

# Università degli Studi di Ferrara



## Determination of polar organic markers in atmospheric aerosol by gas chromatography - ion trap tandem mass spectrometry

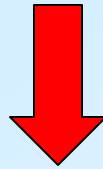
M. Visentin

M. C. Pietrogrande

**PM2014**

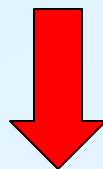
Genova, 21/05/2014

- **Marker Molecolari:** sostanze emesse solamente da determinati tipi di sorgente



Informazioni su origine e processi che il particolato subisce

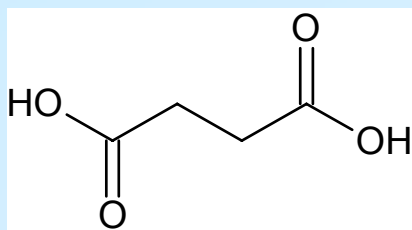
- **Gas cromatografia-spettrometria di massa:** alta efficienza e sensibilità, adatta all'analisi di miscele complesse



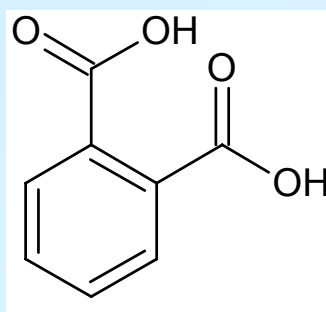
Valutazione della **qualità dell'aria**  
e dell'effetto delle **attività antropiche**

# Acidi carbossilici a basso peso molecolare

- Emissioni primarie antropogeniche: combustione incompleta di combustibili fossili, combustione plastiche
- Indicatori di particolato secondario di origine biogenica e antropica: ossidazione in atmosfera di idrocarburi, IPA, acidi grassi

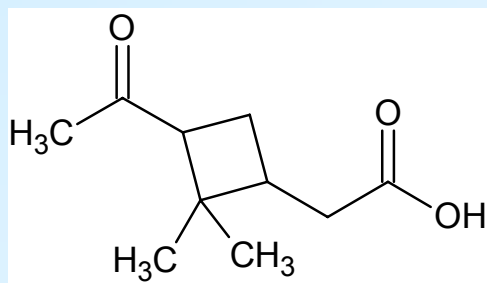


Acido succinico (C<sub>4</sub>)



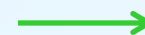
Acido ftalico

**Emissioni primarie:**  
combustione incompleta

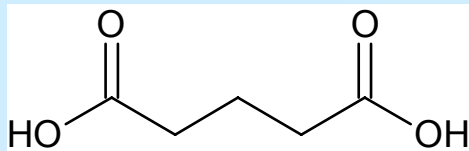


Acido pinonico

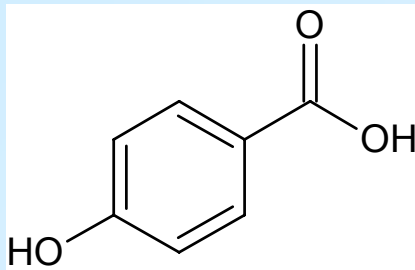
**Emissioni biogeniche  
secondarie:** ossidazione di  
precursori



Ossidazione  
α- pinene

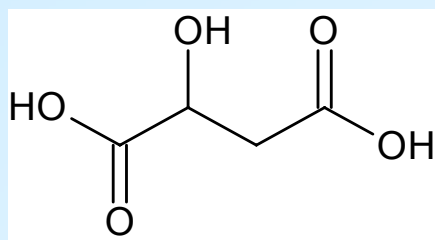


Acido glutarico (C<sub>5</sub>)

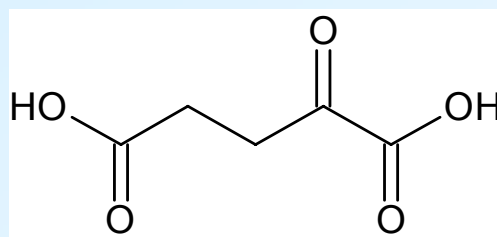


Acido 4-idrossibenzoico

**Emissioni antropogeniche secondarie:** Ossidazione di precursori (idrocarburi, IPA)



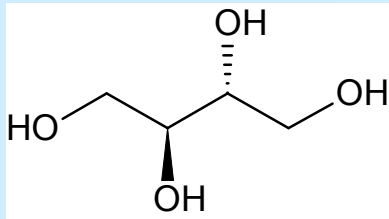
Acido malico



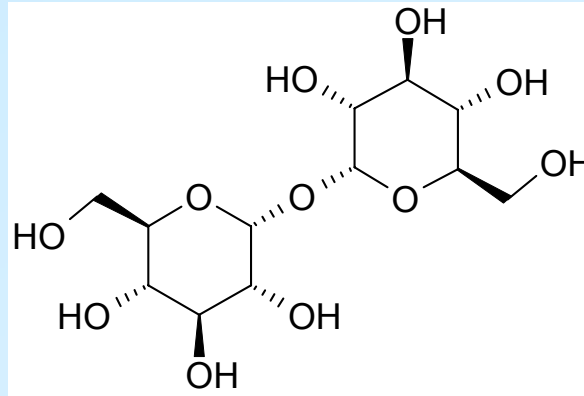
Acido 2-chetoglutarico

**Emissioni antropogeniche secondarie:** Ulteriore fotossidazione degli acidi carbossilici

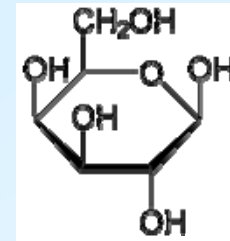
# Zuccheri



Eritritolo

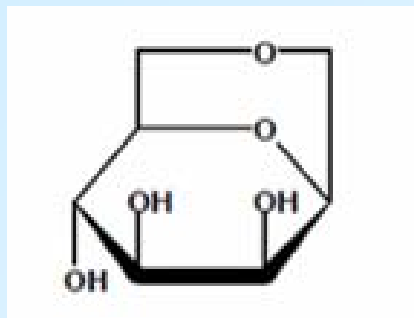


Micoso

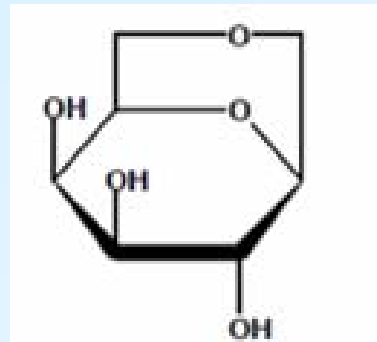


Galattoso

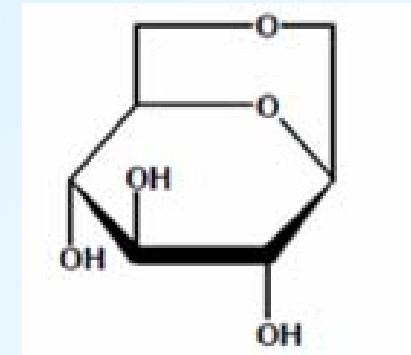
**Biogenici:** risospensione del suolo, attività di microorganismi e vegetali



Galattosano



Mannosano

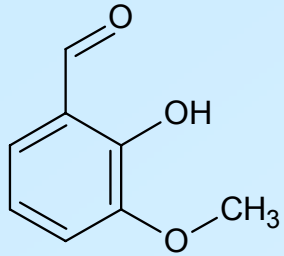


Levoglucosano

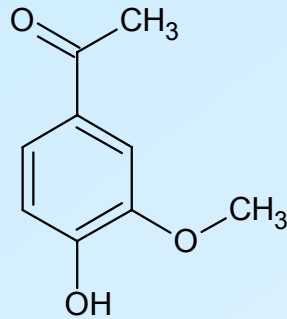
**Tipici marker di combustione di biomassa:** pirolisi cellulosa ed emicellulosa

# Fenoli

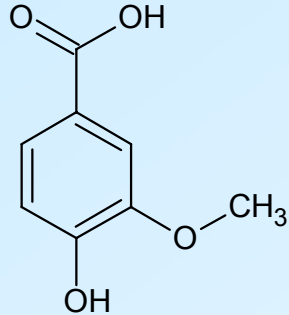
Derivano dalla **combustione** della lignina



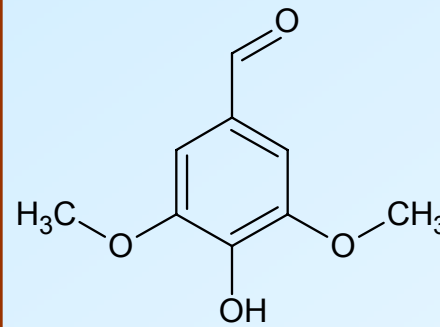
Vanillina



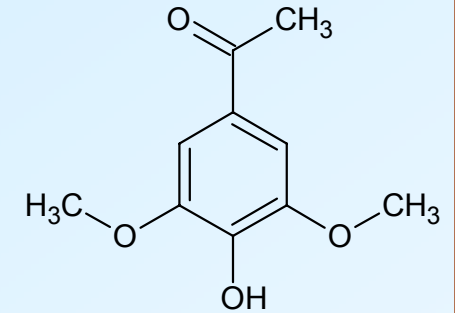
Acetovanillone



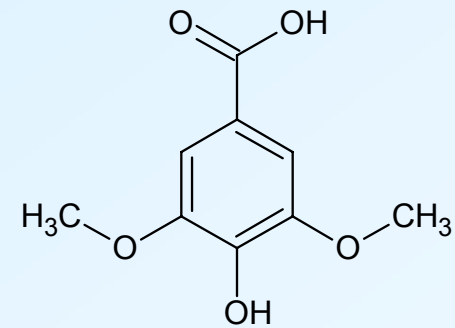
Acido vanillico



Siringaldeide



Acetosiringone



Acido siringico



Alti livelli dalla  
combustione di  
**legni teneri**:  
abete, pino

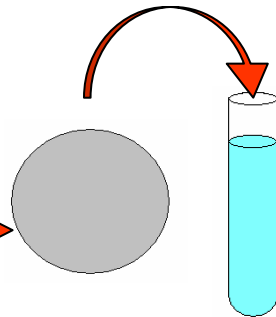


Alti livelli dalla  
combustione di  
**legni duri**:  
faggio, quercia,  
olmo

# Procedura di Analisi



Campionamento



Estrazione  
con solvente



Evaporazione  
del solvente



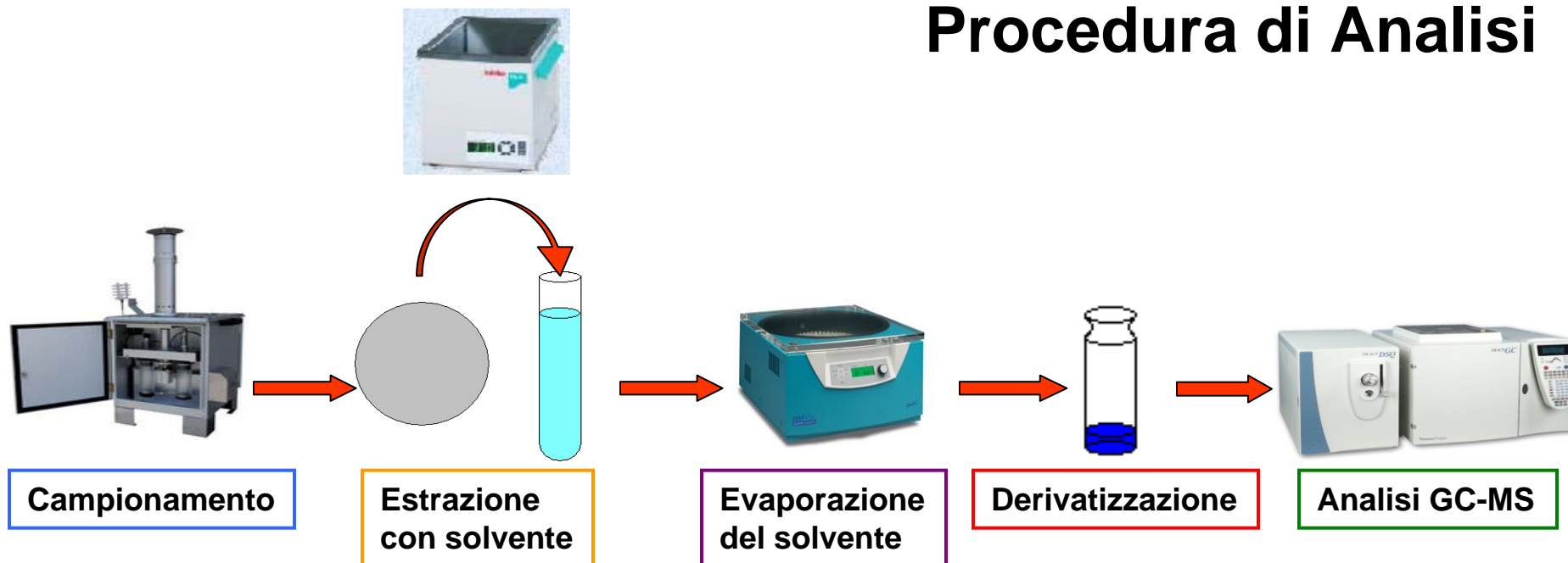
Derivatizzazione



Analisi GC-MS

55m<sup>3</sup> o 280m<sup>3</sup> in  
base alle esigenze

# Procedura di Analisi



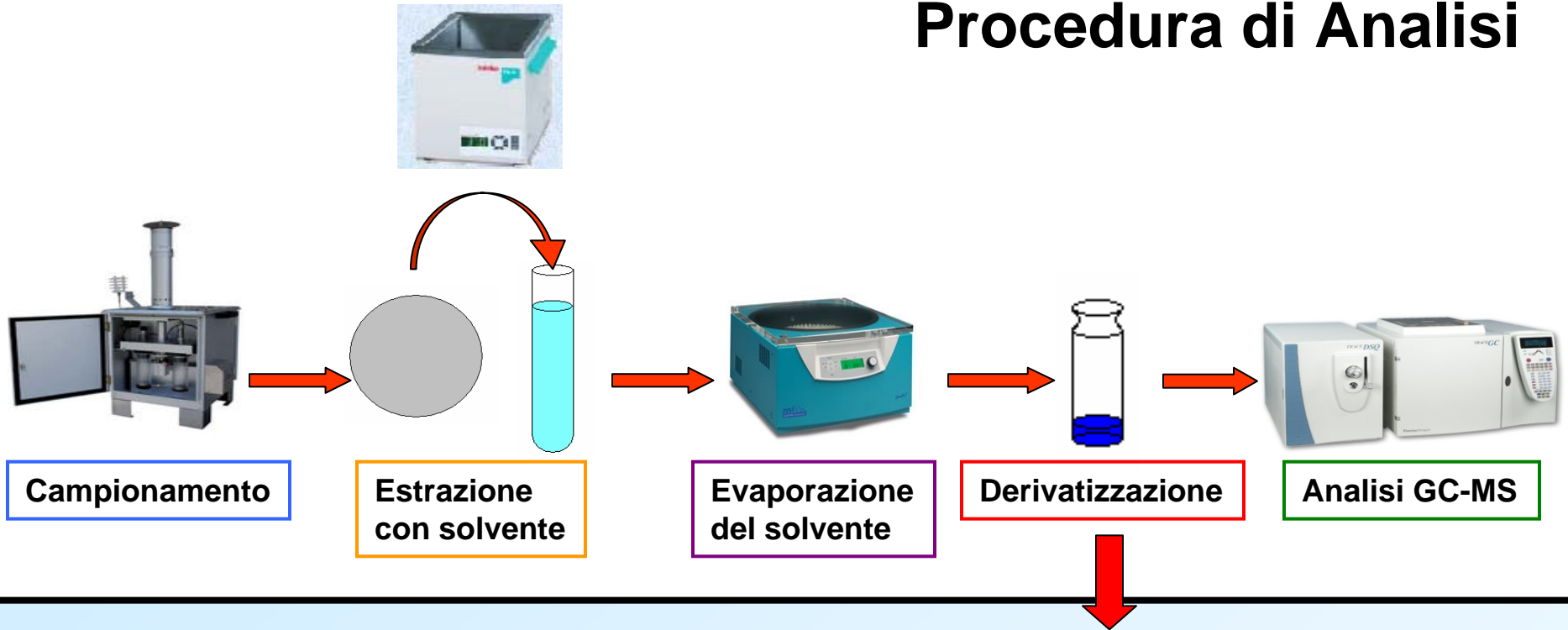
MeOH/DCM 90:10

Miscela adatta all'estrazione di  
composti polari

Recovery  $\approx$  90%

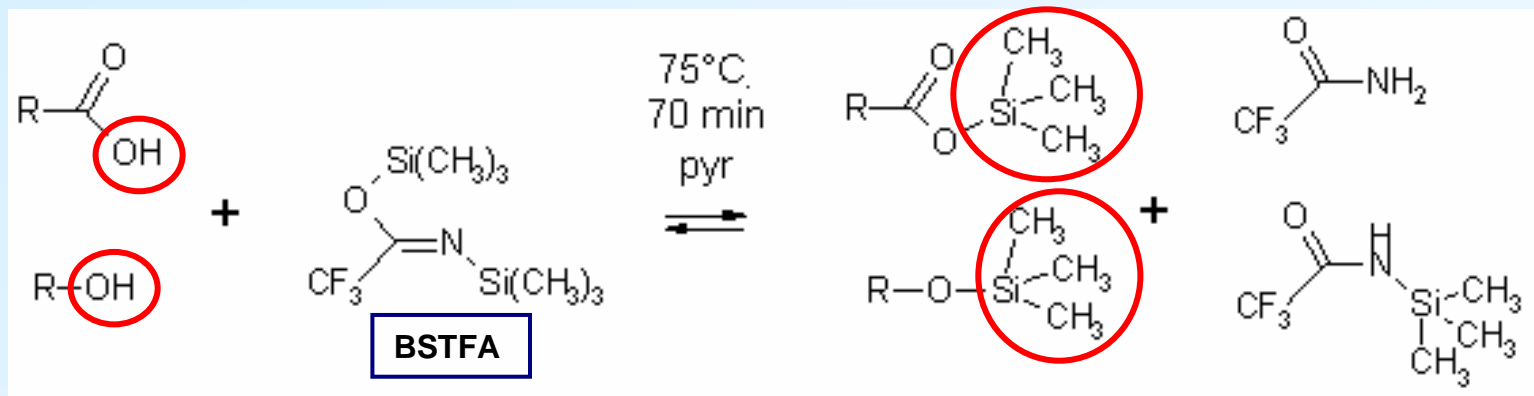


# Procedura di Analisi

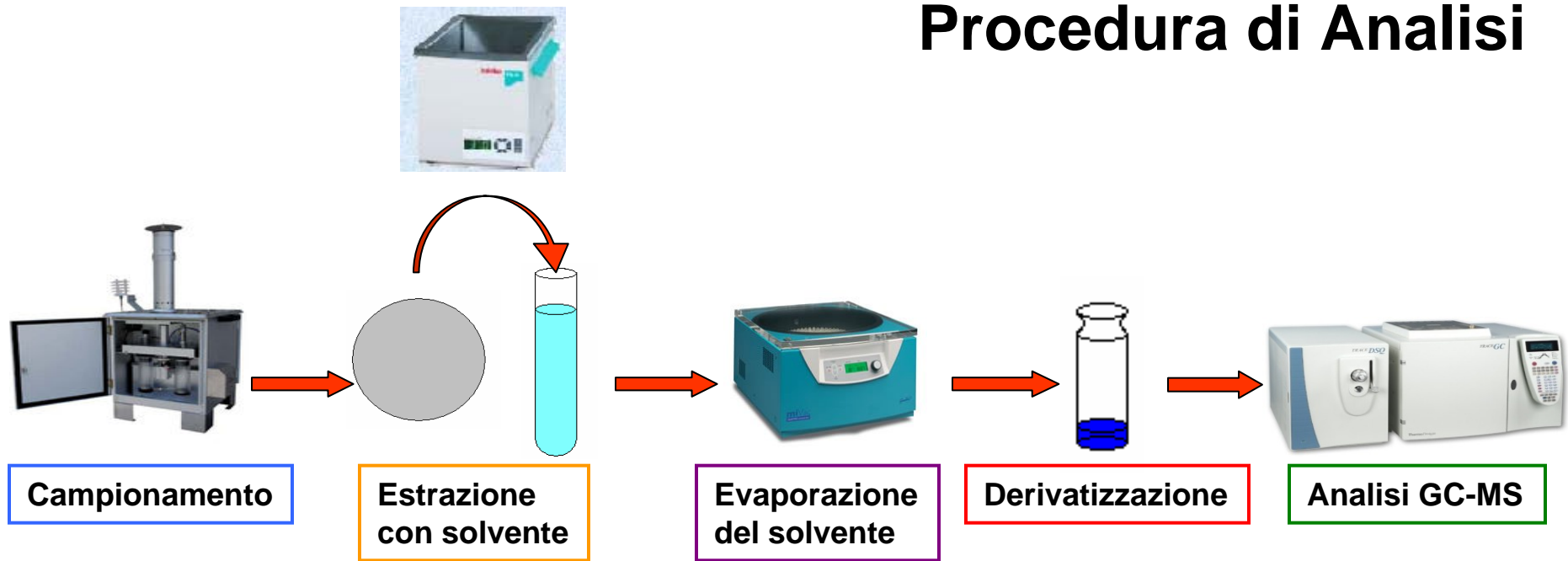


## REAZIONE DI SILILAZIONE

**N, O- bis-(trimetilsilil)trifluoroacetamide (BSTFA)**  
stabilità termica e volatilità degli analiti polari



# Procedura di Analisi



↓  
Acquisizione  
segnale in TIC ed  
estrazione del  
cromatogramma con  
ioni selezionati



## **Analisi GC-MS**

alta efficienza e sensibilità



Maggior parte dei marker presenti in tracce  
Matrice ambientale molto complessa  
Molti interferenti e rumore di fondo



Difficoltà nella rilevazione degli analiti

## Range di concentrazione di alcuni analiti in siti urbani

ACIDI	Conc. (ng/m <sup>3</sup> )
Acido malonico	0.3-473
Acido succinico	0.5-440
Acido adipico	0.4-139
Acido pimelico	0.5-32
Acido ftalico	0.7-242
Acido malico	0.1-144

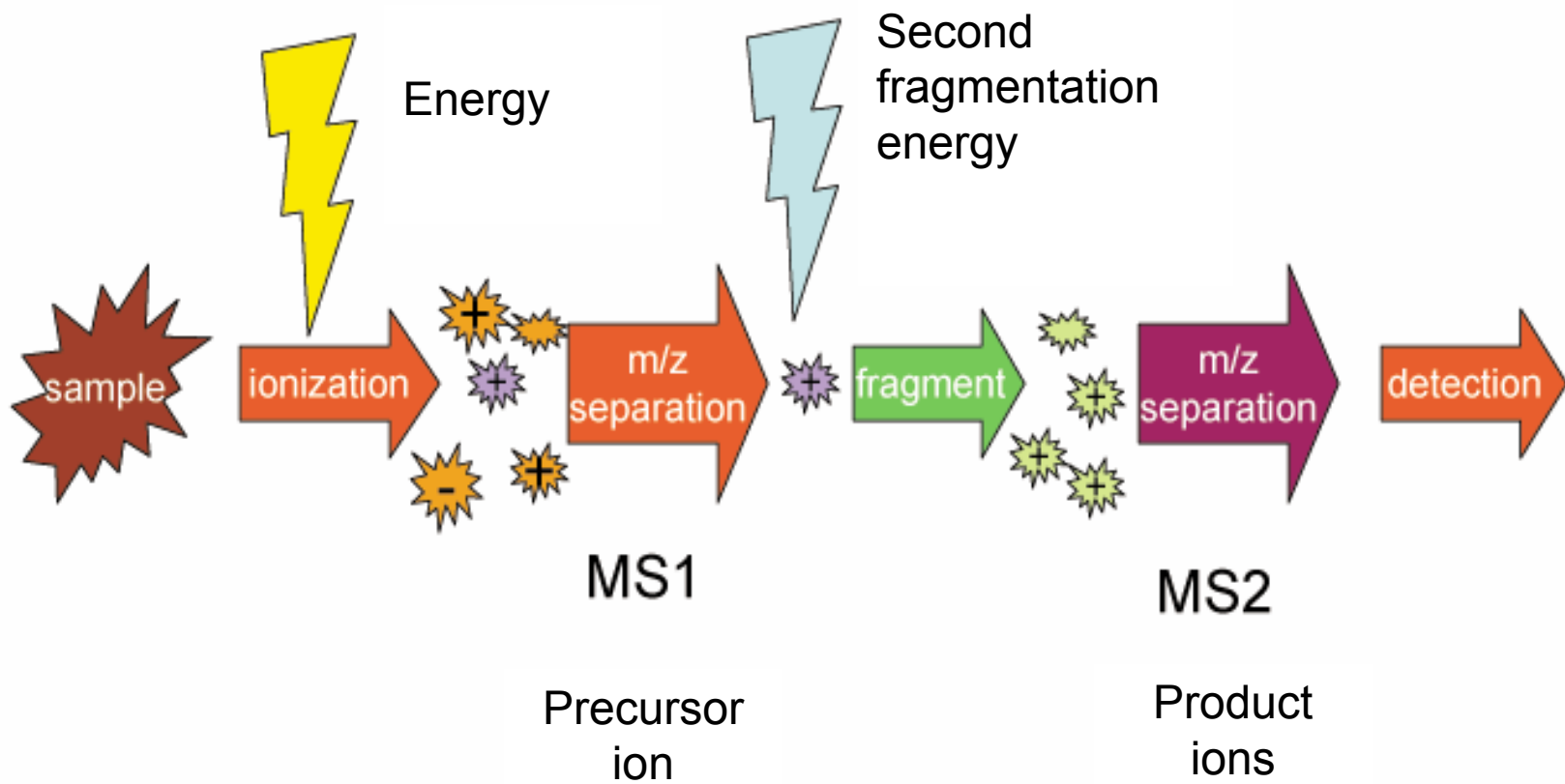
FENOLI	Conc. (ng/m <sup>3</sup> )
Vanillina	0.02-18.9
Acido vanillico	0.04-11
Acetovanillone	0.01-7.05
Acido siringico	0.03-13
Siringaldeide	0.08-23
Syringol	0.13-0.30

Nei campioni in analisi spesso valori vicini al limite di concentrazione inferiore (non più di qualche ng/m<sup>3</sup>)



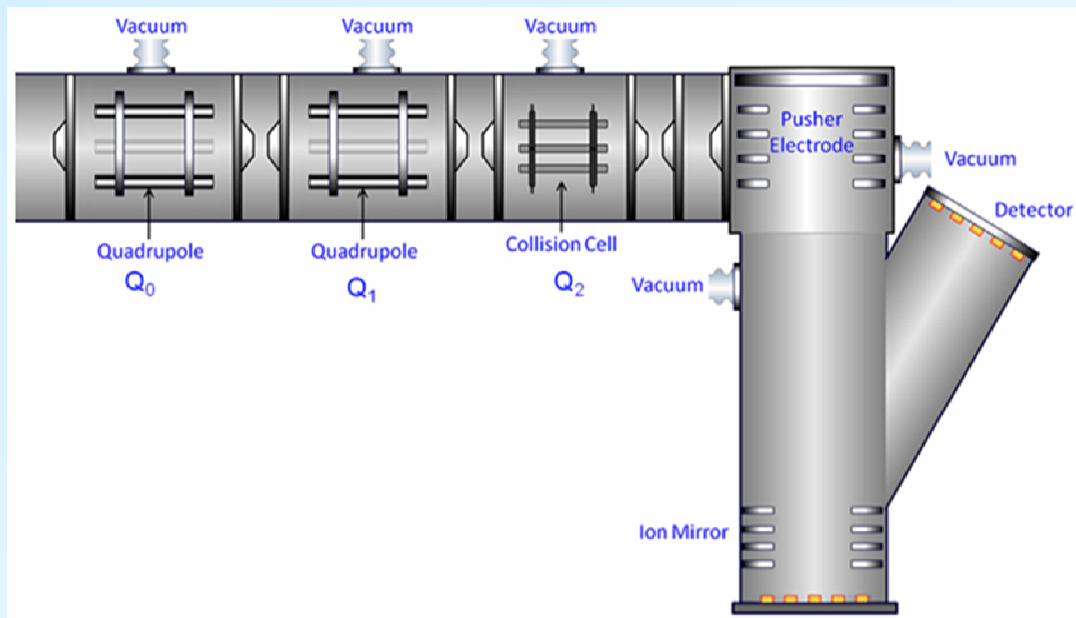
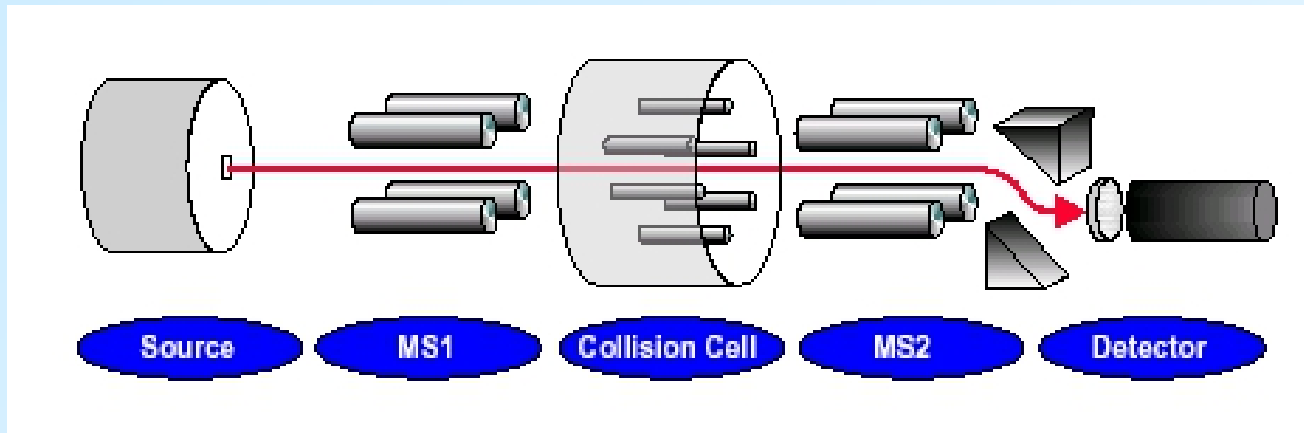
**Analisi GC-MS tandem**

Aumento della sensibilità diminuendo il rumore di fondo e le interferenze della matrice



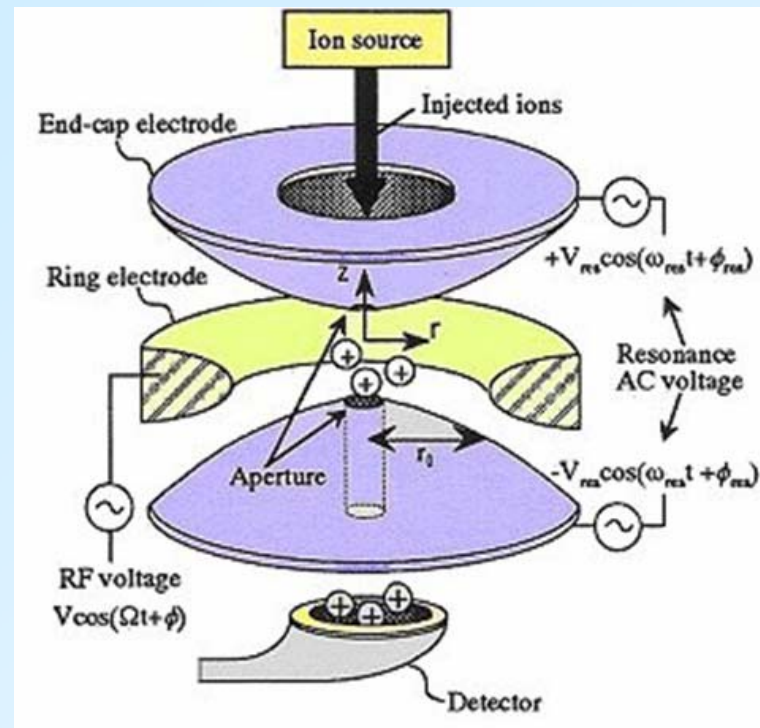
# Tecniche in-space

Triplo quadrupolo  
Qq-TOF



# Tecniche in-time

## Trappola ionica

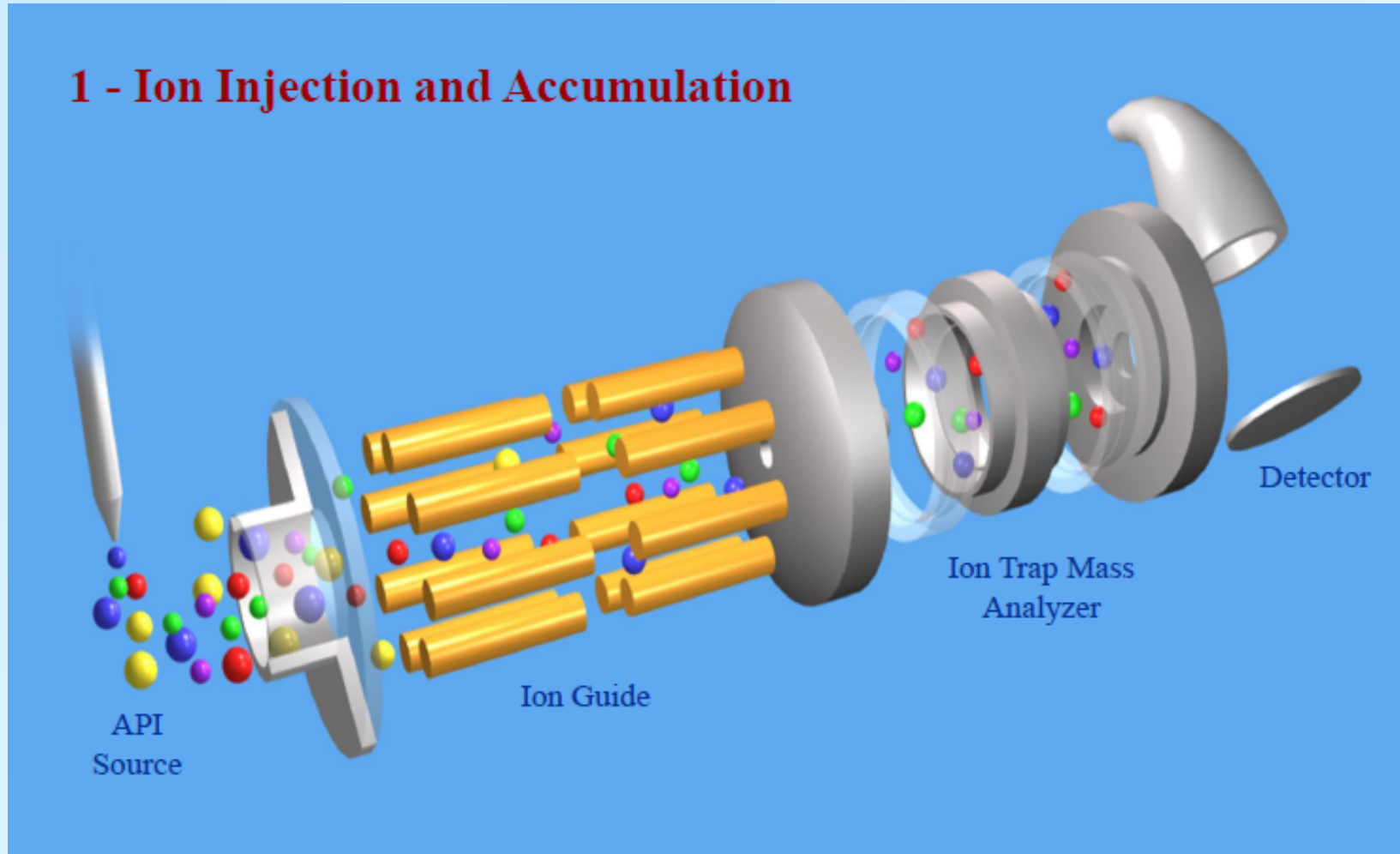


Costi ridotti

Tecnica utilizzata in questo lavoro

# Ion trap MS/MS

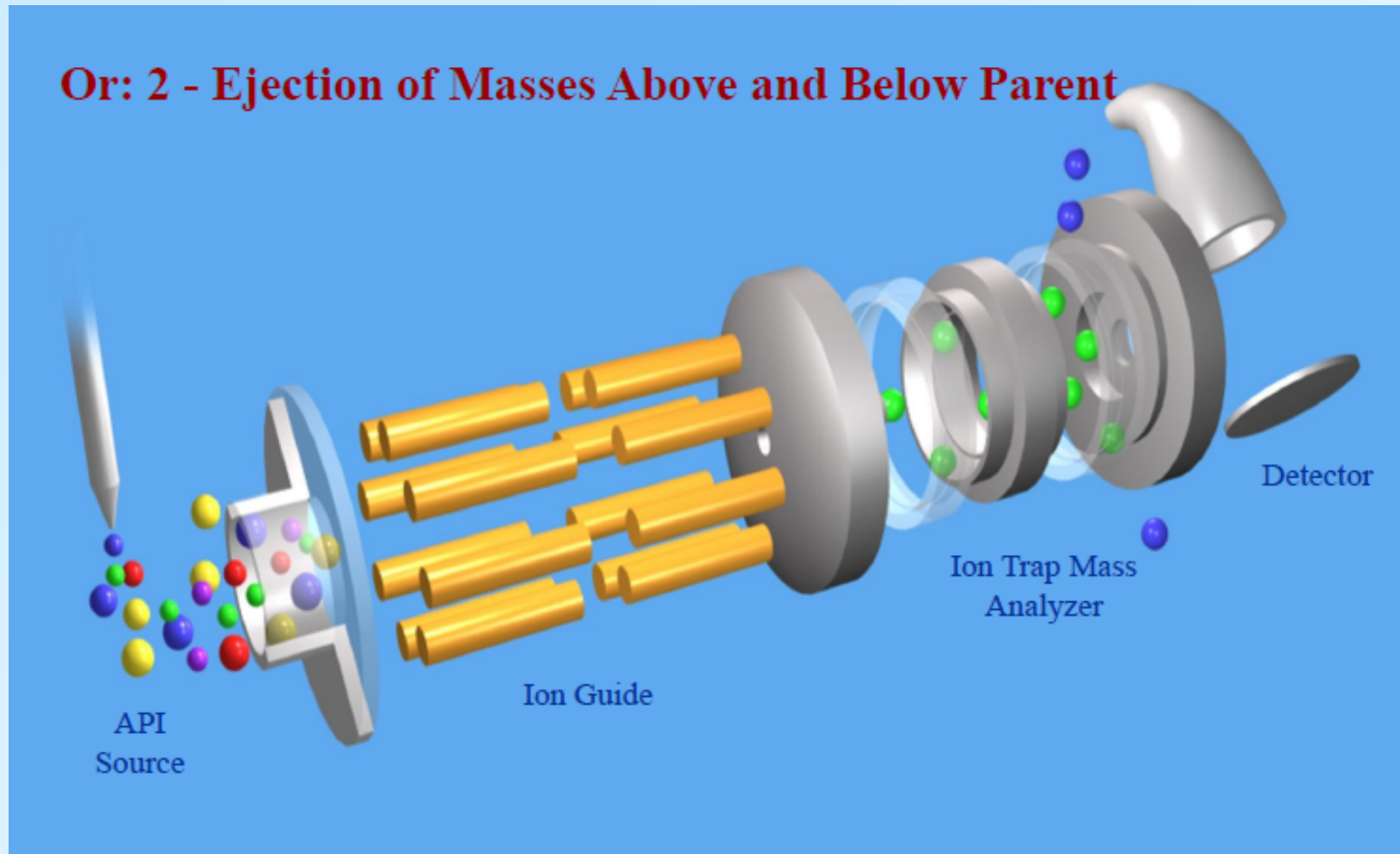
## 1 - Ion Injection and Accumulation





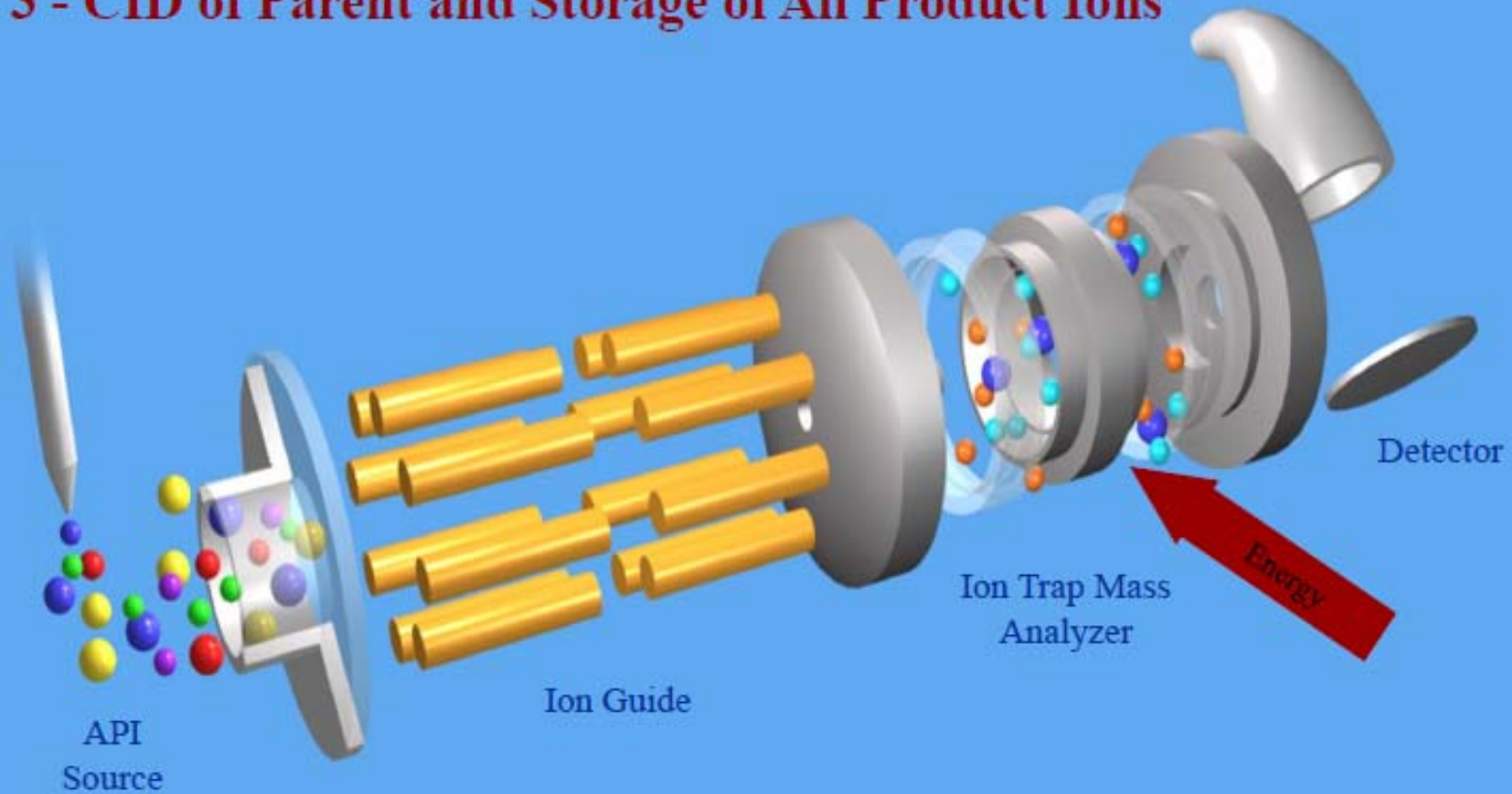
# Ion trap MS/MS: isolation

**Or: 2 - Ejection of Masses Above and Below Parent**



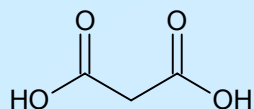
# Ion trap MS/MS: fragmentation

## 3 - CID of Parent and Storage of All Product Ions

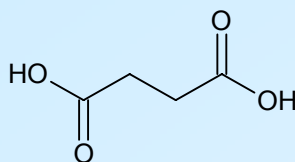


# Considerati acidi carbossilici a basso peso molecolare e fenoli

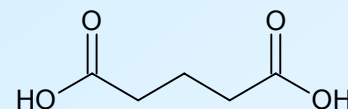
## •Acidi dicarbossilici



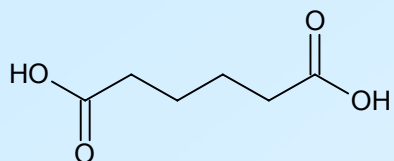
ACIDO MALONICO



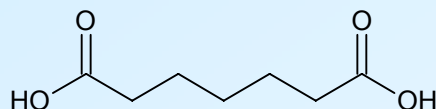
ACIDO SUCCINICO



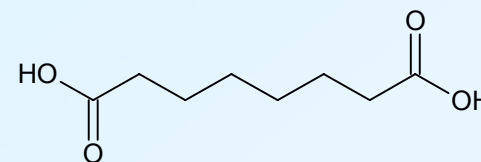
ACIDO GLUTARICO



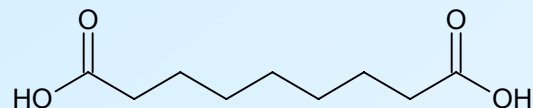
ACIDO ADIPICO



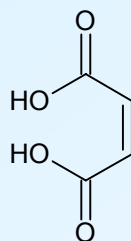
ACIDO PIMELICO



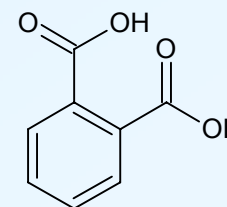
ACIDO SUBERICO



ACIDO AZELAICO

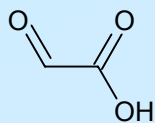


ACIDO MALEICO

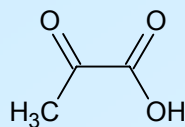


ACIDO FTALICO

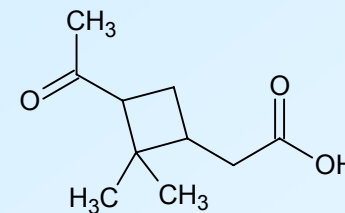
•Acidi oxo- e idrossicarbossilici



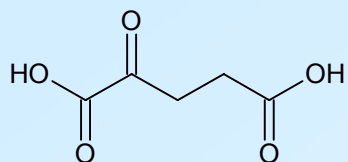
ACIDO GLIOSSILICO



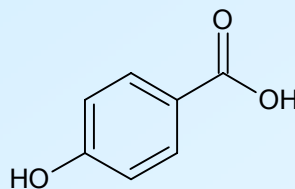
ACIDO PIRUVICO



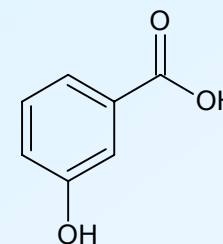
ACIDO PINONICO



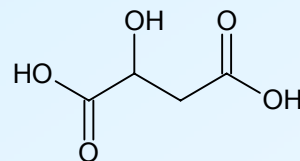
ACIDO 2-CHETOGLUTARICO



ACIDO 4-IDROSSIBENZOICO

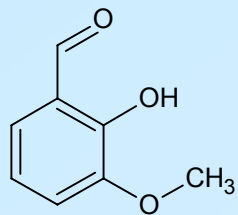


ACIDO 3-IDROSSIBENZOICO

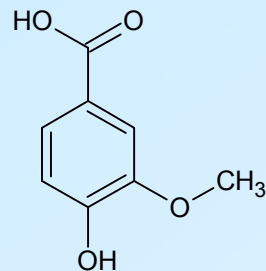


ACIDO MALICO

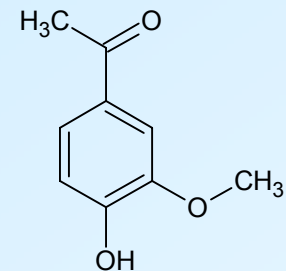
## •Fenoli vanillici



VANILLINA

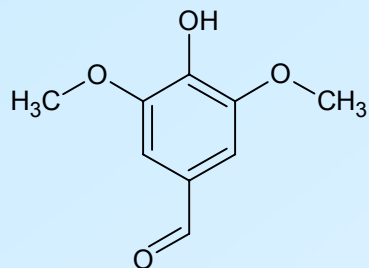


ACIDO VANILLICO

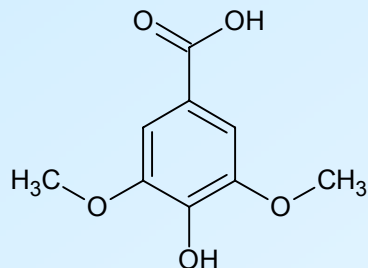


ACETOVANILLONE

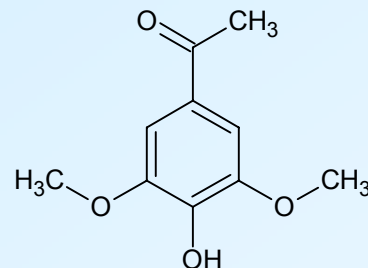
## •Fenoli siringici



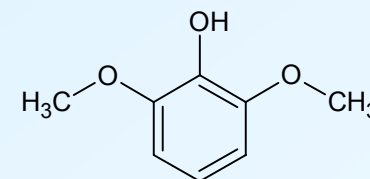
SIRINGALDEIDE



ACIDO SIRINGICO

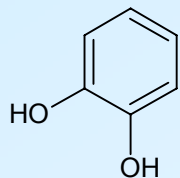


ACETOSIRINGONE

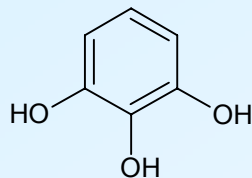


SYRINGOL

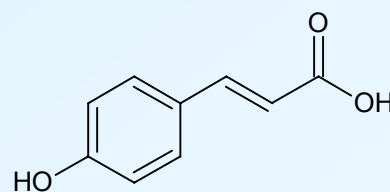
## •Altri fenoli



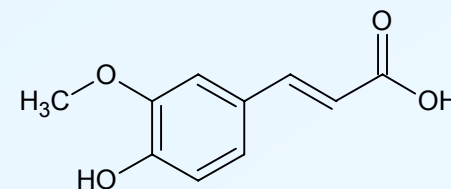
CATECOLO



PIROGALLOLO



ACIDO p-CUMARICO



ACIDO FERULICO

Oltre alla quantità di analiti si possono ricavare altre informazioni utili

$C_3/C_4$ : stima dell'attività ossidativa dell'atmosfera

$C_6/C_9$ : stima dell'origine biogenica o antropogenica dell'aerosol organico

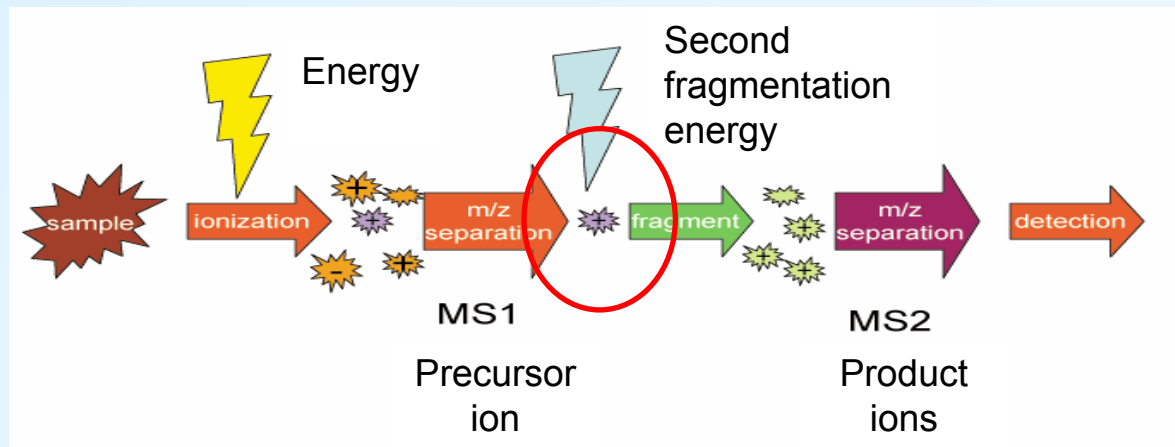
$Ph/C_9$ : stima dell'origine biogenica o antropogenica dell'aerosol organico

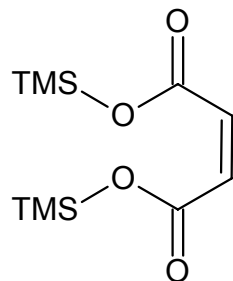
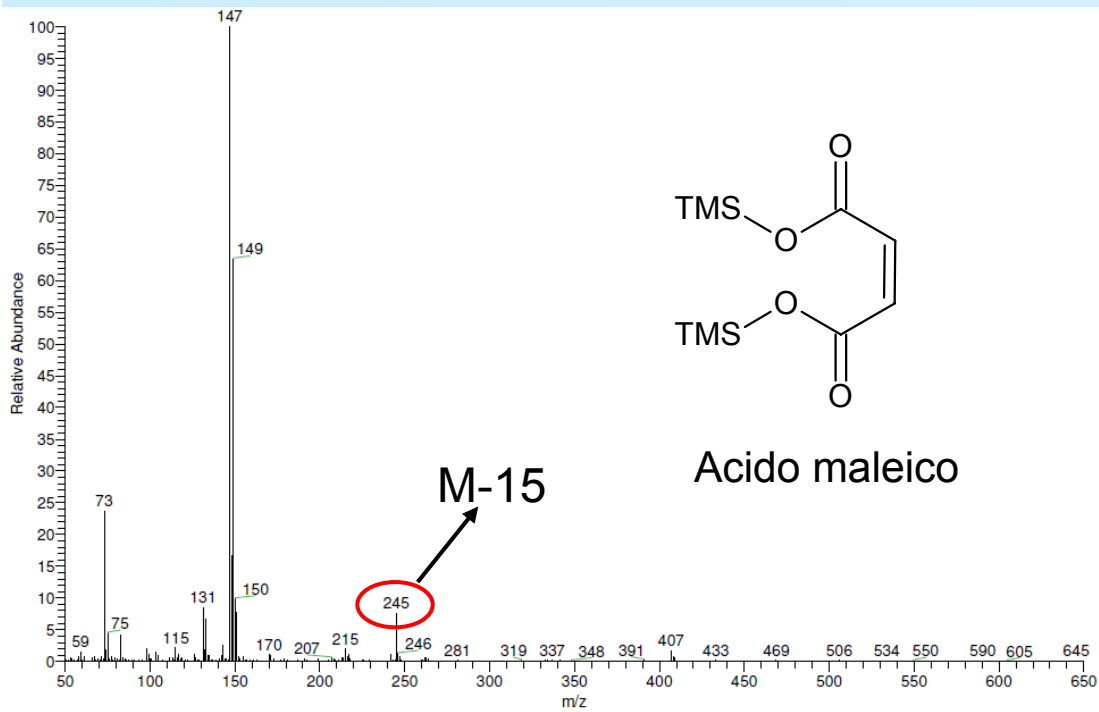
$S/N$ : stima del tipo di biomassa bruciata

Analisi GC/MS usata per ottimizzare la separazione e per ottenere gli spettri di massa da cui selezionare il frammento su cui eseguire la seconda frammentazione

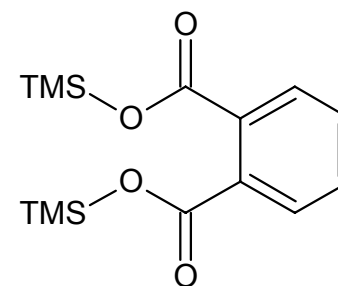
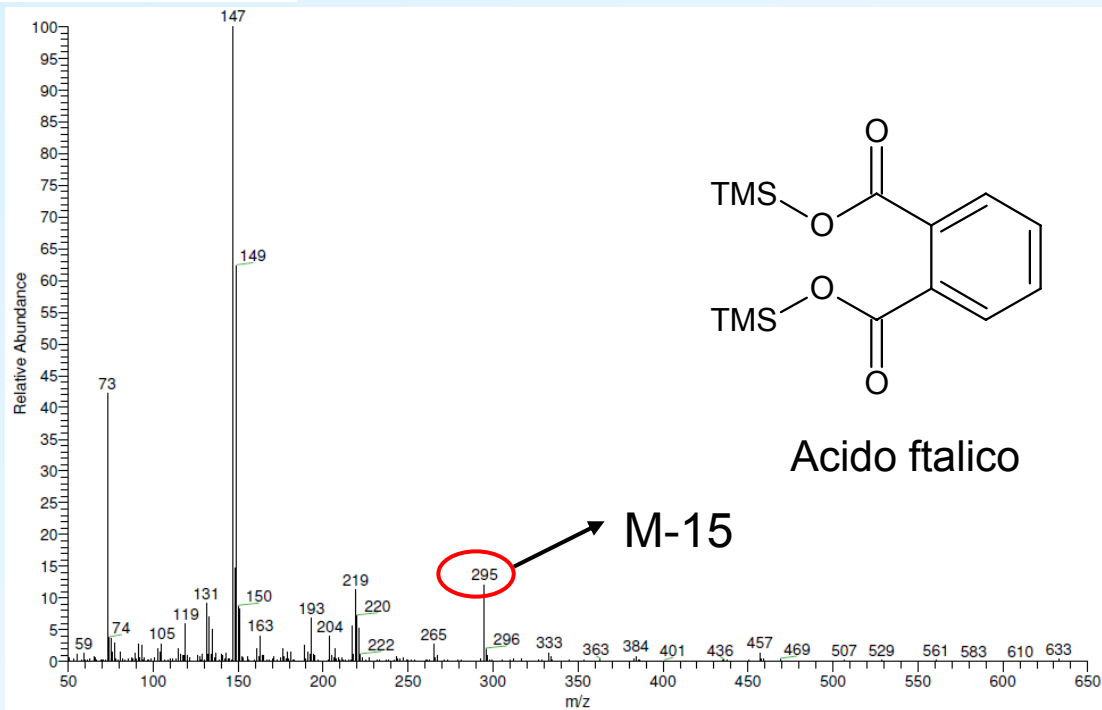


Frammento caratteristico e/o più intenso

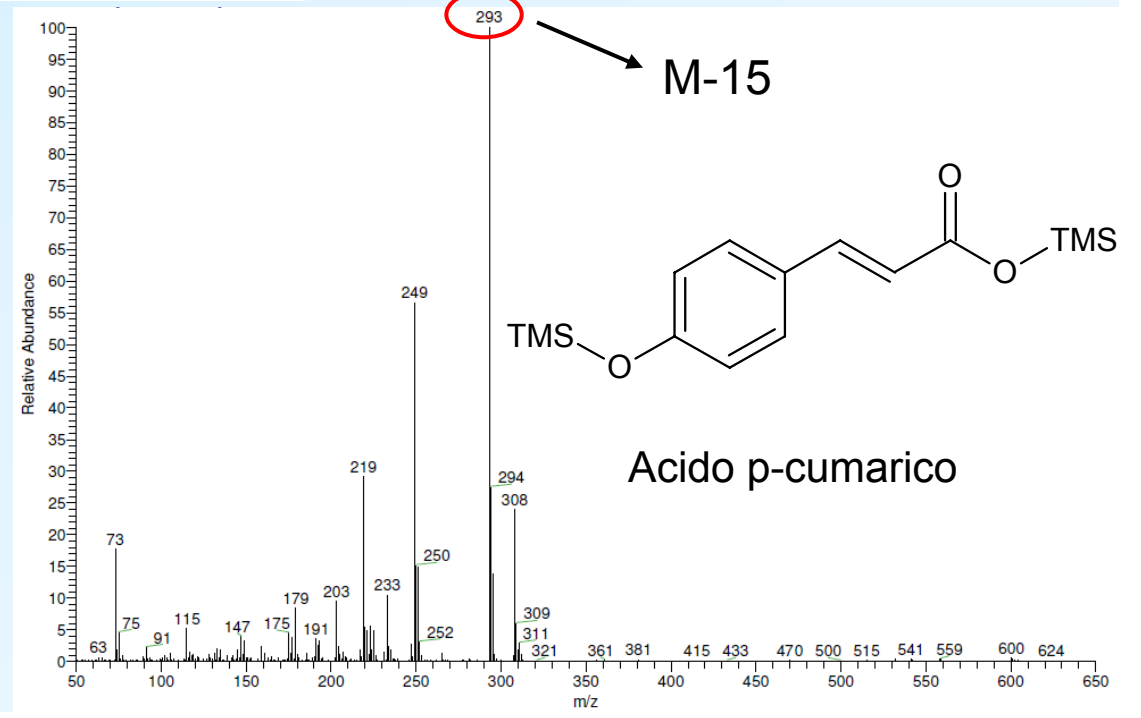
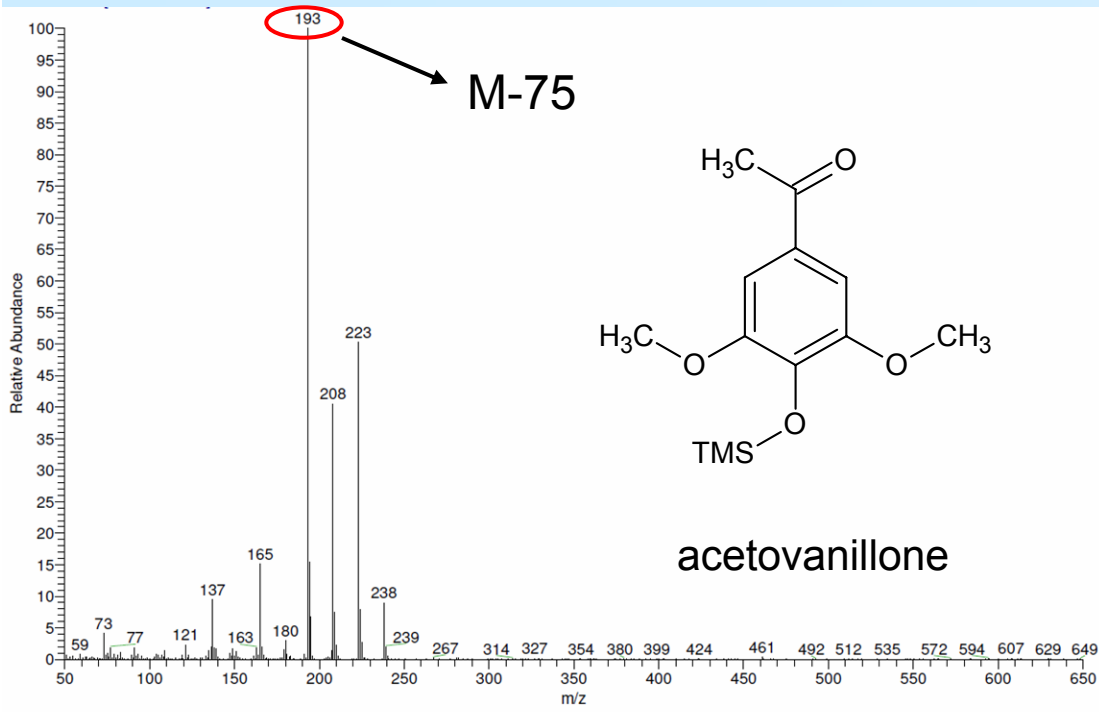




Acido maleico



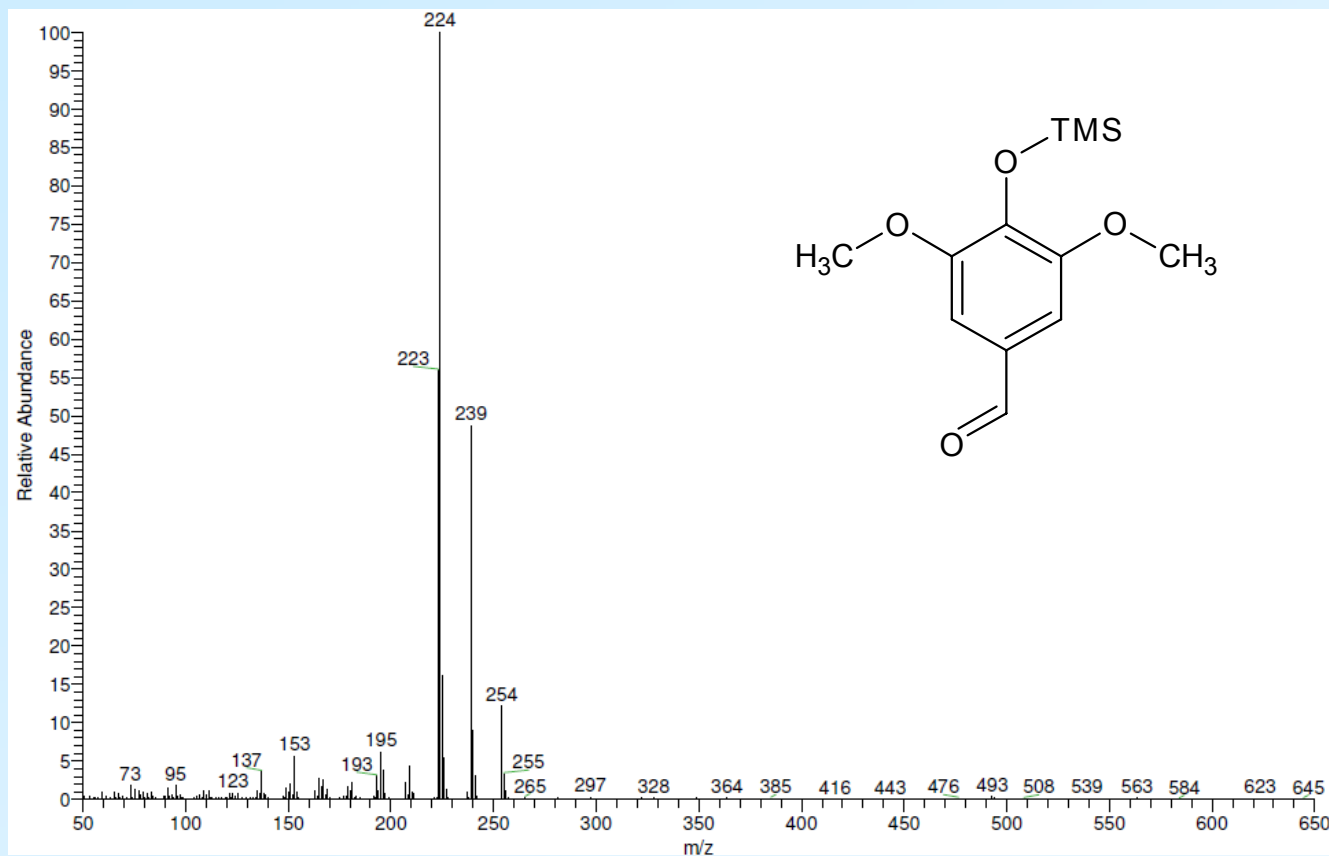
Acido ftalico



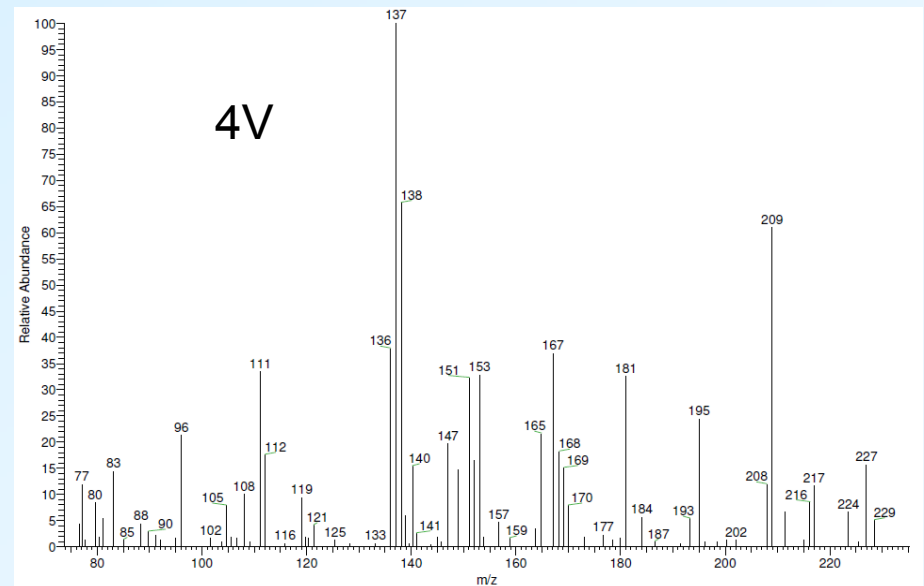
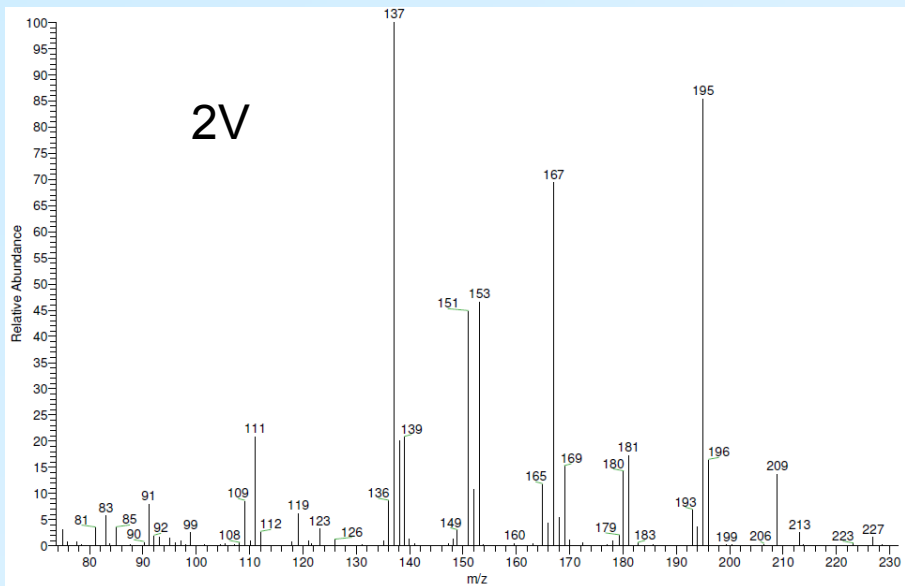
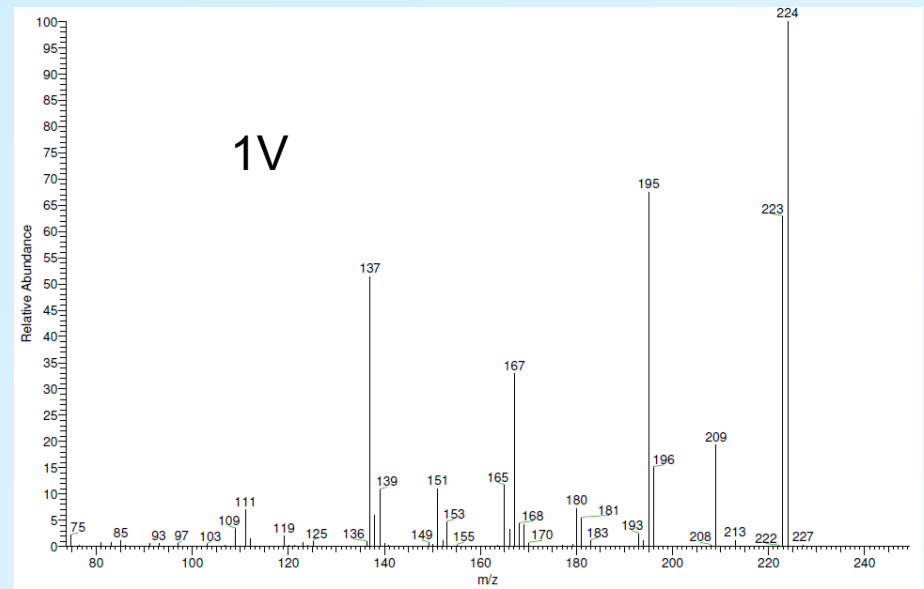
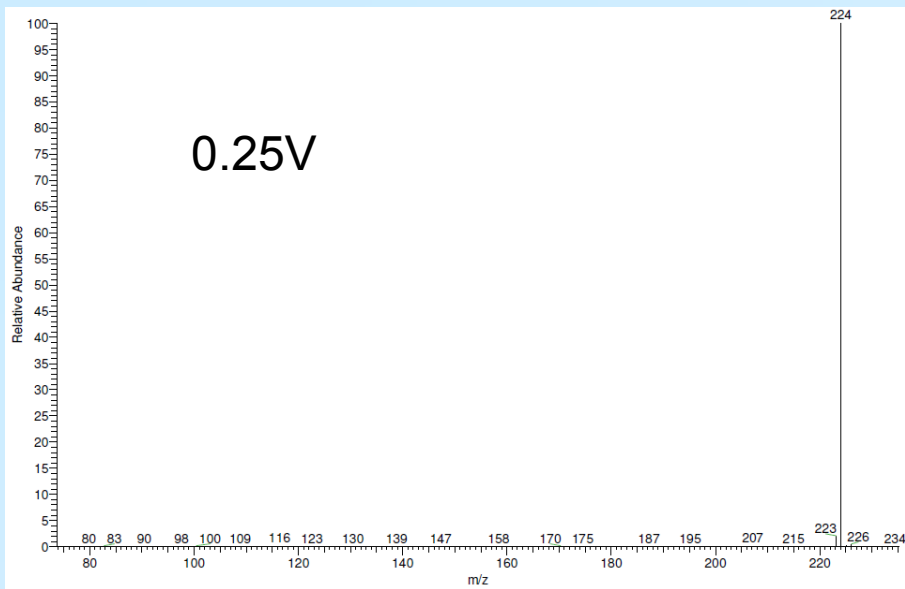
**Studio dell'energia di  
seconda frammentazione**



Seconda frammentazione deve dare spettri con pochi frammenti caratteristici e di buona intensità



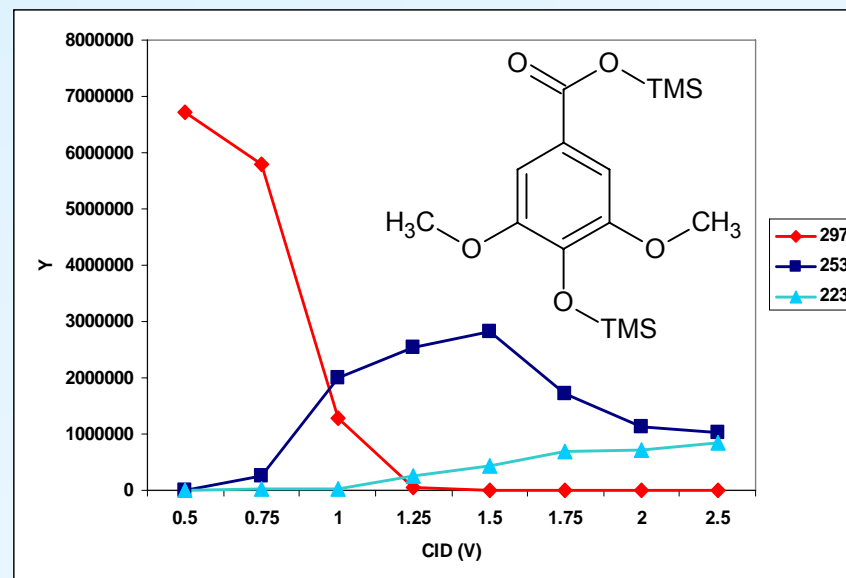
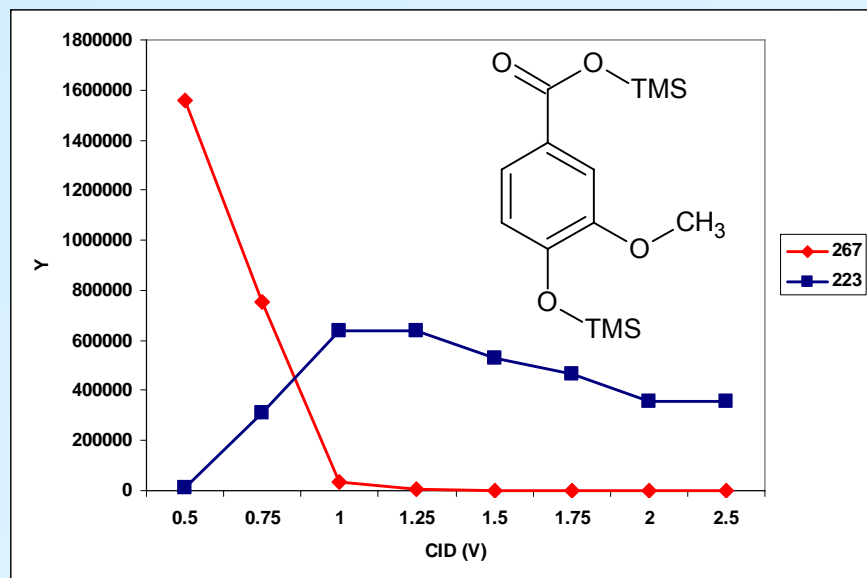
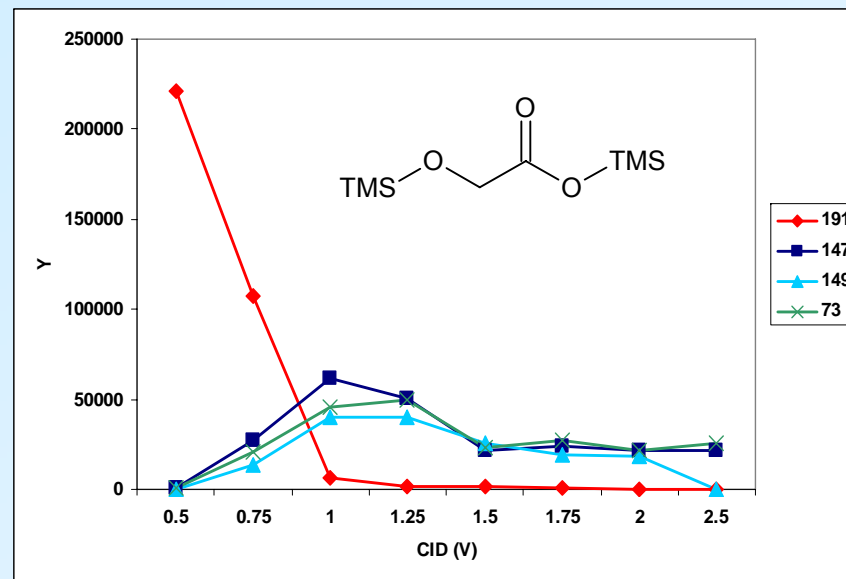
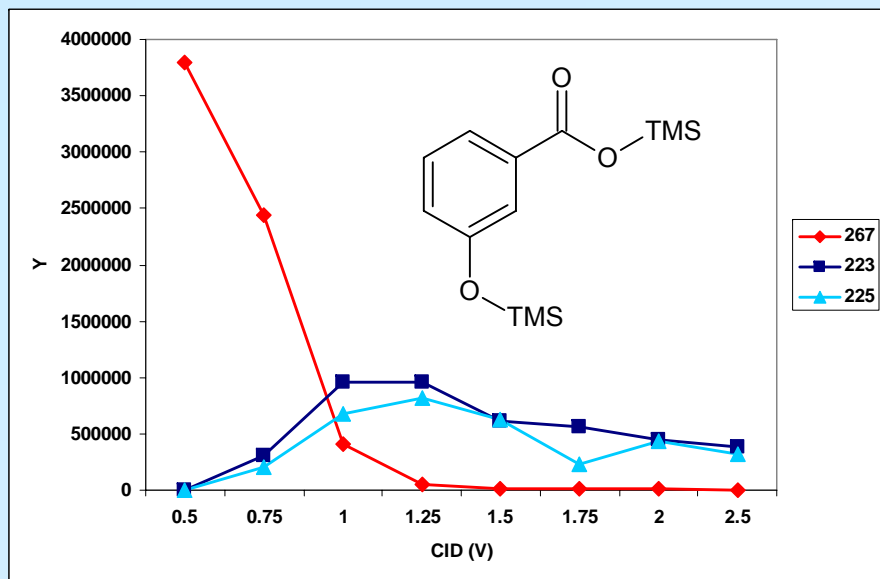
SIRINGALDEIDE: ione precursore m/z 224



Bassa energia di frammentazione: pochi frammenti, nessuna informazione

Energia di frammentazione troppo alta: troppi frammenti, spettro confuso

## Energia di seconda frammentazione ottimale compresa tra 0.75V e 1.5V per tutti i composti



## Curve di calibrazione

ACIDS	R <sup>2</sup>	LOD MSMS (ngm <sup>-3</sup> )	LOD MS (ngm <sup>-3</sup> )	CID Voltage (V)
malonic acid	0.9959	0.46	1.25	1.00
glyoxylix acid	0.9980	0.32	3.01	1.00
maleic acid	0.9986	0.27	1.25	1.00
succinic acid	0.9991	0.22	3.89	1.00
glutaric acid	0.9979	0.33	2.23	1.25
malic acid	0.9940	0.55	0.73	1.25
pyruvic acid	0.9967	0.39	4.21	1.25
adipic acid	0.9987	0.25	4.28	0.75
pinonic acid	0.9974	0.37	1.76	1.00
3-hydroxybenzoic acid	0.9985	0.28	2.03	1.25
pimelic acid	0.9935	0.59	3.03	1.00
2-ketoglutaric acid	0.9980	0.32	3.67	1.25
4-hydroxybenzoic acid	0.9921	0.64	2.95	1.25
phthalic acid	0.9988	0.25	1.79	1.00
suberic acid	0.9962	0.44	4.48	1.00
azelaic acid	0.9952	0.52	4.82	1.25

Volumi riferiti a un campionamento a basso volume: 55m<sup>3</sup>

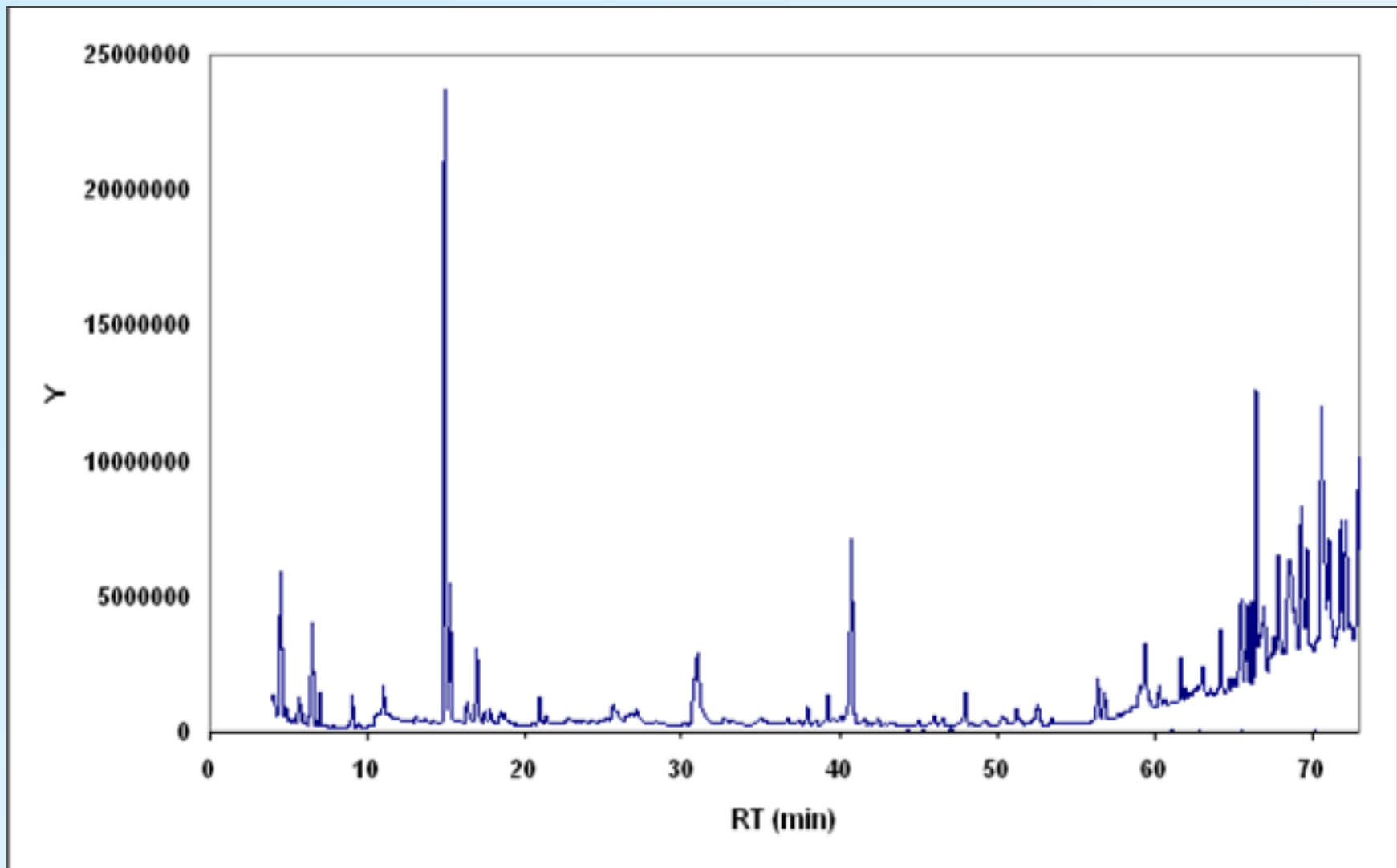
<b>PHENOLS</b>	<b>R<sup>2</sup></b>	<b>LOD MSMS (ngm<sup>-3</sup>)</b>	<b>LOD MS (ngμm<sup>-3</sup>)</b>	<b>CID Voltage (V)</b>
catechol	0.9983	0.33	2.72	1.00
syringol	0.9970	0.47	4.27	1.25
vanillin	0.9937	0.54	4.71	1.50
pyrogallol	0.9976	0.33	3.70	1.25
acetosyringone	0.9921	0.68	3.66	1.25
syringaldehyde	0.9905	0.70	2.28	1.25
acetovanillone	0.9912	0.65	3.43	1.00
vanillic acid	0.9945	0.53	4.21	1.25
syringic acid	0.9933	0.57	3.50	1.50
p-coumaric acid	0.9973	0.42	2.83	1.50
ferulic acid	0.9949	0.54	3.12	1.50

Volumi riferiti a un campionamento a basso volume: 55m<sup>3</sup>

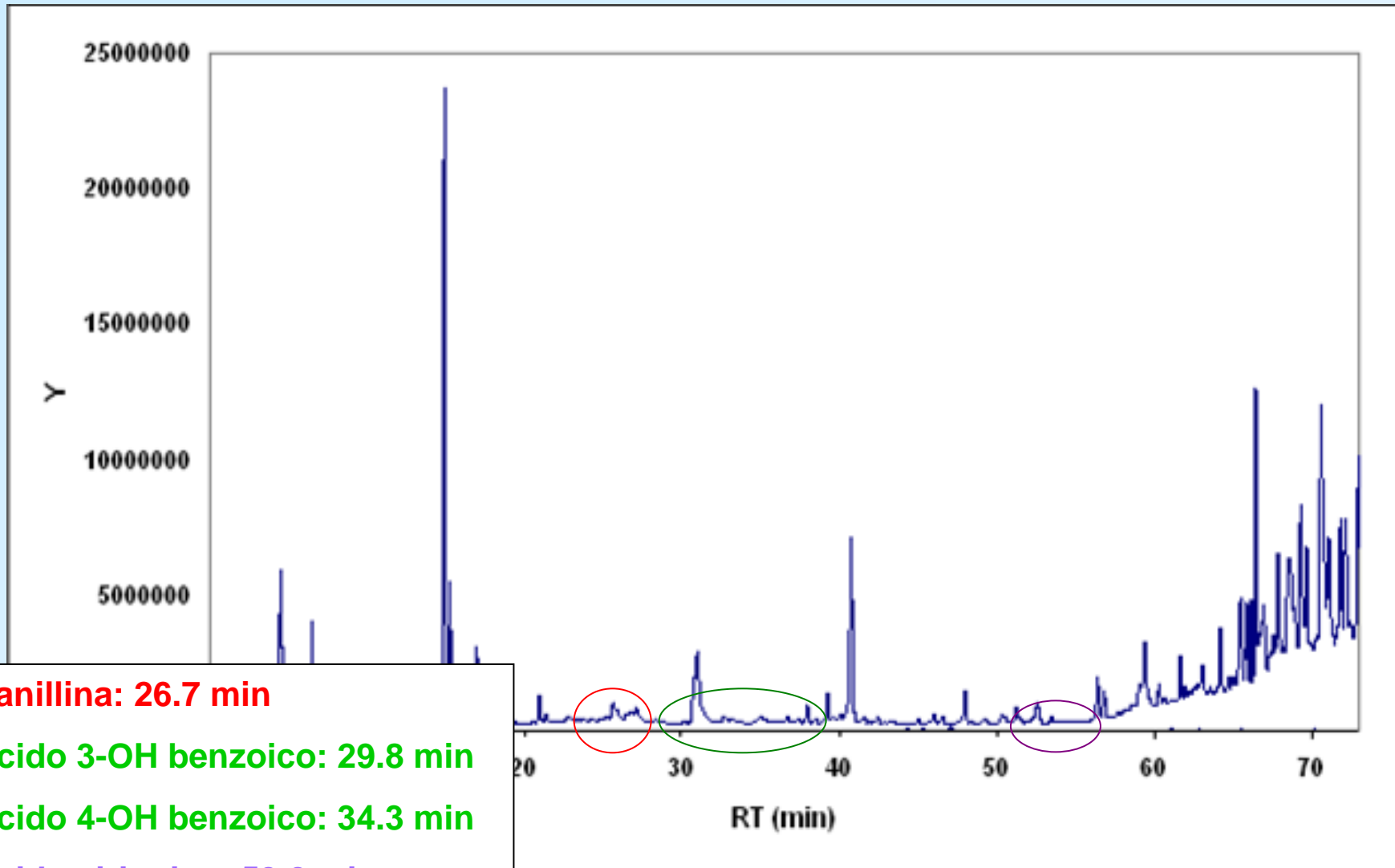
Buona linearità delle curve di calibrazione

Sensibilità migliorata di circa 6 volte

# Applicazione a campioni reali di PM<sub>2.5</sub>



# Applicazione a campioni reali di PM<sub>2.5</sub>



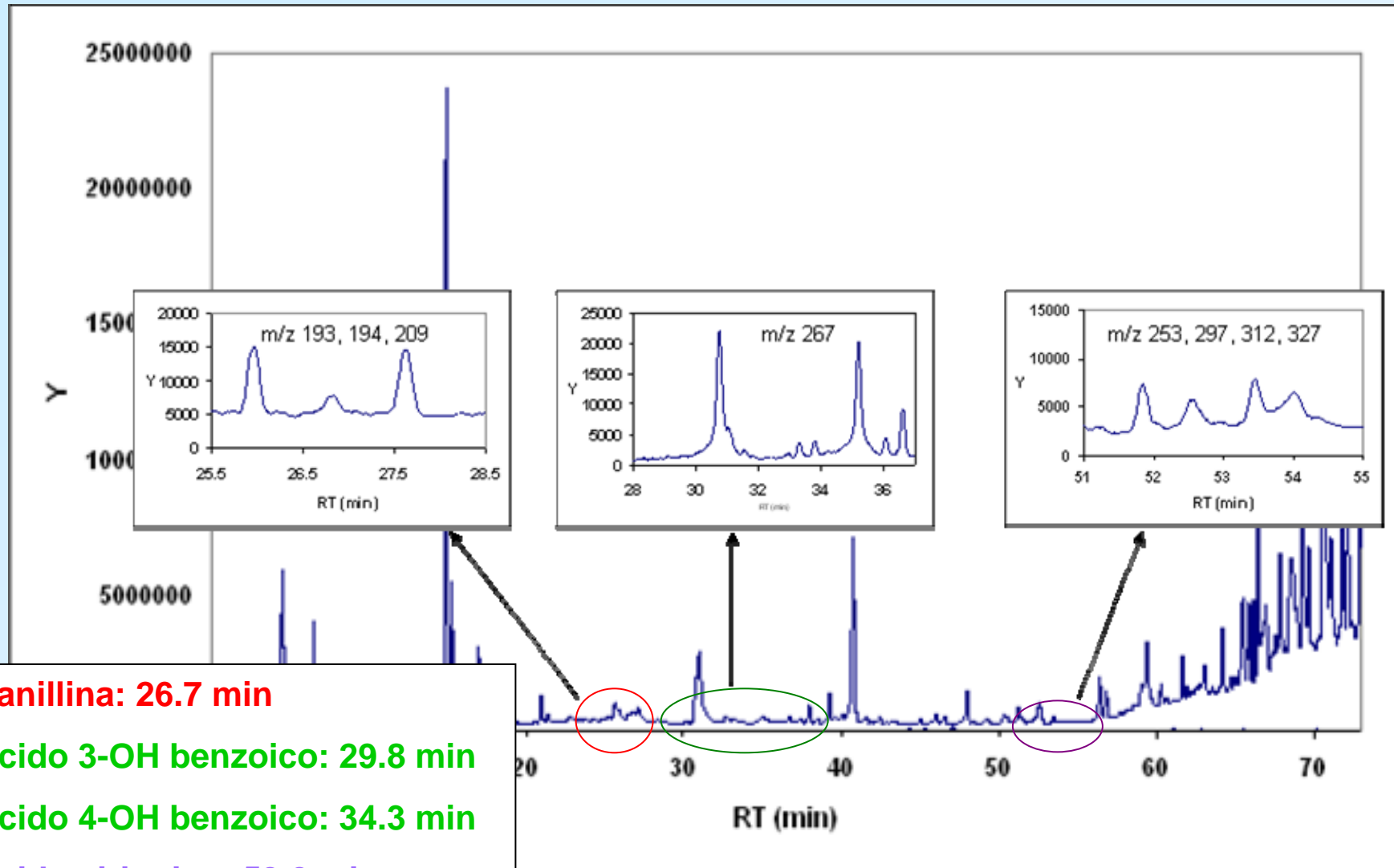
**Vanillina: 26.7 min**

**Acido 3-OH benzoico: 29.8 min**

**Acido 4-OH benzoico: 34.3 min**

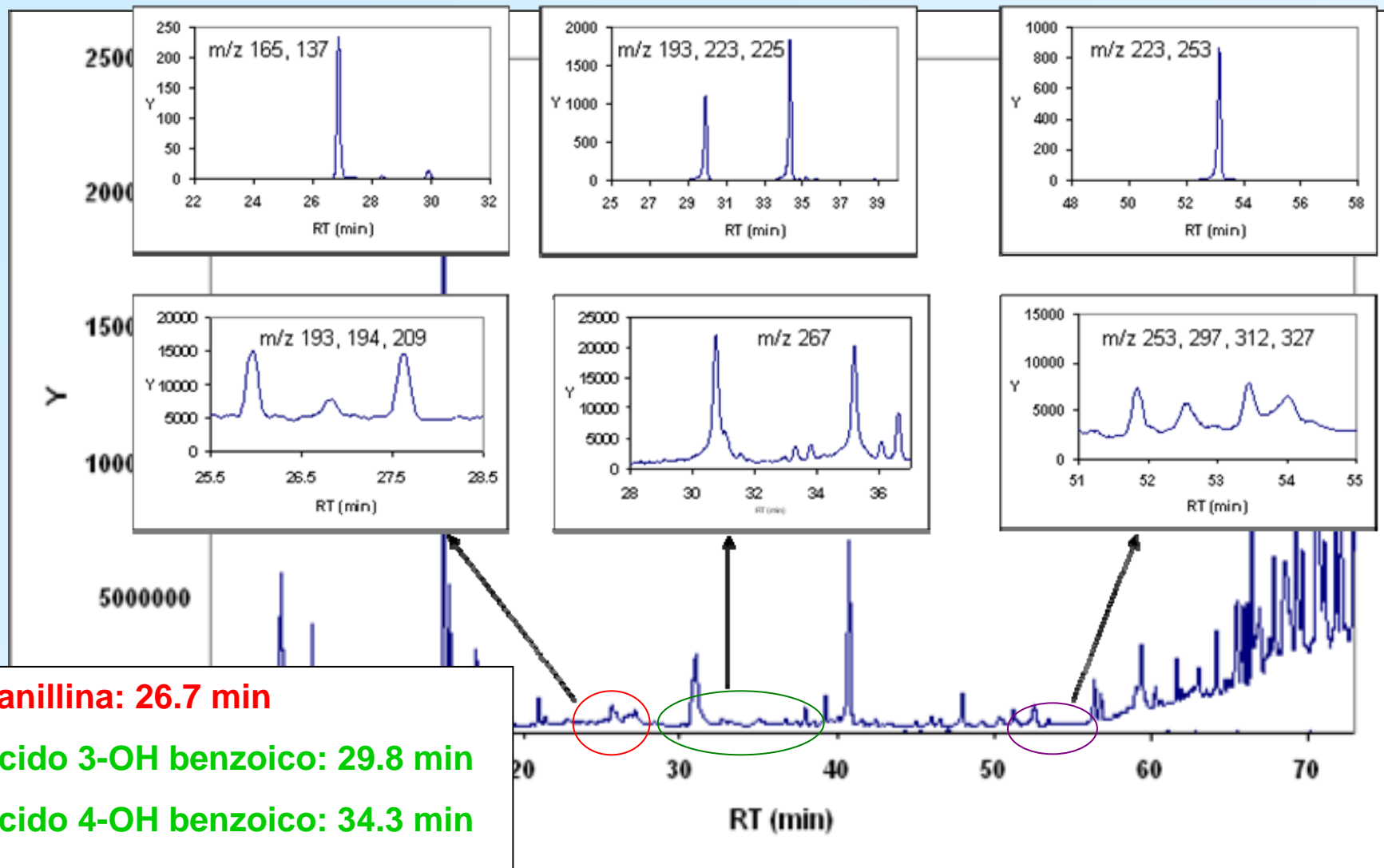
**Acido sirringico: 53.0 min**

# Applicazione a campioni reali di PM<sub>2.5</sub>





# Applicazione a campioni reali di PM<sub>2.5</sub>



# Risultati

## Campione invernale Bologna (V campionato $\approx 55\text{m}^3$ )

ACIDS	MS (ngm <sup>-3</sup> )	MSMS (ngm <sup>-3</sup> )
glycolic acid	6.9	
malonic acid	n.d.	1.1
glyoxylix acid	n.d.	n.d.
maleic acid	15.2	
succinic acid	18.1	
glutaric acid	1.4	
malic acid	n.d.	n.d.
pyruvic acid	n.d.	<LOD
adipic acid	<LOD	1.6
pinonic acid	n.d.	n.d.
3-hydroxybenzoic acid	<LOD	0.4
pimelic acid	n.d.	0.7
2-ketoglutaric acid	n.d.	n.d.
4-hydroxybenzoic acid	<LOD	0.6
phthalic acid	2.8	
suberic acid	n.d.	n.d.
azelaic acid	n.d.	2.1

PHENOLS	MS (ngm <sup>-3</sup> )	MSMS (ngm <sup>-3</sup> )
catechol	<LOD	<LOD
syringol	n.d.	<LOD
vanillin	n.d.	0.3
pyrogallol	n.d.	<LOD
acetosyringone	n.d.	n.d.
syringaldehyde	<LOD	0.7
acetovanillone	<LOD	<LOD
vanillic acid	n.d.	<LOD
syringic acid	n.d.	0.4
p-coumaric acid	n.d.	<LOD
ferulic acid	n.d.	n.d.

- Molti acidi che in MS erano <LOD vengono rilevati e possono essere quantificati in MSMS
- Fenoli che non venivano rilevati in MS sono rilevati in MSMS anche se non per tutti è stata possibile la quantificazione

# Fenoli

Derivano dalla combustione della lignina

Parametri diagnostici	Legni teneri	Legni duri	Tessuti erbosi
S/V	0,02-0,05	0,9-1,7	0,4-0,8

	S/V
Winter	1.5
Spring	0.9



} Indicativi di combustione legni duri  
} Indicativi di combustione tessuti erbosi

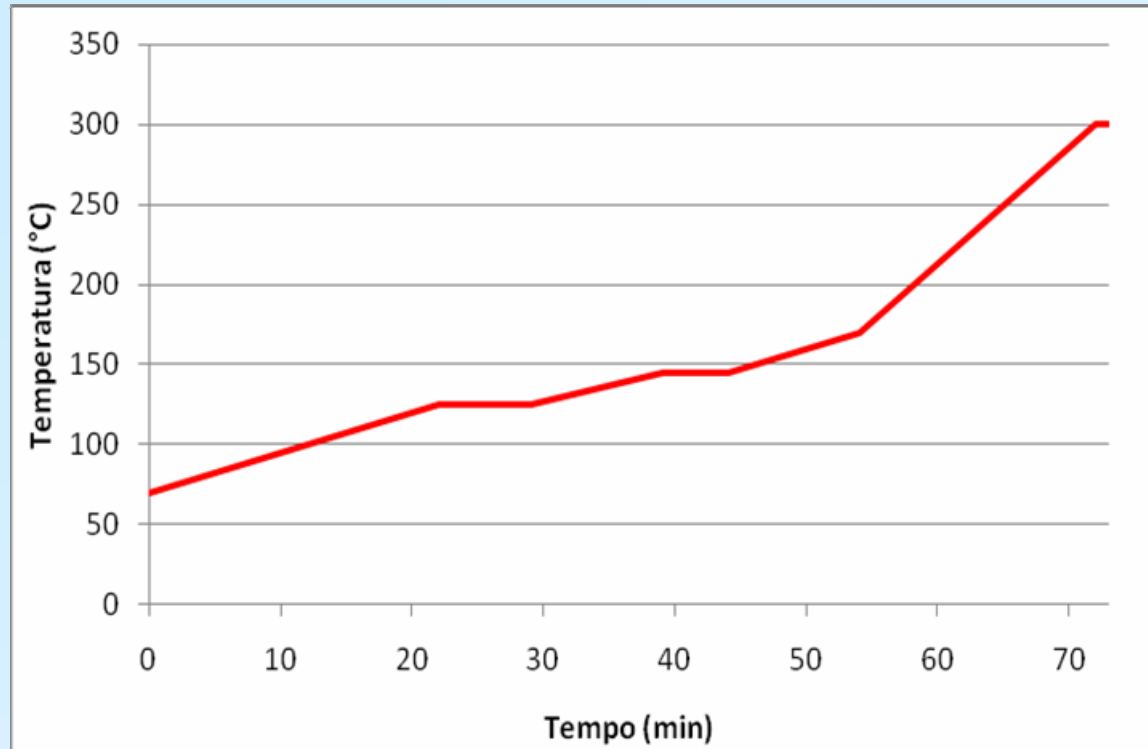
# Conclusioni

- Metodo utile allo studio e ricerca di composti in tracce nel PM
- Vantaggi rispetto GC/MS:
  - Riduzione dei limiti di rilevabilità
  - Riduzione del rumore di fondo e delle interferenze da matrice
  - Miglioramento della selettività
- Costi strumentali contenuti e risultati paragonabili ad alcuni strumenti ad alta risoluzione
- Possibilità di combinare acquisizioni in modalità TIC e MSMS in una singola corsa cromatografica

A bright sun shining through a blue sky with scattered white clouds. The sun is positioned in the upper center, creating a lens flare effect. The clouds are fluffy and white, scattered across the deep blue sky.

Grazie per l'attenzione

# Condizioni operative



- Colonna capillare: lunghezza 30m, diametro interno 0,25mm, spessore fase stazionaria 0,25 $\mu$ m.
- Carrier gas: He flusso 1,5mL/min.
- Tempo di splitless: 1min.
- Temperatura iniettore: 250°C.

- Temperatura transfer line: 280°C.
- Sorgente elettroni: 250°C.
- Energia elettroni: 70eV
- Volume di campione iniettato: 2 $\mu$ L.

Fig. 1.18: Comune di Ferrara. Giorno tipo dell'altezza di rimescolamento, 2005

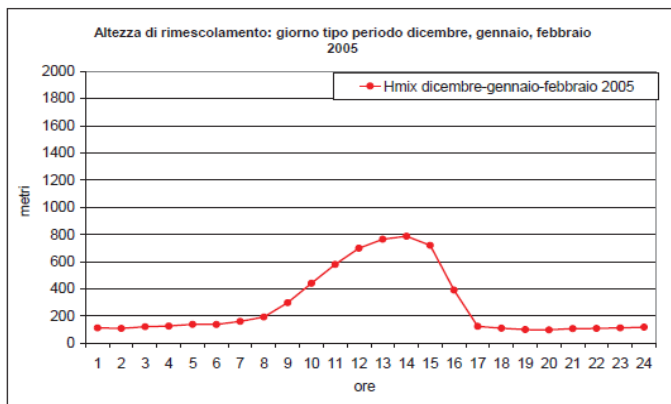
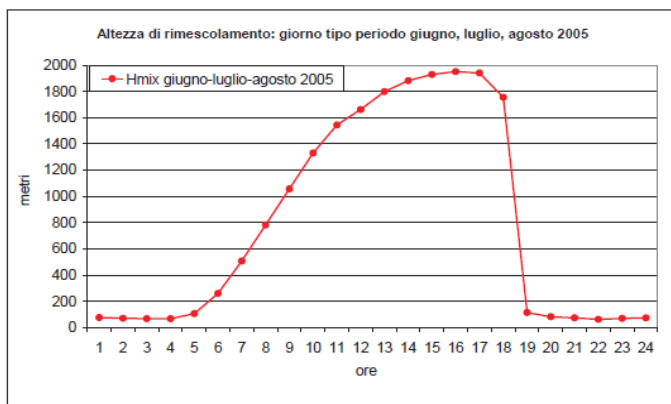
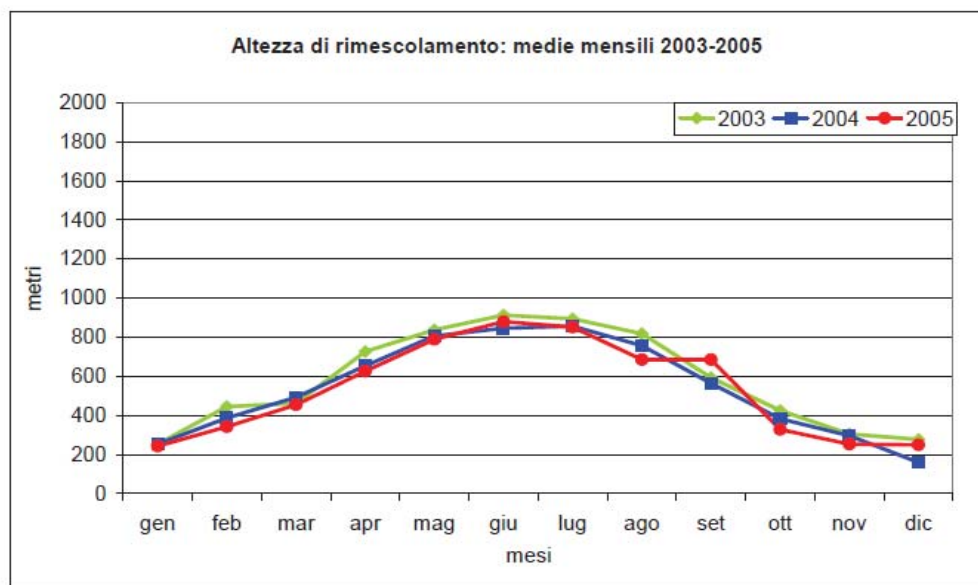
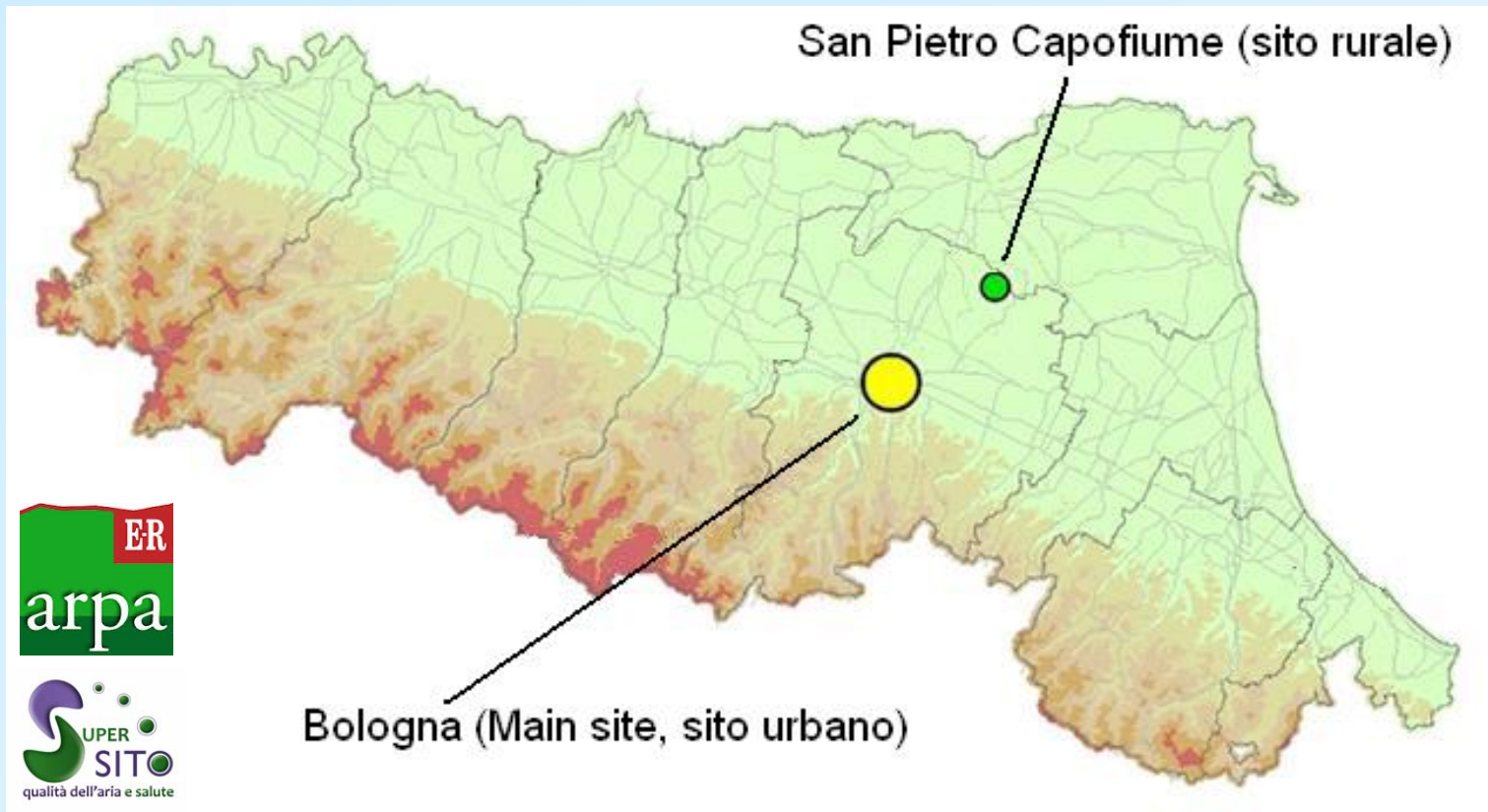


Fig. 1.17: Media mensile dell'altezza di rimescolamento, anni 2003-2005



	<b>Inverno 2011</b>		<b>Estate 2012</b>		<b>Autunno 2012</b>		<b>Inverno 2013</b>		<b>Primavera 2013</b>	
	<b>MS</b>	<b>SPC</b>	<b>MS</b>	<b>SPC</b>	<b>MS</b>	<b>SPC</b>	<b>MS</b>	<b>SPC</b>	<b>MS</b>	<b>SPC</b>
<b>Altezza strato rimescolamento (m)</b>	229	169	974	854	376	273	398	296	955	793





### Main Site

