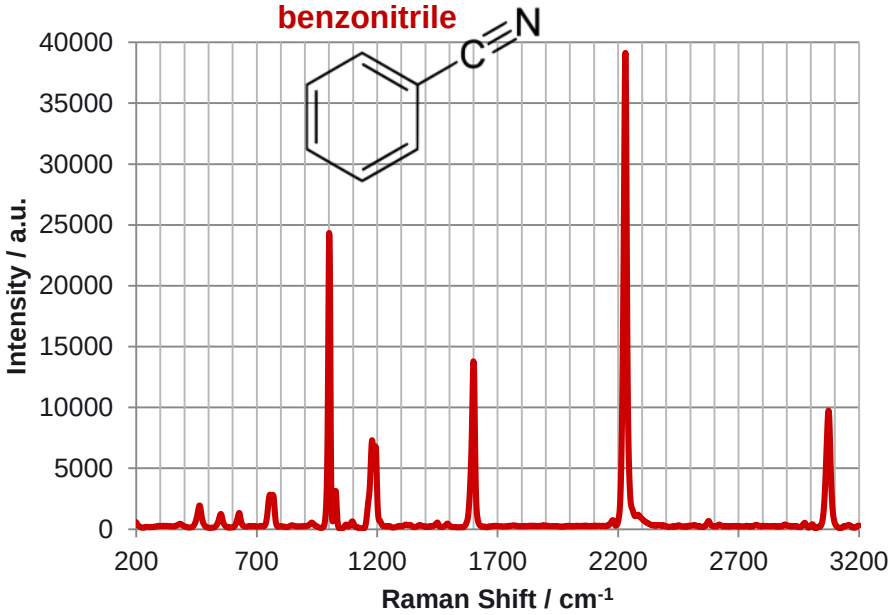
Types of Analyses

- **Identification** of unknown substance (what's in this bag / bottle / container?)
- **Confirmation** (e.g. incoming goods)
- **Chemical composition** and its changes (e.g. oxidation)
- **Molecular structure** and its changes (e.g. conformation of proteins, polymorphism in drugs, structure of soot etc.)
- **Chemical monitoring** (e.g. reactions, curing, matureness, turning points, switching points, phase transitions, real-time adjustments)

Spettroscopia Raman

Spectral information



- **Identification** (unknown substance)
- **Confirmation**
- **Chemical composition**
- **Molecular structure**
- **Chemical monitoring**

Spettroscopia Raman

Benefits

- Analysis through containers (e.g. glass or plastic bags)
- Measurement of aqueous solution is possible due to the low influence of water
- Easy chemical and structural identification: “chemical fingerprinting”
- Raman bands are typically narrow, sharp, not overlapping
- Fast and easy measurement
- Measurements are mostly non-contact and non-destructive
- Tolerant to various samples (solid or liquid)
- No or little sample preparation

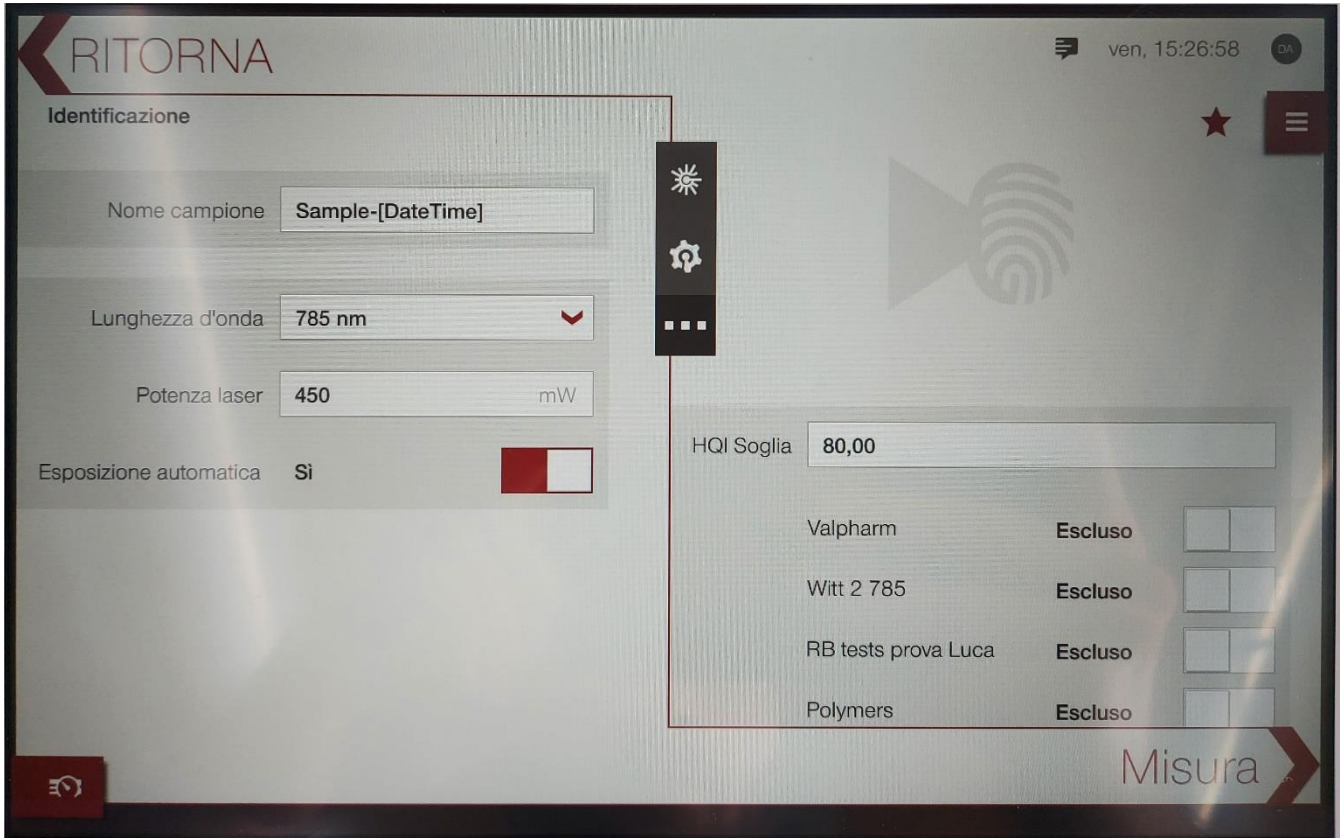
Spettroscopia Raman

Limitations

- Raman effect is weak (probability approx. $1/10^8$), signals may be weak for weakly scattering samples
- Raman signal obscured by fluorescence (depending on excitation wavelength)
- Not possible (no Raman effect) with metals and alloys
- Higher detection limit for Raman compared to mass spectrometry (factor 1000 less sensitive) → higher concentration needed

Spettroscopia Raman

Cora 5001



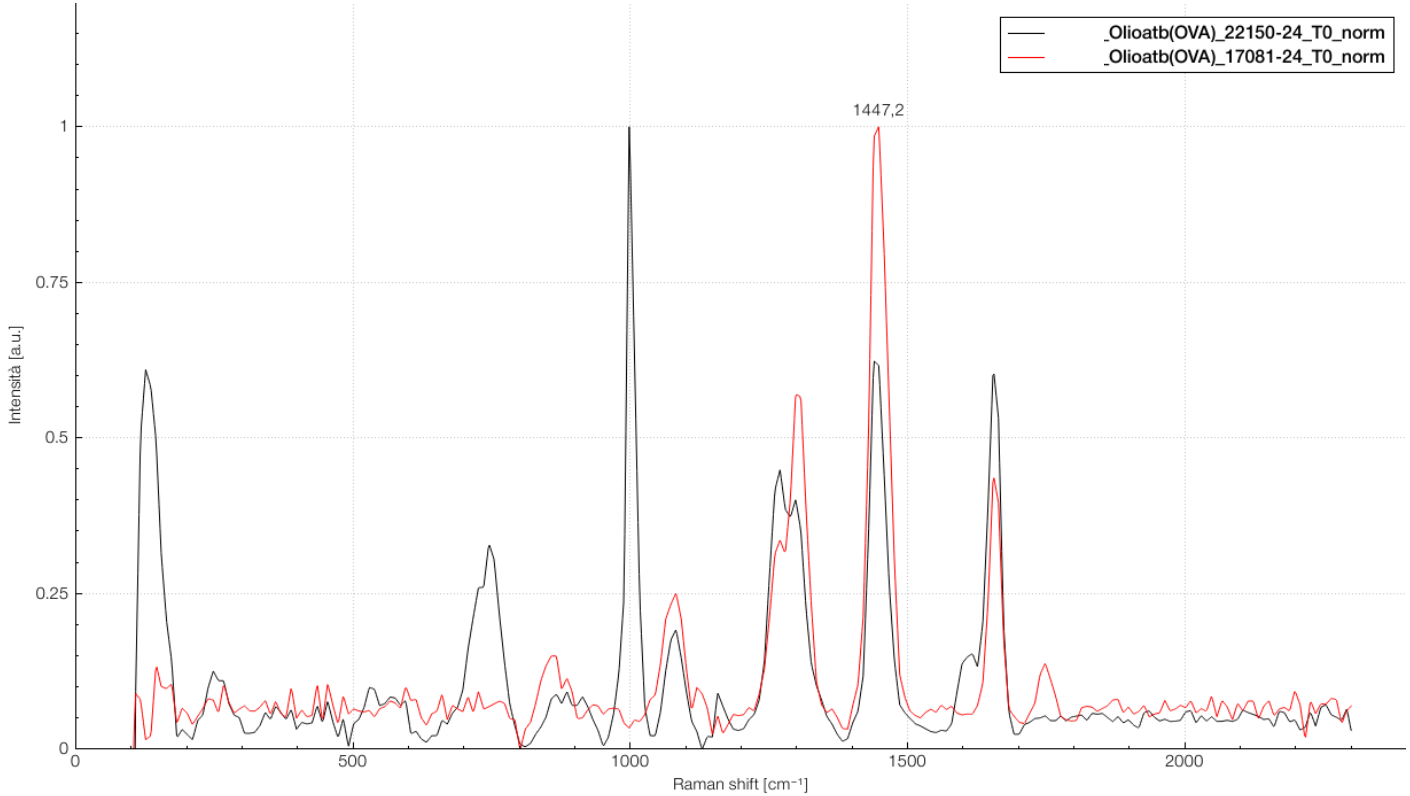
Analisi svolta: **misurazione singola + identificazione**

Parametri dell'analisi:

- Lunghezza d'onda **1064 nm**
- Potenza laser: **200 mW**
- Tempo di esposizione **10000 ms**
- **Normalizzazione** min-max dello spettro

Spettroscopia Raman

Risultati – Campioni 17081 vs 22150 a t0



Spettroscopia Raman

Risultati – Identificazione a t0

17081

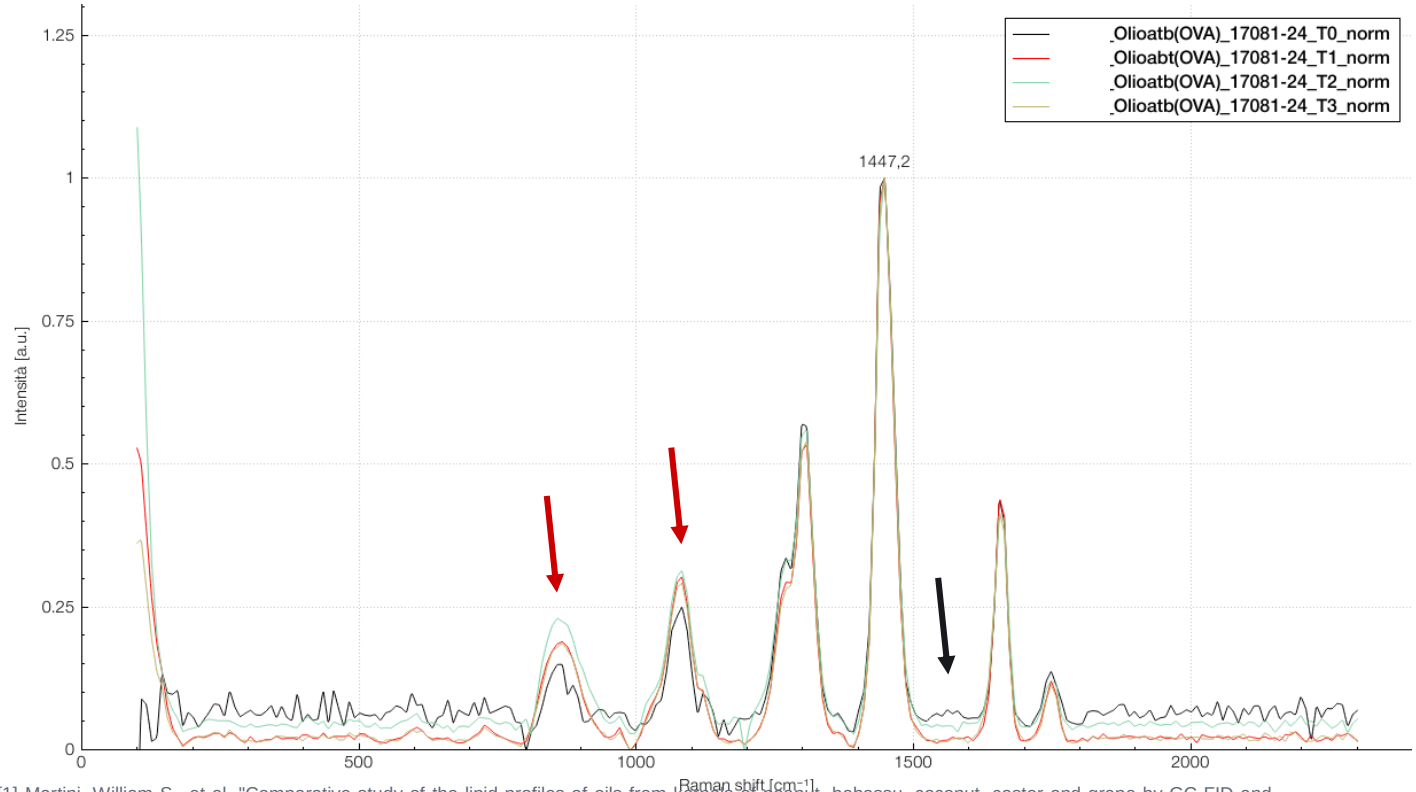
	Match	Libreria	HQI
1	Castor oil	AP Factory (1064)	96,46
2	PENTAERYTHRITOL TETRAOLEATE	S.T. Japan Raman	94,98
3	Cis-9-Tricosene	S.T. Japan Raman	94,38

22150

	Match	Libreria	HQI
1	CARDOLITE NC 513	S.T. Japan Raman	70,87
2	Poly(styrene:butadiene) block filled	S.T. Japan Raman	67,03
3	POLY(BUTADIENE:STYRENE)	S.T. Japan Raman	63,50

Spettroscopia Raman

Risultati – 17081



Picchi a 860 e 1080 cm^{-1} relativi alla **produzione di perossidi**, legata all'ossidazione di oli [1], aumentano fino a T2 poi diminuiscono di nuovo per bassa stabilità

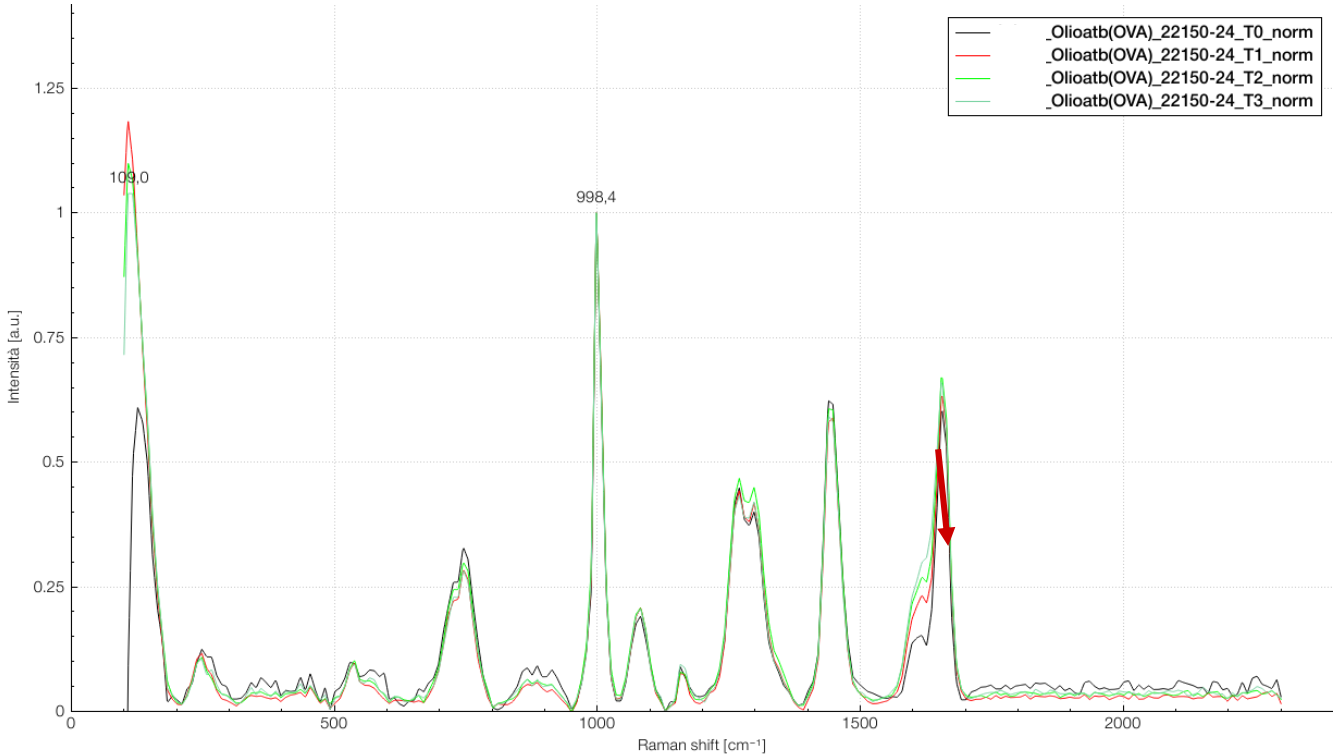
Scomparsa del picco a 1526 cm^{-1}, relativo ai **carotenoidi** e indice di ossidazione [2]

[1] Martini, William S., et al. "Comparative study of the lipid profiles of oils from kernels of peanut, babassu, coconut, castor and grape by GC-FID and Raman spectroscopy." Journal of the Brazilian Chemical Society 29.2 (2018): 390-397.

[2] Vaskova, Hana, and Martina Buckova. "Thermal degradation of vegetable oils: spectroscopic measurement and analysis." Procedia Engineering 100 (2015): 630-635.

Spettroscopia Raman

Risultati – 22150



Progressivo aumento della spalla a 1615 cm^{-1} relativa a **legami C=C** [1] a loro volta collegata alla produzione di **prodotti di degradazione** dell'olio [2]

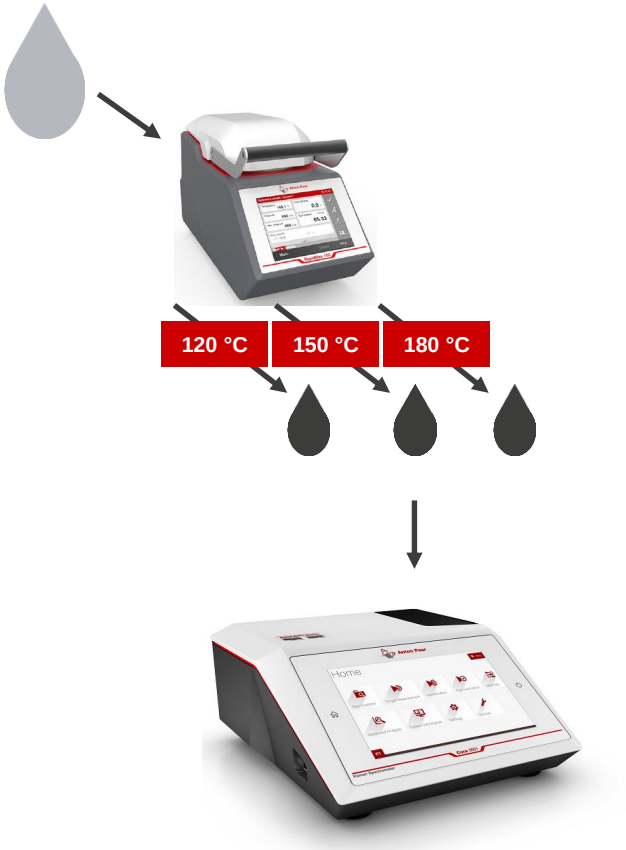
[1] Socrates, George. Infrared and Raman characteristic group frequencies: tables and charts. John Wiley & Sons, 2004.

[2] Vaskova, Hana, and Martina Buckova. "Thermal degradation of vegetable oils: spectroscopic measurement and analysis." Procedia Engineering 100 (2015): 630-635.

Conclusioni

Analisi Stabilità Ossidativa e Analisi Qualitativa Pre/Post Ossidazione

- È stato possibile utilizzare il Rapidoxy per simulare ossidazione in colonna e velocizzare processo
- Analisi effettuate sui due campioni in 4 condizioni:
  - T0: pre ossidazione
  - T1: post ossidazione con RapidOxy a 120 °C
  - T2: post ossidazione con RapidOxy a 150 °C
  - T3: post ossidazione con RapidOxy a 180 °C
- Tramite spettroscopia Raman è stato possibile seguire la formazione di nuove specie chimiche durante il processo ossidativo



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