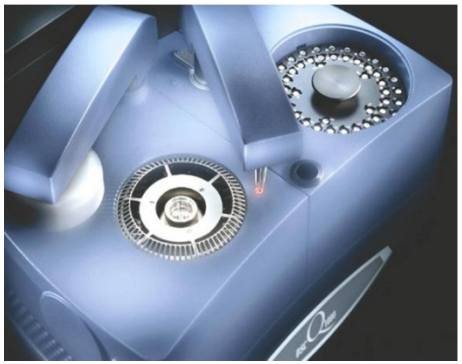
DİFERANSİYEL TARAMALI KALORİMETRE İLE ZEYTİNYAĞI KARAKTERİZASYONU

Huri İLYASOĞLU[1], Cemalettin BALTACI[2], Beraat ÖZÇELİK[3]

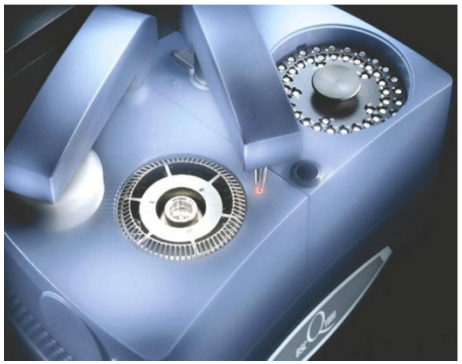
[1] Gümüşhane Üniversitesi, Beslenme ve Diyetetik Bölümü
[2] Gümüşhane Üniversitesi, Gıda Mühendisliği Bölümü
[3] İstanbul Teknik Üniversitesi, Gıda Mühendisliği Bölümü

İÇERİK



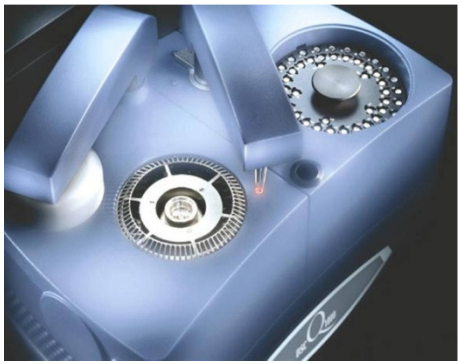
- Termal Analiz
- Diferansiyel Taramalı Kalorimetre (DSC)
- DSC Kullanım Alanları
- DSC Yağ Analizlerinde Kullanımı
- DSC ile Zeytinyağı Karakterizasyonu Üzerine Yapılan Çalışmalar
- Sonuç

TERMAL ANALİZ



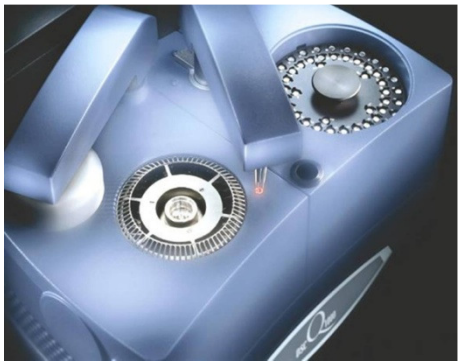
- Maddelerin fiziksel özelliklerini sıcaklığının fonksiyonu olarak ölçen teknikler
- Termodinamik özelliklerin (sıcaklık, ısı, entalpi vb.) belirlendiği analiz yöntemleri

TERMAL ANALİZ

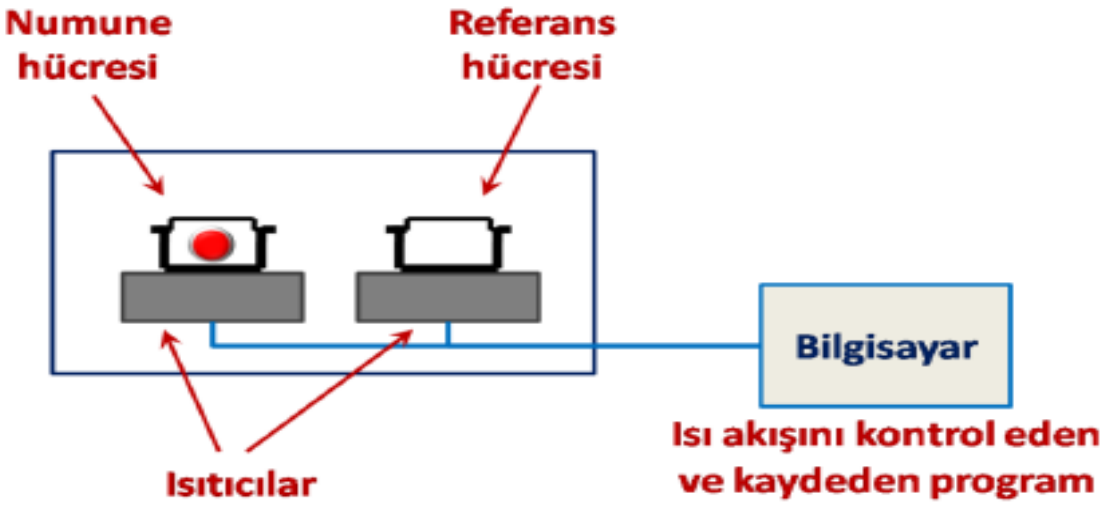


- Termogravimetrik analiz
- Diferansiyel taramalı analiz
- Diferansiyel taramalı kalorimetre

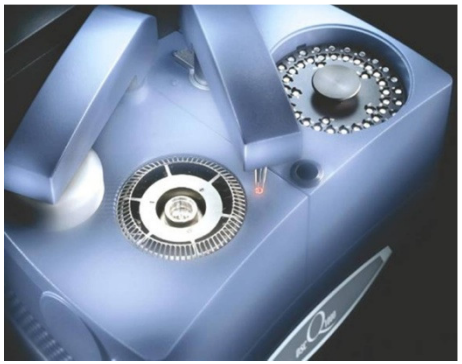
DİFERANSİYEL TARAMALI KALORİMETRE



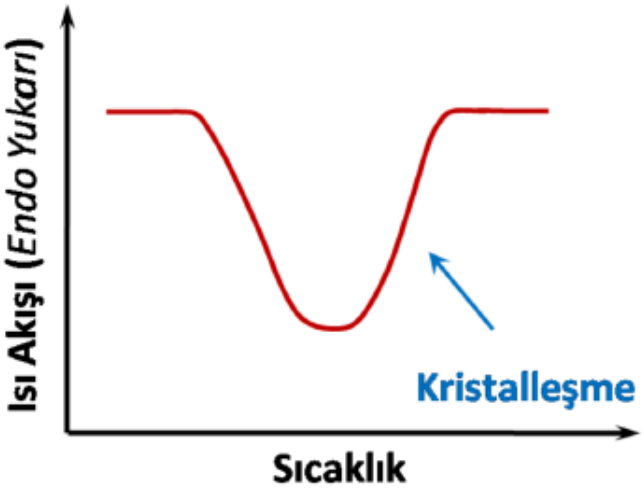
- Kontrollü atmosfer koşullarında,
- Zaman ve sıcaklığın fonksiyonu olarak,
- Maddedeki fiziksel değişimlere bağlı enerji değişimlerinin ölçümü

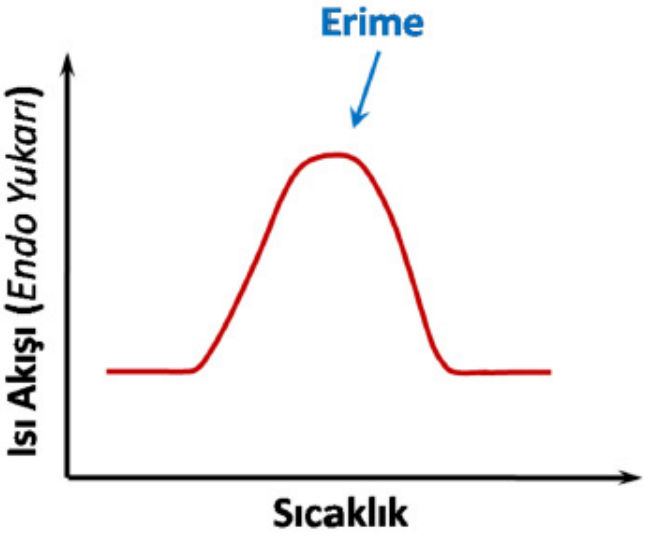


DİFERANSİYEL TARAMALI KALORİMETRE

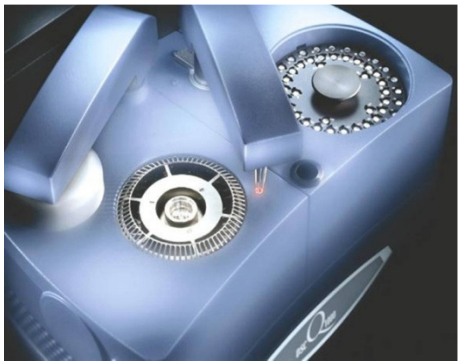


- Ekzotermik ve endotermik prosesler esnasında meydana gelen
  - fiziksel ve kimyasal değişimler ile ilgili kalitatif ve kantitatif bilgi sağlayan termal analiz yöntemi



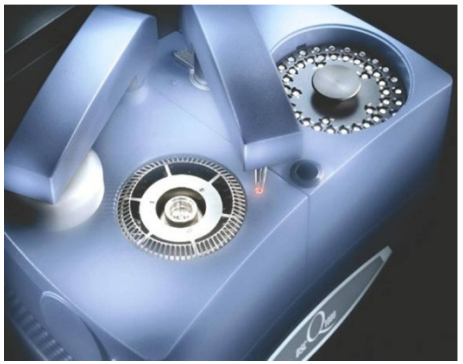


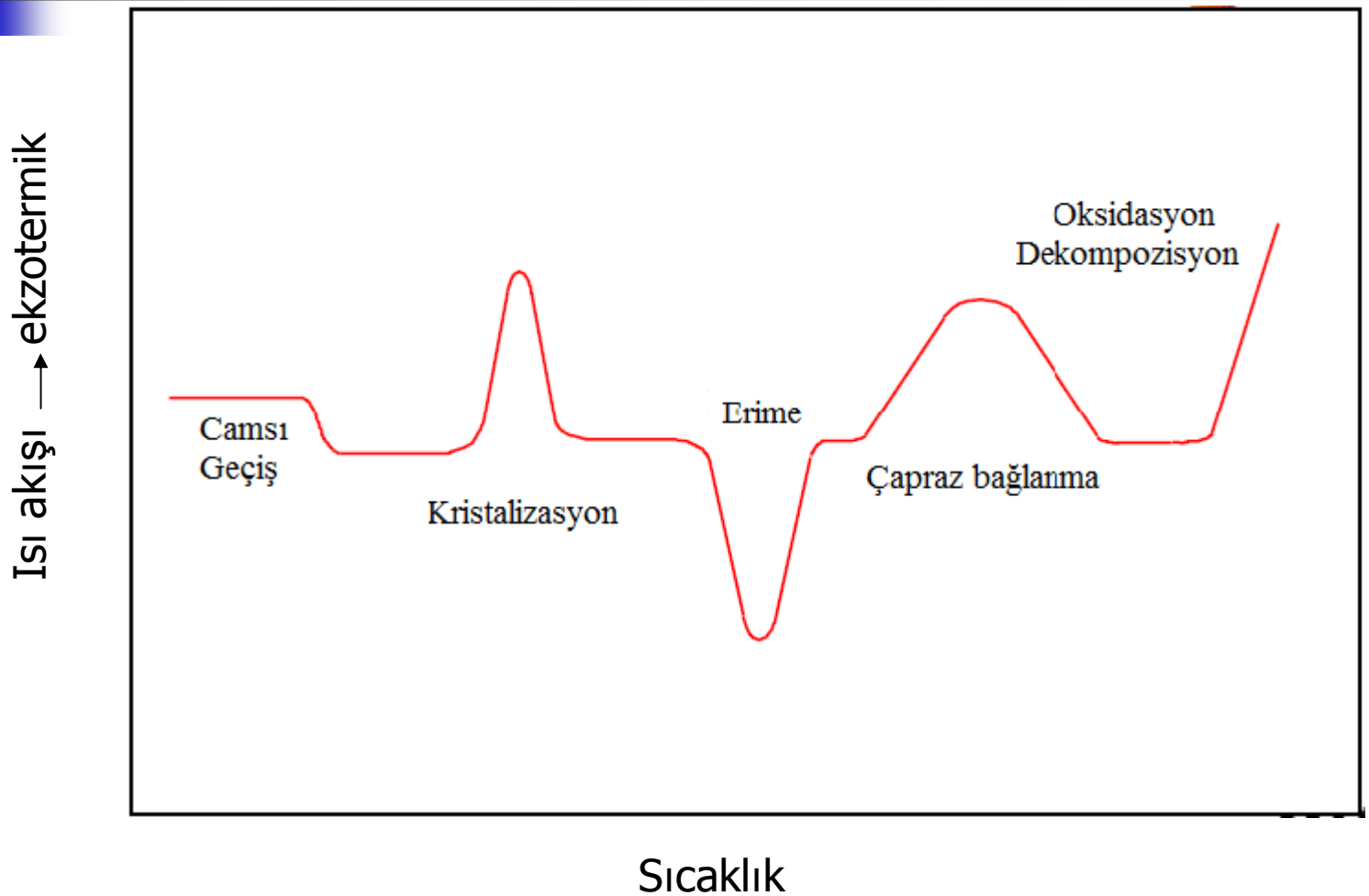
DİFERANSİYEL TARAMALI KALORİMETRE



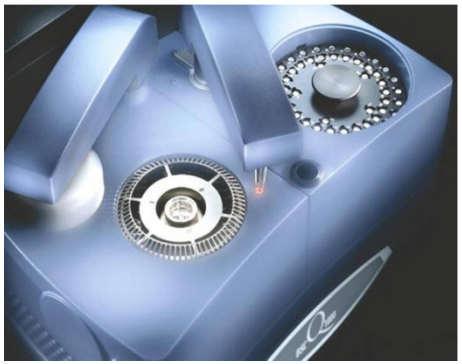
- Camsı geçiş sıcaklığı
- Erime noktası sıcaklığı
- Kristalizasyon sıcaklığı
- Isı kapasitesi
- Entalpi
- Oksidatif stabilite
- Termal stabilite

DİFERANSİYEL TARAMALI KALORİMETRE



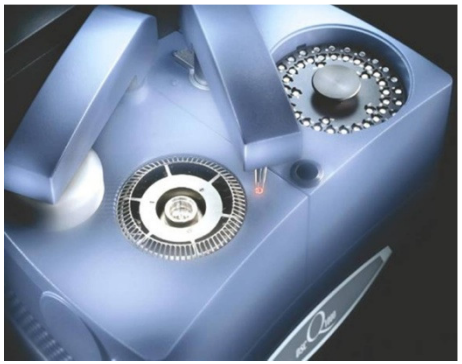


DSC UYGULAMA ALANLARI



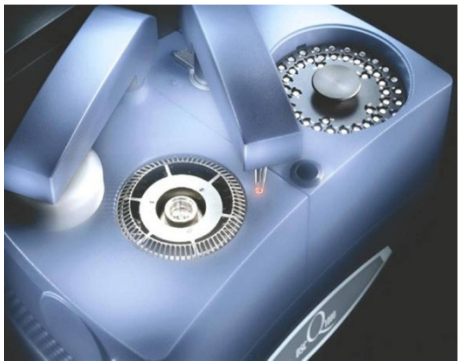
- Polimer
- Gıda
- Seramik
- Cam

DSC YAĞ ANALİZLERİNDE KULLANIMI



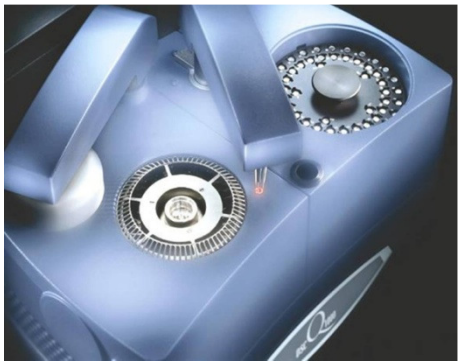
- Termal stabilite
- Oksidatif stabilite
- Yapı belirlenmesi
- Orijin belirlenmesi

DSC İLE ZEYTİNYAĞI KARAKTERİZASYONU

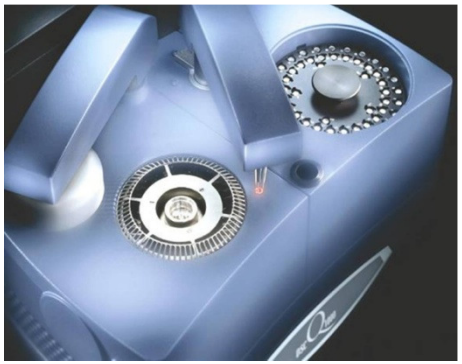


- Her yağın kendine özgü TAG kompozisyonu vardır
- Katı ⟷ sıvı faz geçişleri molekülün kompozisyonundan etkilenmektedir
- Kristalizasyon ve erime grafiklerinden yağların orijini hakkında bilgi elde edilebilir

DSC İLE ZEYTİNYAĞI KARAKTERİZASYONU



- Kristalizasyon ve erime grafikleri yağların kimyasal kompozisyonu ile ilgili direkt bilgi vermez
- Faz geçişleri sırasında termodinamik özelliklerde meydana gelen değişimler kimyasal kompozisyon hakkında bilgi verir
- Termodinamik özelliklerde meydana gelen değişimler kalitatif ve kantitatif değerlendirmede kullanılabilir



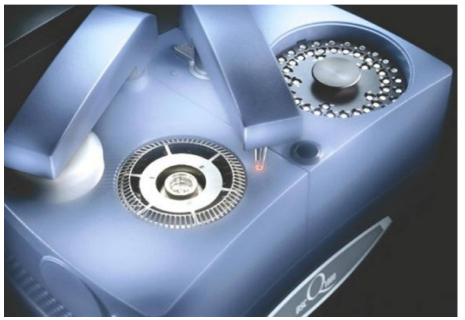
Tan ve Man (2000)

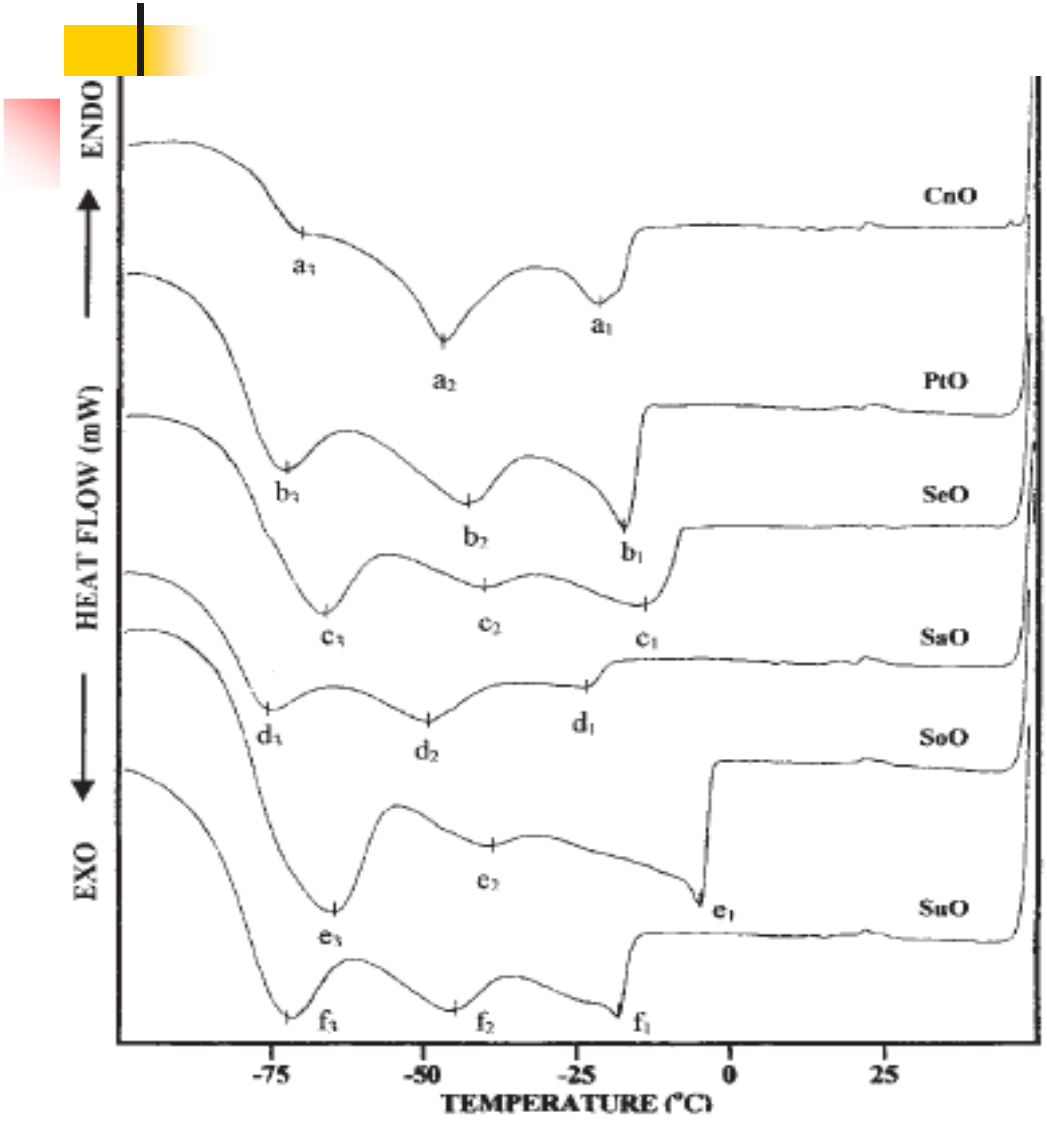
- Kanola (CnO), fıstık (PtO), aspir (SaO), susam (SeO), soya (SoO), ayçiçek yağı(SuO)
- Kimyasal kompozisyon
- Termal özellikler

Tablo : Yağ asitleri kompozisyonu

Örnek	Yağ asitleri yüzdesi (%)		
	SFA	MUFA	PUFA
CnO	15.9 ± 0.1^{h}	27.5 ± 0.2^{i}	56.7 ± 0.4^{e}
PtO	22.5 ± 0.8^{f}	50.1 ± 0.2^{d}	27.4 ± 0.6^{h}
SaO	10.4 ± 0.0^{h}	13.9 ± 0.2^{m}	75.7 ± 0.1^{a}
SeO	$19.1 \pm 0.1^{f,g}$	40.6 ± 0.1^{g}	40.3 ± 0.1^{f}
SoO	16.9 ± 0.1^{g}	23.6 ± 0.1^{j}	59.5 ± 0.1^{d}
SuO	12.8 ± 0.8^{h}	17.8 ± 0.0^{l}	69.4 ± 0.2^{c}

Tan ve Man (2000)





Kristalizasyon grafiği

Örnek	T_{on} (°C)
CnO	−16.20 ± 0.19[k]
PtO	−2.96 ± 0.16[g]
SaO	−19.56 ± 0.56[n]
SeO	−7.23 ± 0.19[h]
SoO	−14.13 ± 0.24[i]
SuO	−15.53 ± 0.07[j]

Örnek	T_{off} (°C)
CnO	−85.71 ± 1.13[i,j,k]
PtO	−85.37 ± 0.04[i,j]
SaO	−89.28 ± 0.70[m]
SeO	−85.78 ± 0.76[i,j,k]
SoO	−86.76 ± 0.05[l]
SuO	−86.14 ± 0.15[j,k,l]

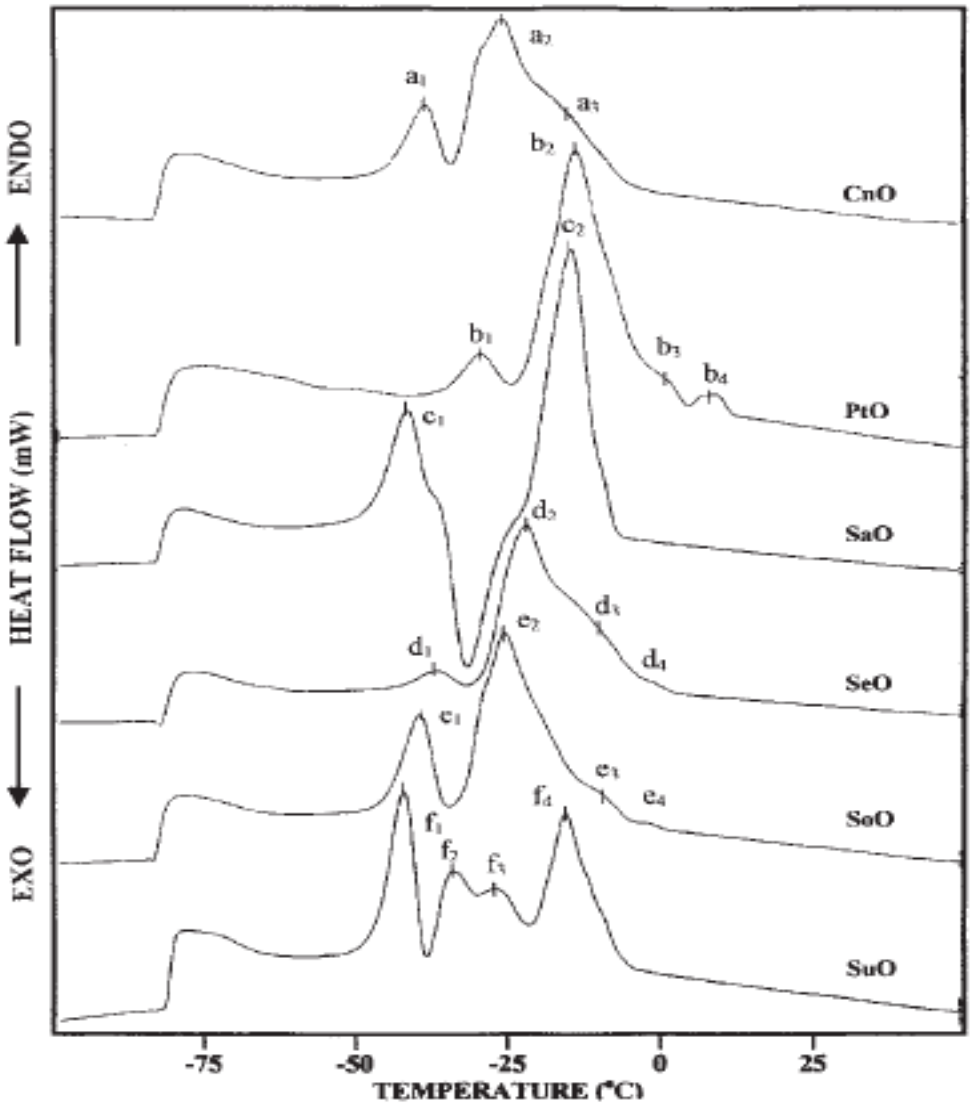
Örnek	T_r (°C)
CnO	69.51 ± 1.32[a,b,c]
PtO	82.42 ± 0.12[a]
SaO	69.72 ± 0.13[a,b,c]
SeO	78.56 ± 0.95[a,b]
SoO	72.63 ± 0.30[a,b,c]
SuO	70.61 ± 0.22[a,b,c]

T_{on} : kristalizasyon başlangıç sıcaklığı

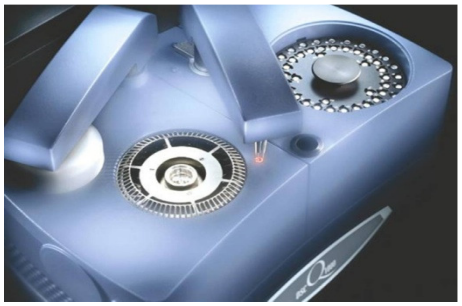
T_{off} :kristalizasyon bitiş sıcaklığı

T_r: kristalizasyonun meydana geldiği sıcaklık aralığı

Tan ve Man (2000)



Erime grafiği



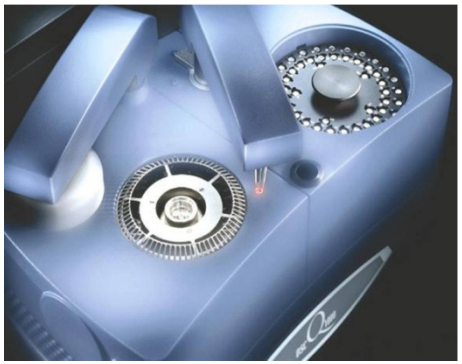
Örnek	T_{on} (°C)
CnO	−46.02 ± 0.09[g]
PtO	−56.52 ± 0.07[k]
SaO	−48.36 ± 0.09[h,i]
SeO	−46.03 ± 0.96[g]
SoO	−46.11 ± 0.06[g]
SuO	−46.79 ± 0.45[g,h]

Örnek	T_{off} (°C)
CnO	−4.21 ± 0.05[l]
PtO	11.83 ± 0.03[f]
SaO	−6.64 ± 0.09[m]
SeO	3.36 ± 0.25[i]
SoO	1.89 ± 0.03[j]
SuO	−4.72 ± 0.06[l]

Örnek	T_r (°C)
CnO	41.31 ± 0.44[g]
PtO	68.35 ± 0.09[b]
SaO	41.72 ± 0.18[g]
SeO	49.40 ± 1.21[e]
SoO	47.75 ± 0.37[e,f]
SuO	42.57 ± 0.06[g]

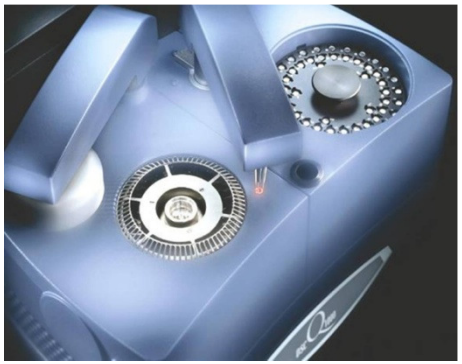
T_{on} : erime başlangıç sıcaklığı
T_{off} : erime bitiş sıcaklığı
T_r: erimenin meydana geldiği sıcaklık aralığı

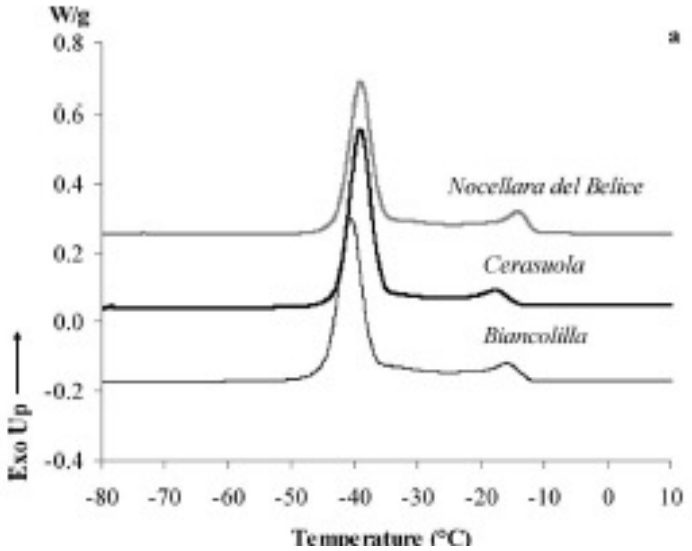
Chiavaro ve diğ. (2007)



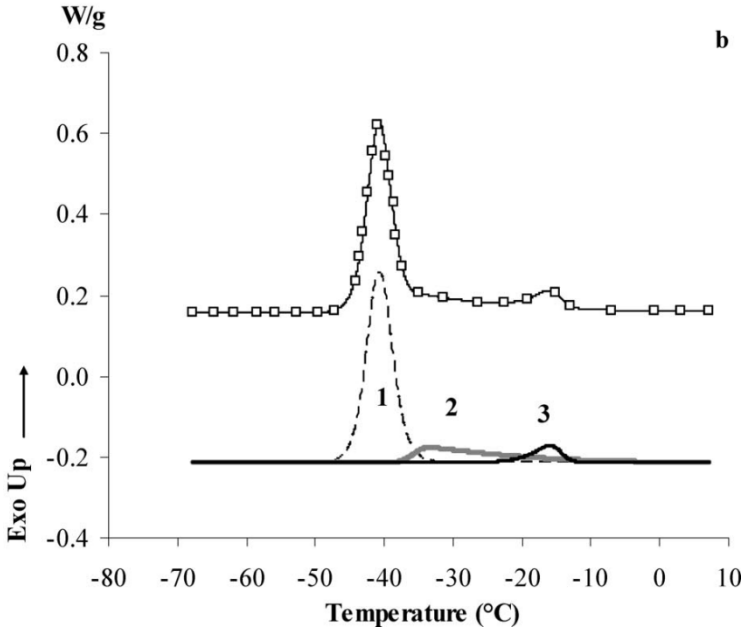
- Sicilya zeytinyağları
  - Biancolila
  - Cerassuola
  - Nocellara del Belice
- Kimyasal kompozisyon
- Termal özellikler

Chiavaro ve diğ. (2007)



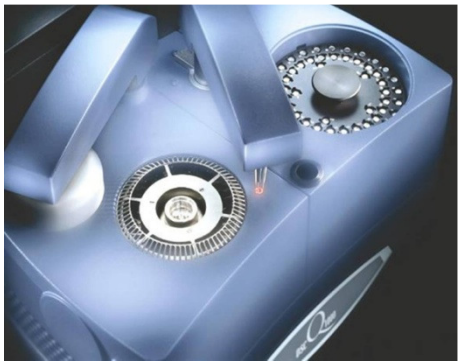


Şekil : Kristalizasyon grafiği



Şekil : Kristalizasyon grafiği (ters evrişim)

Chiavaro ve diğ. (2007)



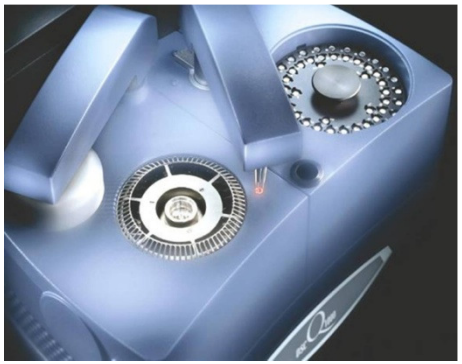
Tablo : Yağ asitleri kompozisyonu

Hasat dönemi	A			B			C		
	Biancolilla	*Cerasuola*	*Nocellara del Belice*	*Biancolilla*	*Cerasuola*	*Nocellara del Belice*	*Biancolilla*	*Cerasuola*	*Nocellara del Belice*
SFA	16.5 b	15.0 c	18.1 a	17.4 a	14.6 b	16.6 c	15.9 a	13.7 b	15.6 a
MUFA	75.1 b	76.3 a	74.8 b	73.6 b	76.1 a	74.4 b	76.0 c	77.7 a	76.4 b
PUFA	8.4 b	8.6 a	7.0 c	8.6 c	9.2 a	9.0 b	8.1 b	8.5 a	8.0 b

Tablo : Termal özellikler

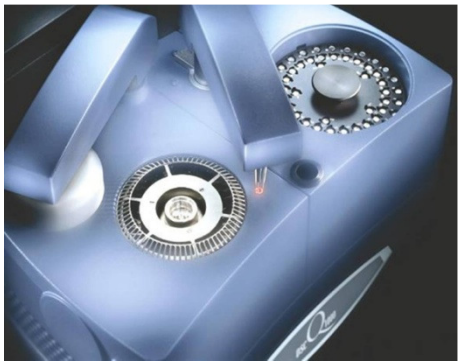
Çeşit	ΔH (J/g)	T_{on} (°C)	range[b] (°C)
Biancolilla	66.7 a	−12.1 b	36.3 a
Cerasuola	67.3 a	−13.6 b	32.5 b
Nocellara del Belice	67.4 a	−10.9 a	35.5 a

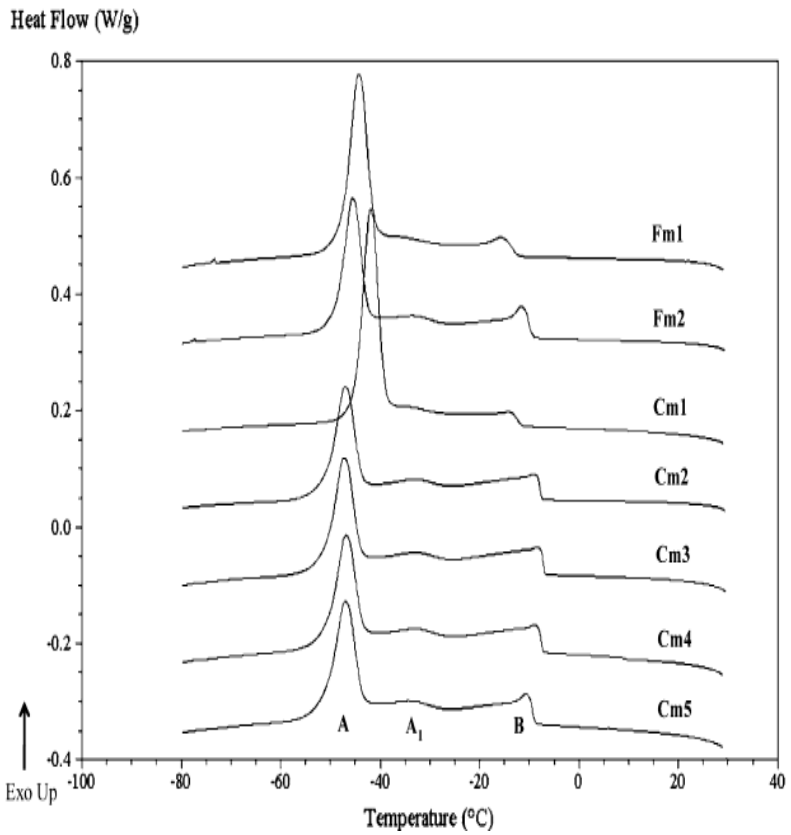
Kotti ve diğ. (2009)

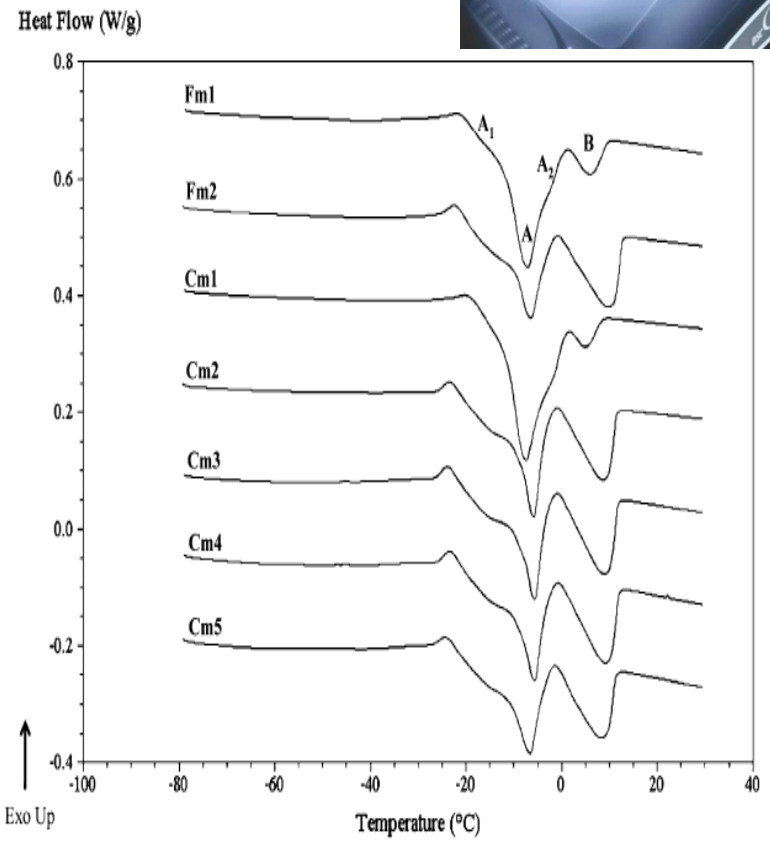


- Tunus
  - Chetoui
  - Chemlali
- Kimyasal kompozisyon
- Termal özellikler

Kotti ve diğ. (2009)





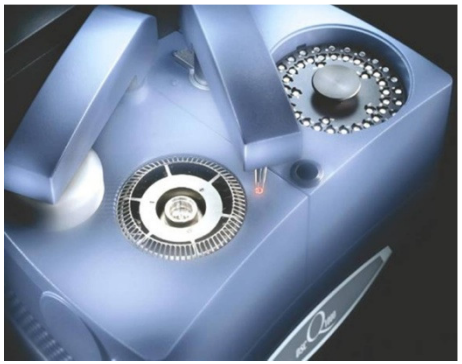


Kristalizasyon grafiği

Erime grafiği

Chetoui (Fm1, Cm1)
Chemlali (Fm2, Cm2, Cm3, Cm4, Cm5)

Kotti ve diğ. (2009)



Tablo : Yağ asitleri yüzdesi

	Fm1	Fm2	Cm1	Cm2	Cm3	Cm4	Cm5
SFA	17.6 ± 0.2^{d}	22.8 ± 0.2^{bc}	17.1 ± 0.3^{d}	23.4 ± 0.1^{ab}	23.8 ± 0.2^{a}	23.7 ± 0.2^{a}	22.4 ± 0.2^{c}
MUFA	63.1 ± 0.4^{b}	58.5 ± 0.4^{c}	65.4 ± 0.5^{a}	56.6 ± 0.2^{d}	56.4 ± 0.3^{d}	57.0 ± 0.3^{d}	58.4 ± 0.4^{c}
PUFA	19.3 ± 0.2^{b}	18.6 ± 0.1^{c}	17.5 ± 0.2^{d}	20.1 ± 0.2^{a}	19.8 ± 0.2^{a}	19.3 ± 0.1^{b}	19.1 ± 0.2^{b}

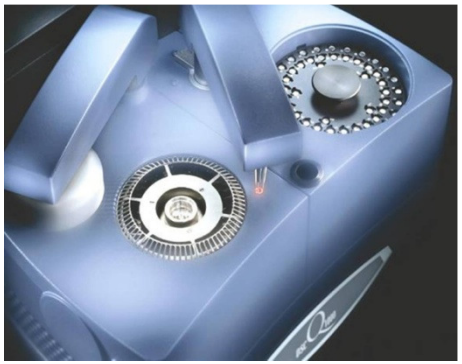
Tablo : Termal özellikler (kristalizasyon)

Sample	ΔH (J/g)	T_{on} (°C)	T_{off} (°C)	Range[a] (°C)
Fm1	64.3 ± 1.5^{bc}	-11.7 ± 0.4^{c}	-52.1 ± 0.4^{b}	40.4 ± 0.8^{d}
Fm2	64.2 ± 1.3^{bc}	-8.8 ± 0.1^{b}	-53.6 ± 0.8^{c}	44.8 ± 1.0^{c}
Cm1	66.1 ± 1.0^{bc}	-11.3 ± 0.1^{c}	-49.9 ± 0.3^{a}	38.6 ± 0.4^{e}
Cm2	63.7 ± 0.5^{c}	-7.1 ± 0.2^{a}	-56.4 ± 0.5^{d}	49.2 ± 0.6^{ab}
Cm3	66.7 ± 0.8^{ab}	-6.7 ± 0.1^{a}	-56.7 ± 0.5^{d}	49.9 ± 0.5^{a}
Cm4	69.5 ± 0.5^{a}	-6.9 ± 0.2^{a}	-57.0 ± 0.5^{d}	50.0 ± 0.4^{a}
Cm5	65.7 ± 1.2^{bc}	-8.6 ± 0.1^{b}	-56.9 ± 0.6^{d}	48.4 ± 0.7^{b}

Tablo : Termal özellikler (erime)

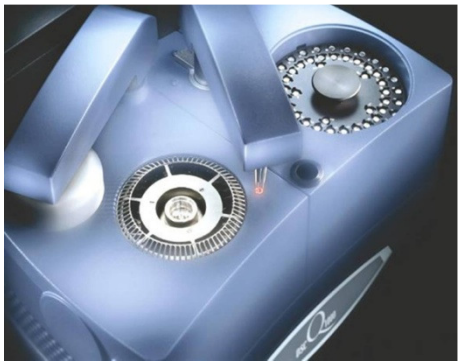
Sample	ΔH (J/g)	T_{on} (°C)	T_{off} (°C)	Range[a] (°C)
Fm1	63.1 ± 2.9^{bc}	-28.9 ± 1.1^{a}	10.2 ± 0.2^{d}	39.1 ± 1.2^{c}
Fm2	61.0 ± 1.4^{c}	-36.6 ± 0.3^{b}	13.0 ± 0.4^{a}	49.8 ± 0.2^{a}
Cm1	74.9 ± 2.2^{a}	-27.4 ± 0.5^{a}	9.1 ± 0.1^{e}	36.4 ± 0.6^{c}
Cm2	66.6 ± 1.7^{b}	-36.4 ± 0.3^{b}	12.2 ± 0.2^{c}	48.6 ± 0.4^{b}
Cm3	54.6 ± 1.7^{d}	-38.4 ± 0.5^{c}	12.7 ± 0.4^{ab}	51.1 ± 0.5^{a}
Cm4	56.5 ± 1.0^{d}	-38.4 ± 0.3^{c}	12.7 ± 0.1^{ab}	51.1 ± 0.3^{a}
Cm5	54.6 ± 2.1^{d}	-38.9 ± 0.3^{c}	12.3 ± 0.1^{bc}	51.2 ± 0.3^{a}

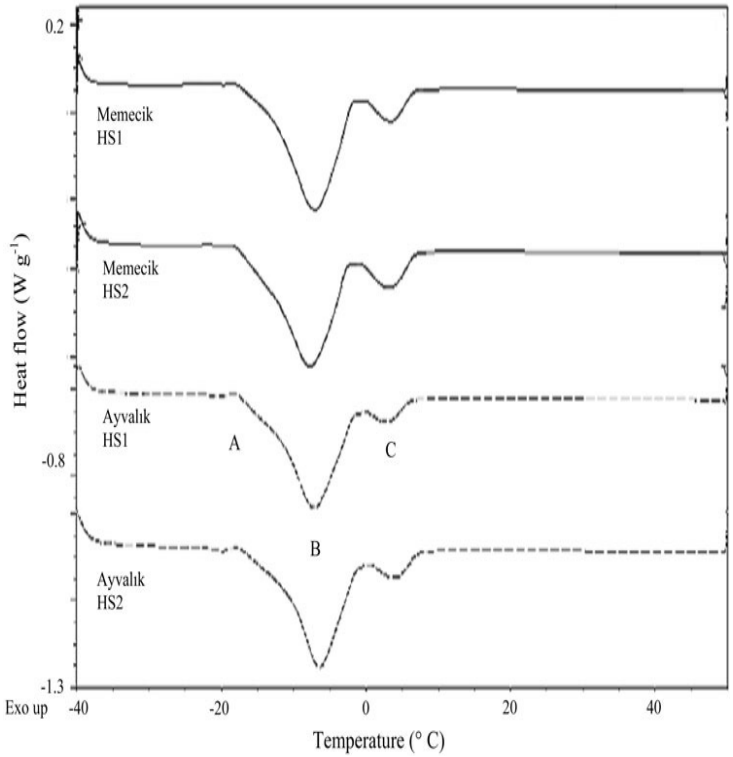
Ilyasoglu ve Ozcelik (2011)

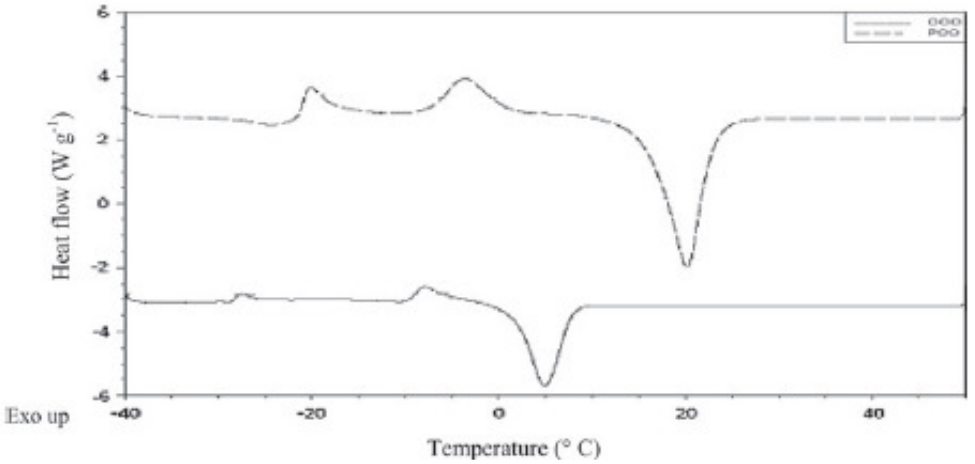


- Türk Sızma Zeytinyağları
  - Ayvalık
  - Memecik
- Hasat sezonu
  - 2006/2007
  - 2007/2008
- Kimyasal kompozisyon
- Termal özellikler

Ilyasoglu ve Ozcelik (2011)

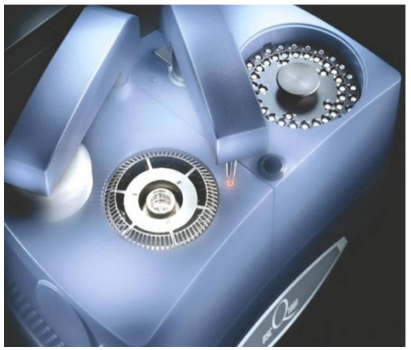






Şekil : Erime grafikleri

Ilyasoglu ve Ozcelik (2011)



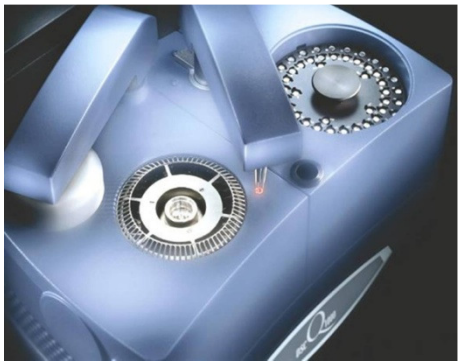
Tablo : Yağ asitleri ve TAG kompozisyonu

Parameters	Ayvalik cultivar (mean ± SD) North Aegean		Memecik cultivar (mean ± SD) South Aegean	
	2006/2007 (*n*:3)	2007/2008 (*n*:5)	2006/2007 (*n*:4)	2007/2008 (*n*:4)
Fatty acids (%)				
C16:0	13.01 ± 0.17	13.87 ± 0.36	12.64 ± 0.80	12.62 ± 0.40
C16:1	0.61 ± 0.02	0.70 ± 0.03	0.68 ± 0.06	0.67 ± 0.06
C18:0	2.83 ± 0.10	2.82 ± 0.06	2.51 ± 0.08	2.62 ± 0.18
C18:1	72.79 ± 0.36	71.08 ± 0.47	75.42 ± 0.38	75.17 ± 0.75
C18:2	10.06 ± 0.21	10.81 ± 0.17	7.98 ± 0.71	8.17 ± 0.24
C18:3	0.71 ± 0.02	0.68 ± 0.05	0.77 ± 0.03	0.76 ± 0.06
SFA	15.84 ± 0.17	16.70 ± 0.33	15.15 ± 0.73	15.24 ± 0.47
MUFA	73.40 ± 0.37	71.79 ± 0.46	76.10 ± 0.38	75.84 ± 0.70
PUFA	10.77 ± 0.20	11.49 ± 0.17	8.74 ± 0.72	8.92 ± 0.26
TAG (%)				
LOO	9.90 ± 0.28	10.38 ± 0.82	7.27 ± 1.38	7.46 ± 0.23
PLO	2.35 ± 0.13	2.92 ± 0.37	1.35 ± 0.10	1.73 ± 0.19
OOO	58.88 ± 2.25	56.79 ± 1.74	65.54 ± 2.24	64.11 ± 1.64
POO	24.02 ± 0.48	26.00 ± 1.10	21.85 ± 2.52	23.97 ± 1.27
POP	0.98 ± 0.23	1.06 ± 0.07	0.84 ± 0.19	0.91 ± 0.09
SOO	1.70 ± 0.06	1.91 ± 0.50	1.60 ± 0.39	1.31 ± 0.32
SUU	28.06 ± 0.60	30.82 ± 1.13	24.81 ± 2.70	27.00 ± 1.40
SSU	0.98 ± 0.23	1.06 ± 0.07	0.84 ± 0.19	0.91 ± 0.09
UUU	68.78 ± 1.99	67.17 ± 1.23	72.81 ± 3.59	71.57 ± 1.48

Tablo :Termal özellikler

	Ayvalik		Memecik	
	2006/2007 (*n*:3)	2007/2008 (*n*:5)	2006/2007 (*n*:4)	2007/2008 (*n*:4)
T_{on} (°C)	−22.30 ± 0.11	−22.25 ± 0.45	−20.99 ± 0.78	−21.05 ± 0.47
T_{off} (°C)	6.31 ± 0.16	7.19 ± 0.49	6.58 ± 1.25	7.47 ± 0.32
T_{range} (°C)	28.61 ± 0.23	29.44 ± 0.71	27.58 ± 0.59	28.52 ± 0.41
ΔH (J g^{-1})	54.23 ± 0.84	51.11 ± 1.91	60.28 ± 6.38	55.26 ± 2.72

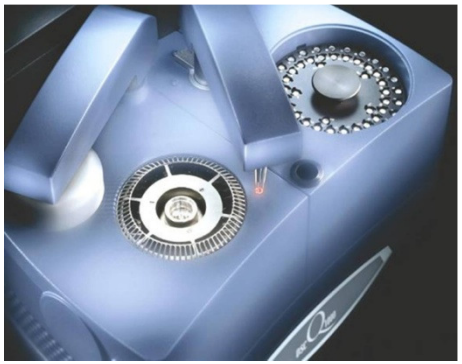
Ilyasoglu ve Ozcelik (2011)



Tablo : Pearson korelasyon katsayıları

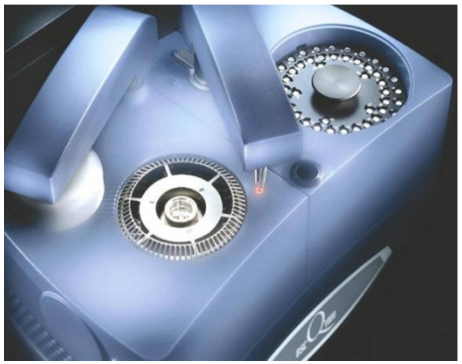
	Chemical characteristics								
	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	SFA	MUFA	PUFA
T_{on}	−0.204	**0.536**	−0.883	**0.740**	−0.864	**0.699**	−0.393	**0.757**	−0.858
T_{off}	**0.781**	**0.751**	−0.234	−0.188	−0.137	0.125	**0.645**	−0.161	−0.135
T_{range}	**0.888**	0.182	**0.601**	−0.847	**0.670**	−0.529	**0.939**	−0.839	**0.666**
ΔH	−0.909	−0.286	−0.456	**0.762**	−0.541	0.379	−0.924	**0.750**	−0.540
	Chemical characteristics								
	LOO	PLO	OOO	POO	POP	SOO	MSTAG	DSTAG	TUTAG
T_{on}	−0.933	−0.788	**0.657**	−0.300	−0.279	−0.055	−0.428	−0.279	0.392
T_{off}	−0.263	0.144	−0.267	**0.696**	0.386	0.019	**0.564**	0.386	−0.504
T_{range}	**0.620**	**0.853**	−0.841	**0.899**	**0.602**	0.068	**0.898**	**0.602**	−0.811
ΔH	−0.394	−0.689	**0.784**	−0.917	−0.725	−0.294	−0.905	−0.725	**0.856**

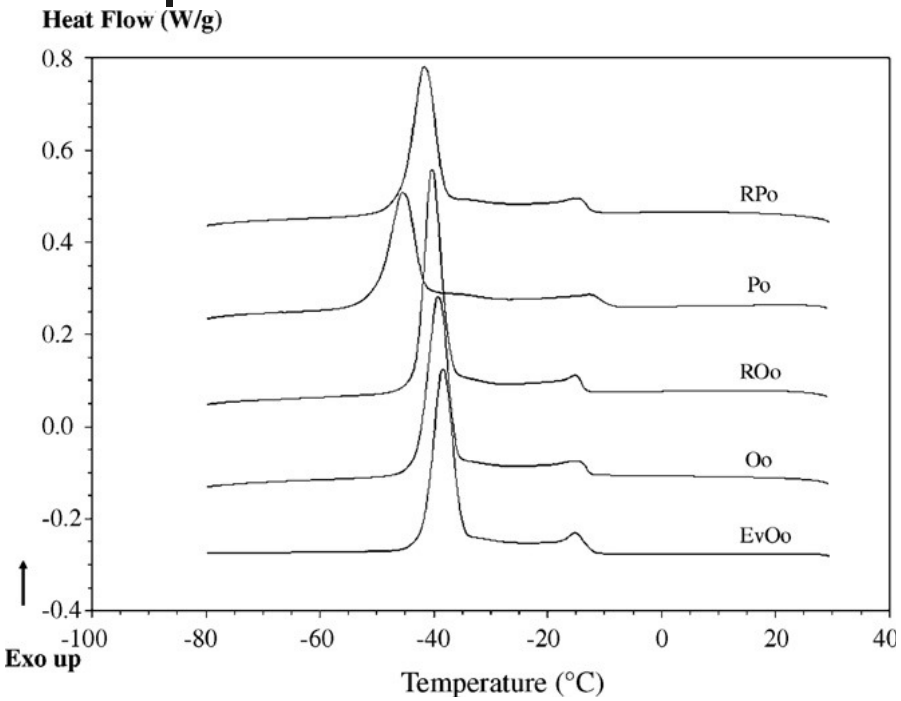
Chiavaro ve diğ. (2008)



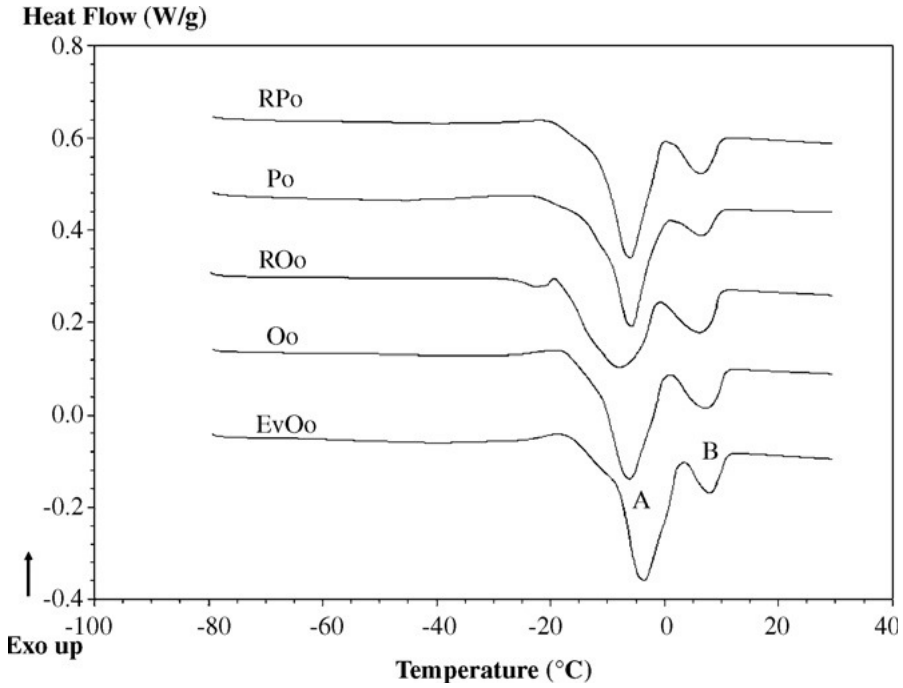
- Ticari zeytinyağlar
  - Sızma zeytinyağı (EVOo)
  - Zeytinyağı (Oo)
  - Rafine zeytinyağı (ROo)
  - Prina yağı (Po)
  - Rafine prina yağı (RPo)
- Kimyasal kompozisyon
- Termal özellikler

Chiavaro et al. (2008)

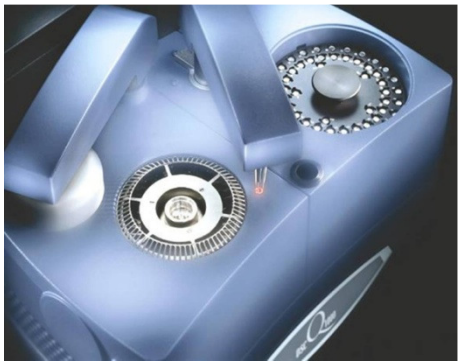




Kristalizasyon grafiği



Erime grafiği



Chiavaro et al. (2008)

Tablo : Yağ asitleri yüzdesi

	EvOo	Oo	ROo	Po	RPo
SFA	15.8 ± 0.2 A	14.2 ± 0.1 E	14.7 ± 0.5 B	15.6 ± 0.2 A	13.8 ± 0.2 C
MUFA	77.6 ± 0.2 A	76.8 ± 0.4 E	76.1 ± 0.5 B	76.4 ± 0.3 B	75.1 ± 0.2 C
PUFA	7.6 ± 0.1 C	9.1 ± 0.1 E	9.2 ± 0.0 B	9.6 ± 0.1 B	9.8 ± 0.1 A

Tablo : Termal özellikler (kristalizasyon)

Sample	ΔH (J g^{-1})	T_{on} (°C)	T_{off} (°C)	Range[b] (°C)
EvOo	65.8 ± 2.9 BC	−10.5 ± 0.2 B	−45.4 ± 0.2 A	34.9 ± 0.4 C
Oo	70.3 ± 0.9 B	−12.2 ± 0.1 C	−48.0 ± 0.7 B	36.0 ± 0.8 C
ROo	77.9 ± 2.3 A	−12.8 ± 0.1 D	−48.5 ± 0.5 B	35.6 ± 0.5 C
Po	63.9 ± 1.9 C	−7.6 ± 0.3 A	−55.1 ± 0.8 D	47.5 ± 1.0 A
RPo	68.4 ± 0.3 BC	−10.7 ± 0.0 B	−50.4 ± 0.1 C	39.7 ± 0.1 B

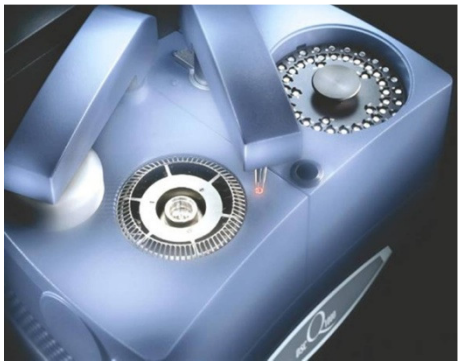
Tablo : Termal özellikler (erime)

Sample	ΔH (J g^{-1})	T_{on} (°C)	T_{off} (°C)	Range[b] (°C)
EvOo	67.1 ± 3.5 C	−26.8 ± 0.7 A	12.2 ± 0.2 A	39.0 ± 0.9 CD
Oo	75.6 ± 2.1 B	−27.1 ± 0.2 A	11.3 ± 0.0 B	38.3 ± 0.2 D
ROo	83.4 ± 1.3 A	−32.0 ± 0.2 C	10.6 ± 0.5 C	42.7 ± 0.3 B
Po	63.5 ± 1.8 C	−38.6 ± 0.2 D	10.5 ± 0.2 C	49.1 ± 0.2 A
RPo	73.3 ± 1.1 B	−28.9 ± 0.2 B	10.4 ± 0.2 C	39.3 ± 0.2 CD

DSC Tekniğinin Klasik Karakterizasyon Yöntemlerine Göre Avantajları

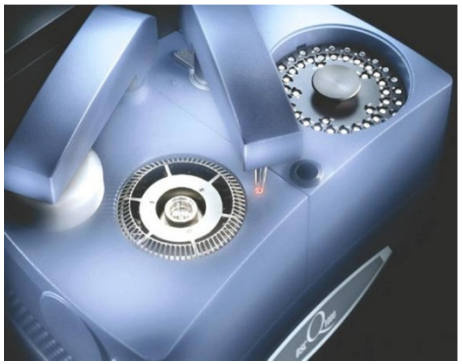
- Örnek hazırlığı basit
- Çözgen kullanılmıyor
- Analiz süresi kısa

SONUÇ

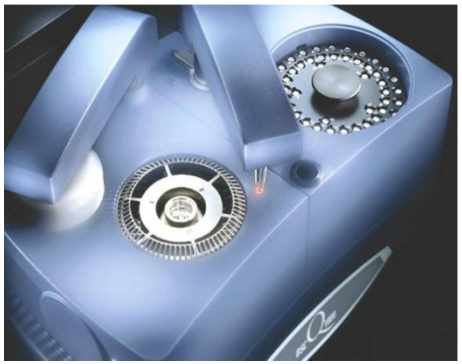


- DSC kristalizasyon ve erime grafiklerinden;
  - Zeytinyağının çeşit ve coğrafi orijine göre tanımlanmasında
  - Hasat sezonlarına göre kimyasal kompozisyonların farklılıkların değerlendirilmesinde yararlanılabilir

SONUÇ



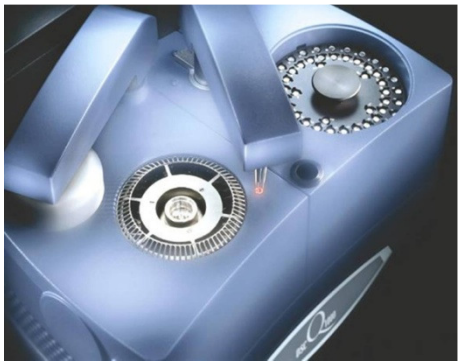
- Örnek sayısı,
- Örneklerin alındığı çeşit ve bölge sayısı artırılarak,
- En az 3 hasat sezonu kapsayacak kapsamlı çalışmalar yapılması ile veri tabanları oluşturabilir
- Oluşturulacak veri tabanlarından karakterizasyon çalışmalarında yararlanılabilir



KAYNAKLAR

- Chiavaro E, Vittadini E, Rodriguez-Estrada, MT, Cerretani L, Bonoli M, Bendini A, Lercker G (2007) Monovarietal extra virgin olive oils : correlation between thermal properties and chemical composition. J Agric Food Chem 55: 10779-10786.
- Chiavaro E, Rodriguez-Estradab MT, Barnaba C, Vittadini E, Cerretani L, Bendini, A (2008) Differential scanning calorimetry: A potential tool for discrimination of olive oil commercial categories. Analytica Chimica Acta 625: 215–226.
- Chiavaro E, Rodriguez-Estradab MT, Bendini A, Cerratani, L (2010) Correlation between thermal properties and chemical composition of Italian virgin olive oils. Eur J Lip Sci Tech 112: 580-592.

KAYNAKLAR



- Ilyasoglu H, Ozcelik B (2011) Determination of seasonal changes in olive oil by using differential scanning calorimetry heating termagrams. J Am Oil Chem Soc 88: 907-913
- Kotti F, Chiavaro E, Cerretani L, Barnaba C, Gargouri M, Bendini, A (2009) Chemical and thermal characterization of Tunusian extra virgin olive oil from Cheutoi and Chemlali cultivars and different geographical origin. Eur Food Res Technol 228: 735-742.
- Tan CP, Che Man, YB (2000) Differential scanning calorimetric analysis of edible oils : comparision of thermal properties and chemical composition. J Am Oil Chem Soc 77: 143-155.