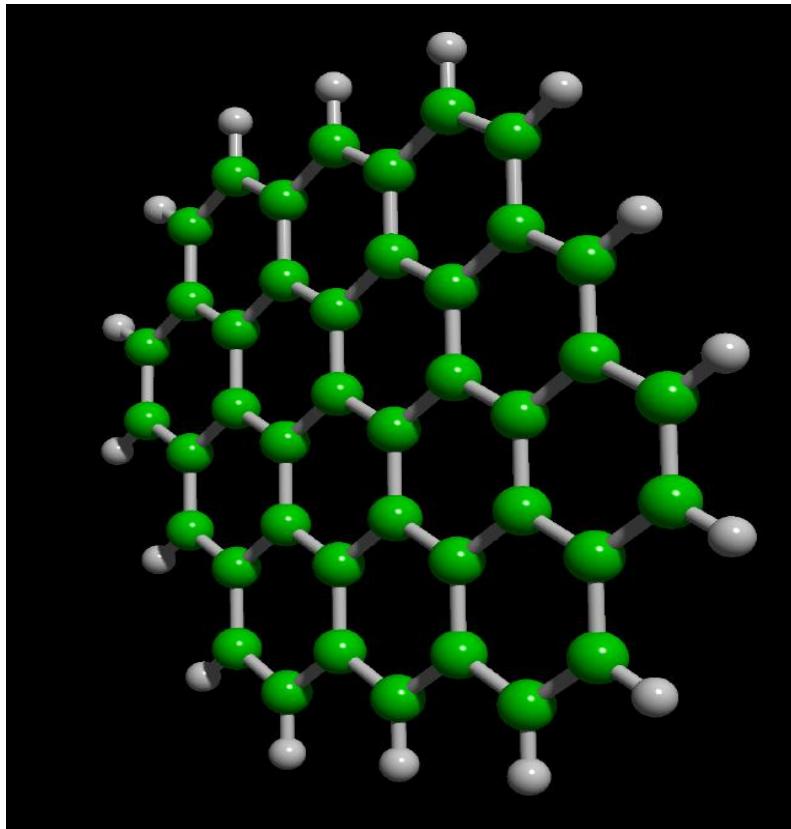


Interconfronto APAT-IC011

Misura della frazione in massa degli IPA in un suolo contaminato: valutazione del processo analitico



Riunione Conclusiva

Roma, 28 ottobre 2008

Stefania Balzamo

Sabrina Barbizzi

Elisa Calabretta

Paolo de Zorzi

Monica Potalivo

Silvia Rosamilia

Servizio Metrologia Ambientale



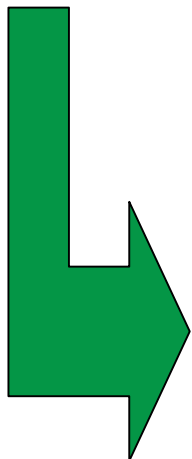
Destinatari

17 agenzie regionali +

2 agenzie provinciali +

1 laboratorio ISS

59 laboratori (adesione)



41 laboratori (70%)
(restituzione risultati)



Obiettivo generale

■ Valutazione del processo analitico

- Processo completo [inclusa estrazione e purificazione];
- Analisi dell'estratto;
- Analisi di una soluzione di riferimento incognita pura

■ 3 materiali di prova:

- APAT RM014 “Polluted Soil-A” [solido];
- APAT RM017 Estratto in n-esano [liquido];
- Soluzione incognita contenente IPA [Chemical Research srl].



Idrocarburi Policiclici Aromatici

Acenaftene	Benzo[k]fluoranteme
Acenaftilene	Benzo[j]fluoranteme
Fluorene	Benzo[e]pirene
Fenantrene	Benzo[a]pirene
Antracene	Perilene
Fluorantene	Indeno[1,2,3-c,d]pirene
Pirene	Benzo[g,h,i]perilene
Benzo[a]antracene	Dibenzo[a,h]antracene
Crisene	Dibenzo[a,e]pirene
Benzo[b]fluoranteme	Somma IPA



■ Esclusione

- Naftalene
- Dibenzo[a,i]pirene
- Dibenzo[a,l]pirene
- Dibenzo[a,h]pirene

■ Somma IPA

- Richiesta ai laboratori di fornire un nuovo valore che tenesse conto delle esclusioni

Valori assegnati [1]

■ APAT RM014

- Valore di consenso laboratori esterni (statistica robusta, ISO 13528:2005)
- Incertezza:
 1. Incertezza di caratterizzazione;
 2. Incertezza composta (caratterizzazione, eterogeneità residua e instabilità)

$$u(c_{RM}) = \sqrt{u_{car}^2 + u_{bb}^2 + u_{smts}^2}$$

$$U = k \times u(c_{RM}) \quad \boxed{k = 2}$$

Valori assegnati [2]

■ APAT RM017

- Valore di consenso laboratori APAT-IC011 (statistica robusta, ISO 13528:2005)
- Incertezza: Scarto tipo robusto

■ Soluzione di riferimento incognita

- Valore ed incertezza associata forniti dal produttore



Criteri di accettazione dei dati [1]

Almeno 2 misure indipendenti

Analita	Fenantrene	
Unità di misura	µg/kg s.s.	
	Valore	Incertezza
Codice Laboratorio	LAB	
misura 1	72,4	
misura 2	71,1	
misura 3		

Valori < LOQ

SI

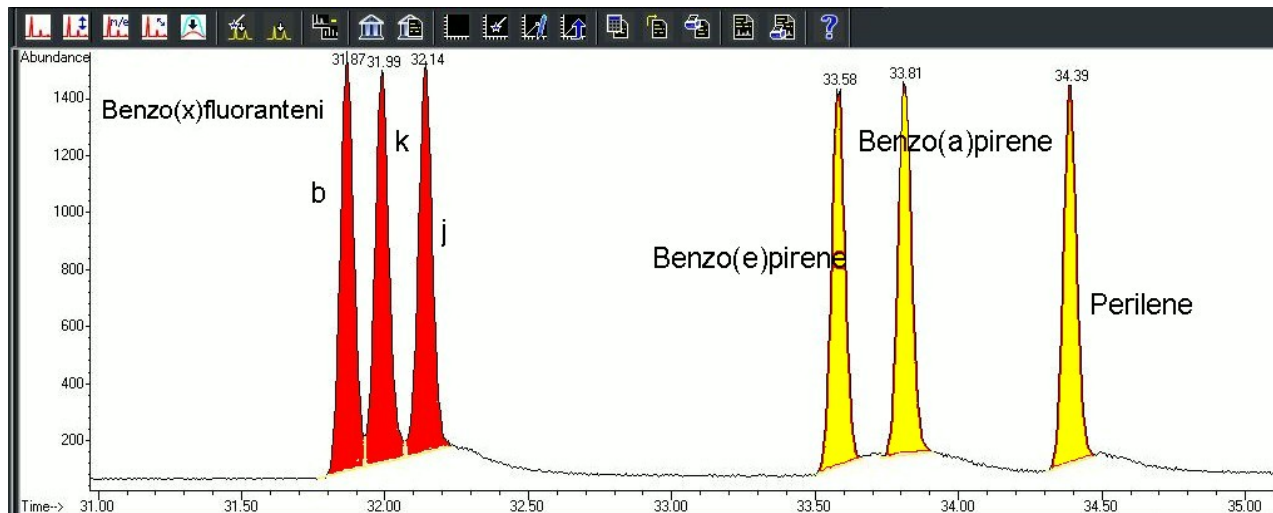
Dibenzo[a,e]pirene	
µg/L	
Valore	Incertezza
LAB	
<2	
<2	
<2	
2	

Valori nulli

NO

Acenaftilene	
µg/L	
Valore	Incertezza
LAB	
0	44%
0	44%
0	44%
100	

Criteri di accettazione dei dati [2]



- Separazione b, k, j [11 laboratori]
- b+j e k+j [k e b separati]
- Quantificazione solo di alcuni isomeri
- Stesso valore per i tre isomeri
- Nessuna separazione

Valutazione statistica

- Analisi preliminare [errori grossolani]
- Test di normalità [Shapiro-Wilk]
- Disaggregazione:
 - Metodo di estrazione [APAT RM014];
 - Tecnica strumentale [APAT RM014, APAT RM017 e Soluzione]



Valutazione dei risultati

- z-score [ISO 13258: 2005 E]

$$|z| = \frac{X_{LAB} - X_{RIF}}{\hat{\sigma}}$$

$\hat{\sigma}$ = scarto tipo del circuito [dati dei laboratori partecipanti]

z-score ≤ 2	Accettabile
z-score ≤ 3	Discutibile
z-score > 3	Non accettabile

Conferma omogeneità

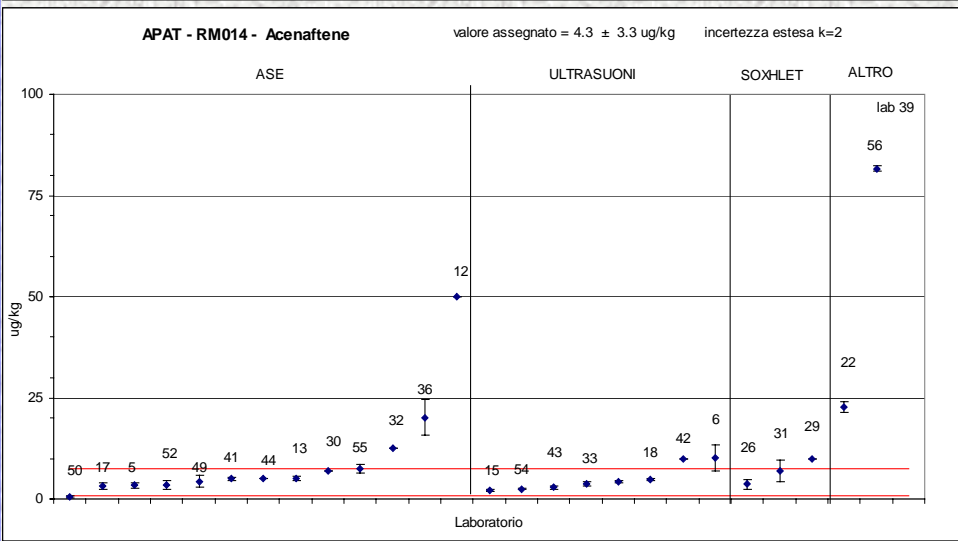
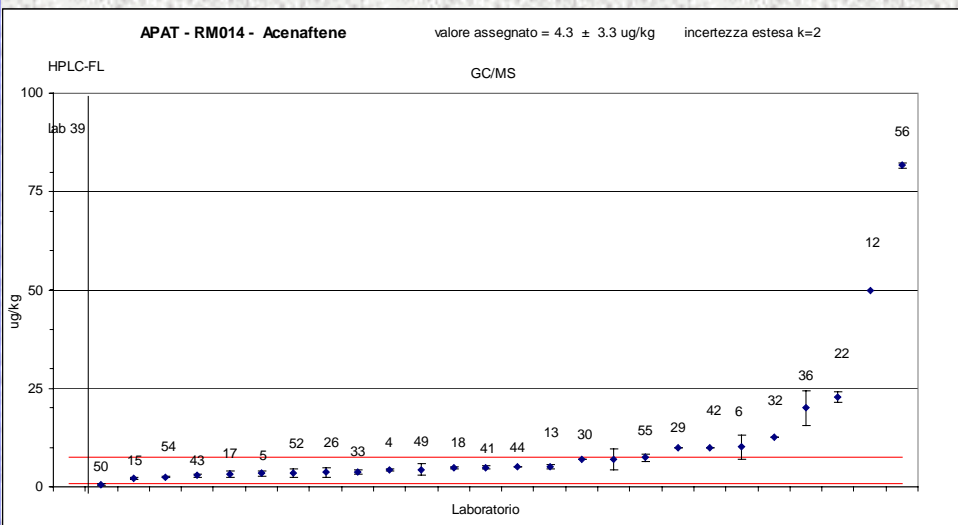
Criterio ISO 13528:2005 – Annex E

$$u_{bb}/\hat{\sigma} < 0.3$$

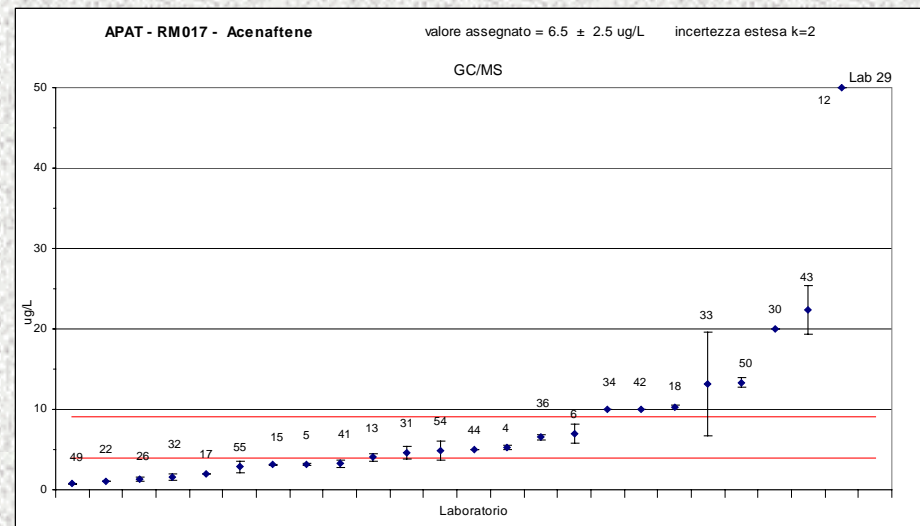
APAT RM014	$u_{bb}/\hat{\sigma}$	APAT RM017	$u_{bb}/\hat{\sigma}$
Fenantrene	0,09	Fenantrene	0,05
Antracene	0,10	Fluorantene	0,03
Fluorantene	0,10	Pirene	0,04
Pirene	0,09	Benzo[a]antracene	0,04
Benzo[a]antracene	0,10		
Crisene	0,04		



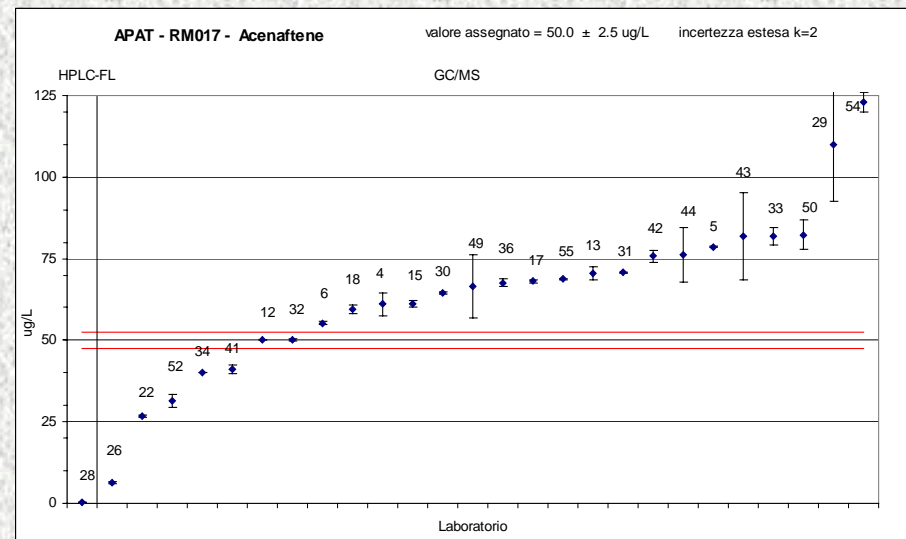
APAT RM014



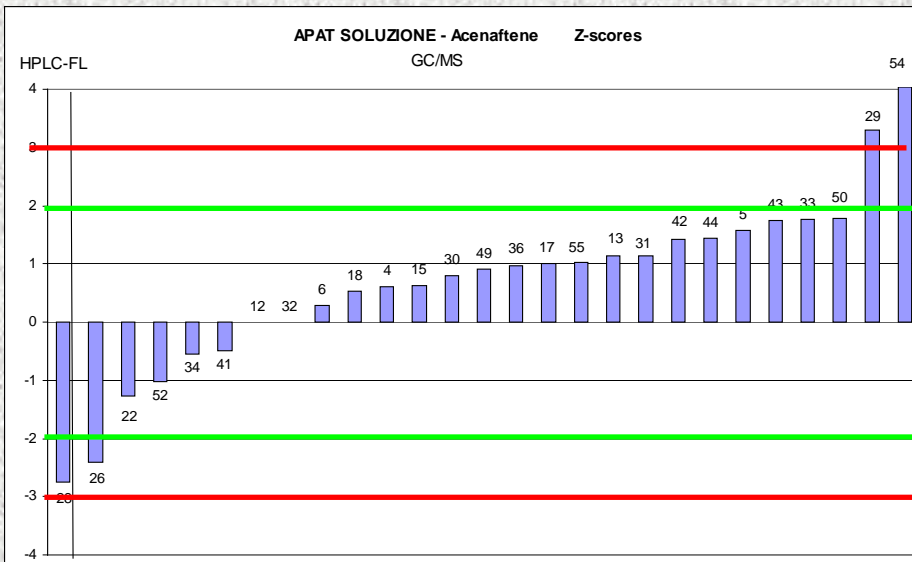
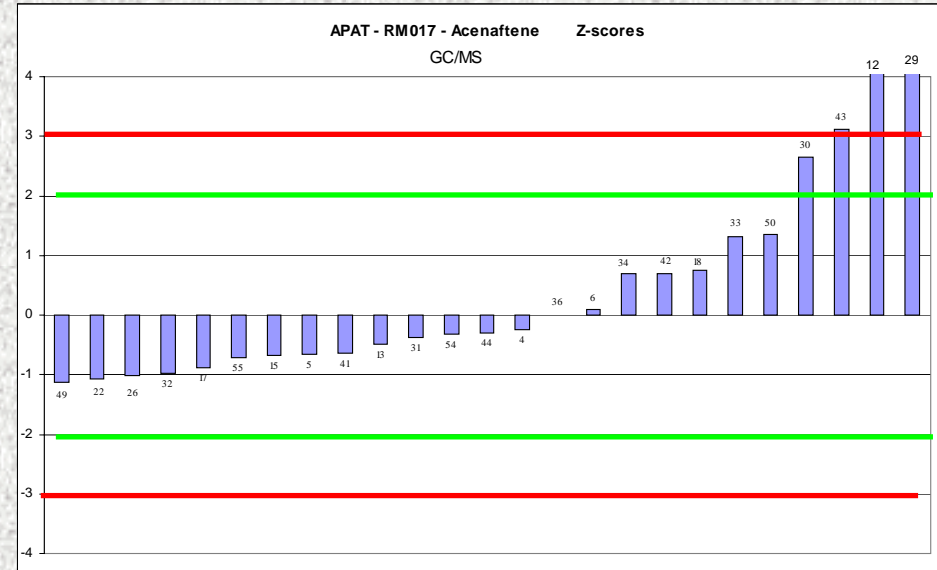
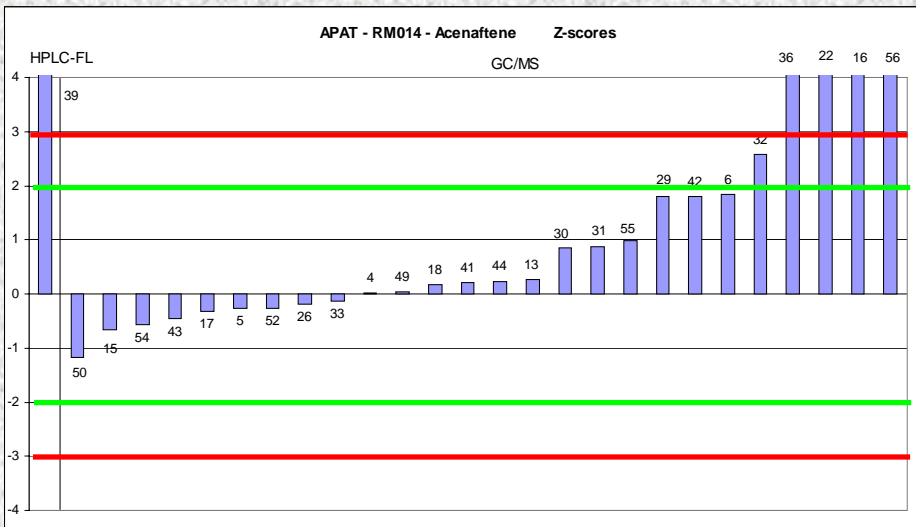
APAT RM017



Soluzione



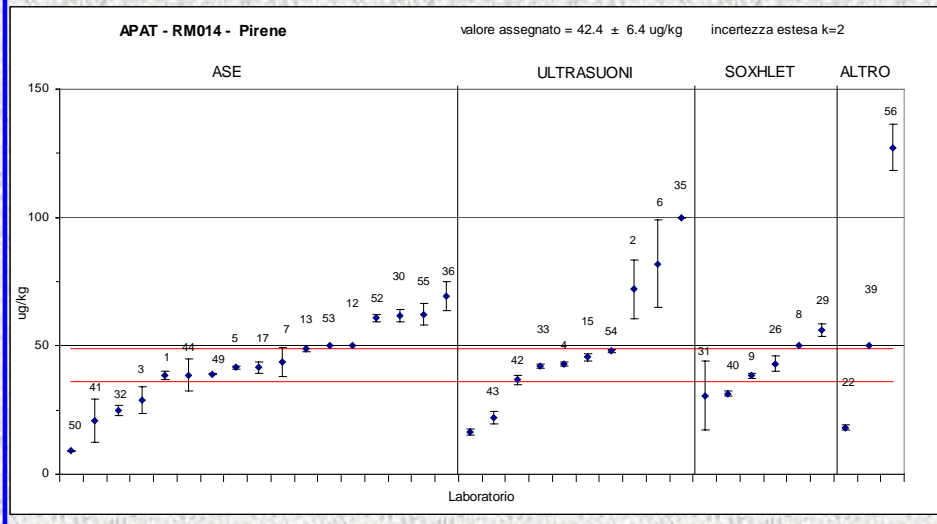
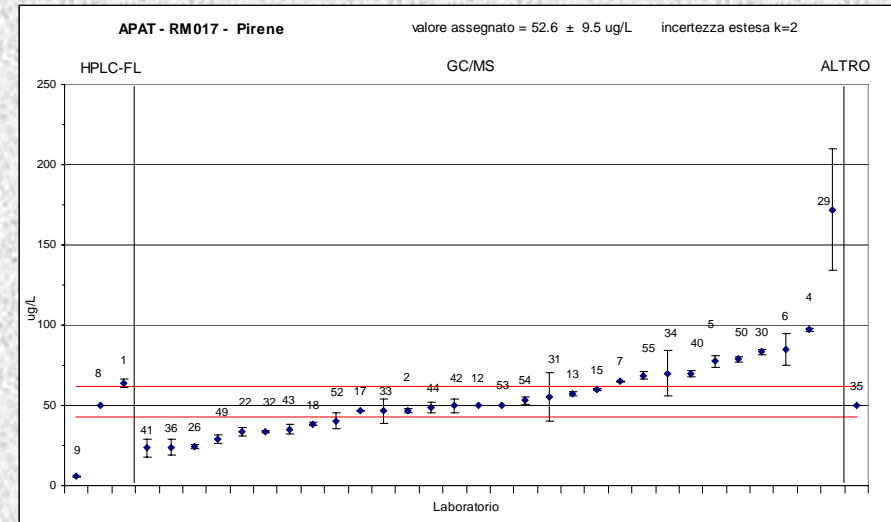
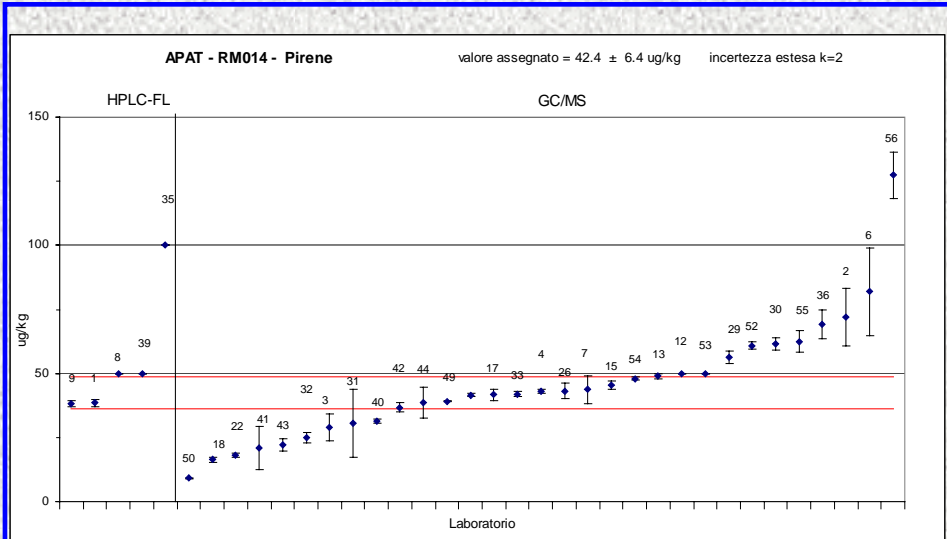
Acenaftene



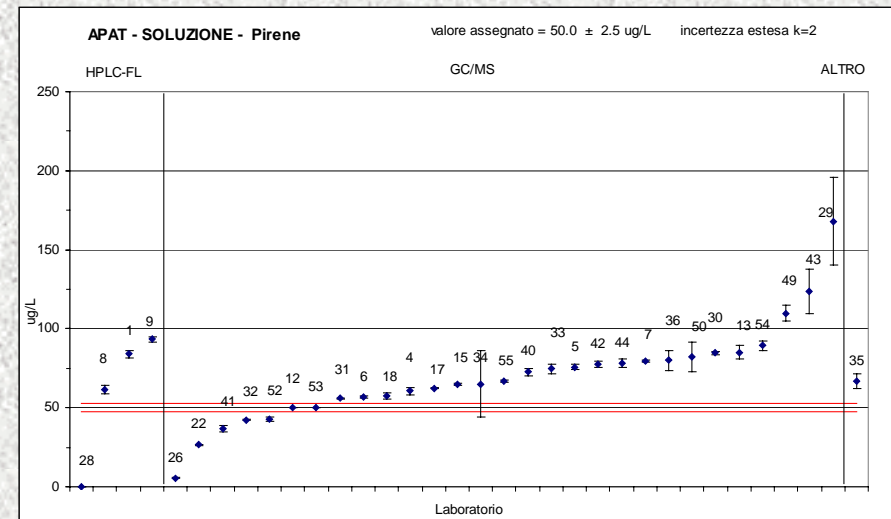
APAT RM014

Pirene

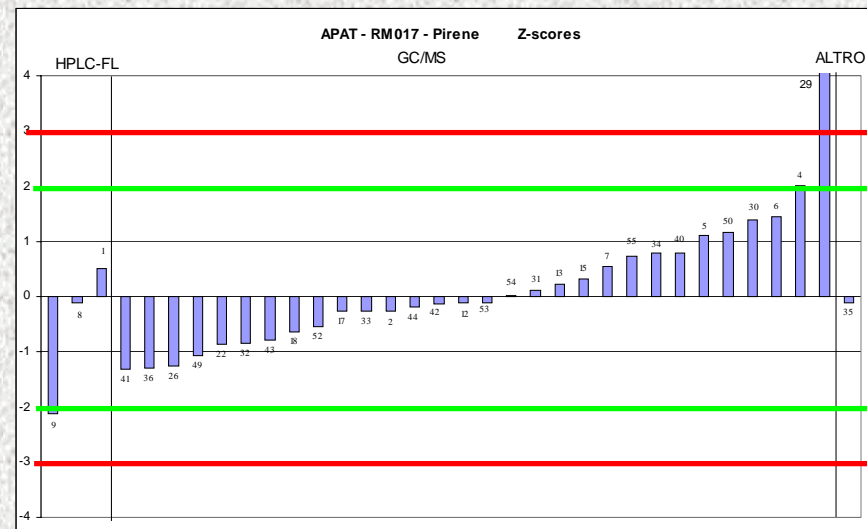
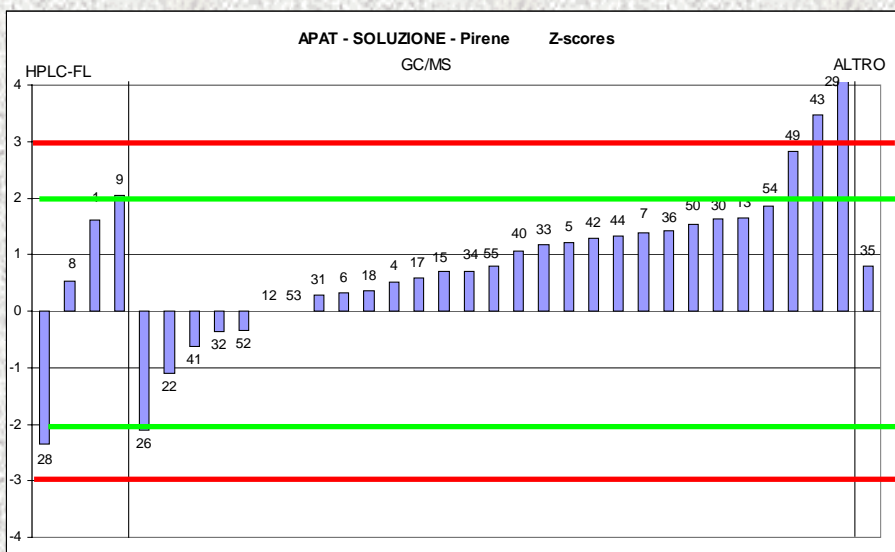
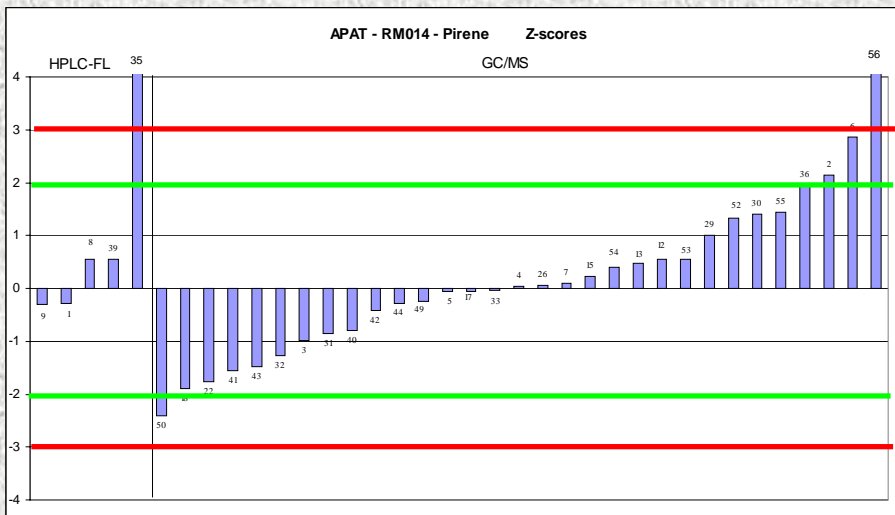
APAT RM017



Soluzione



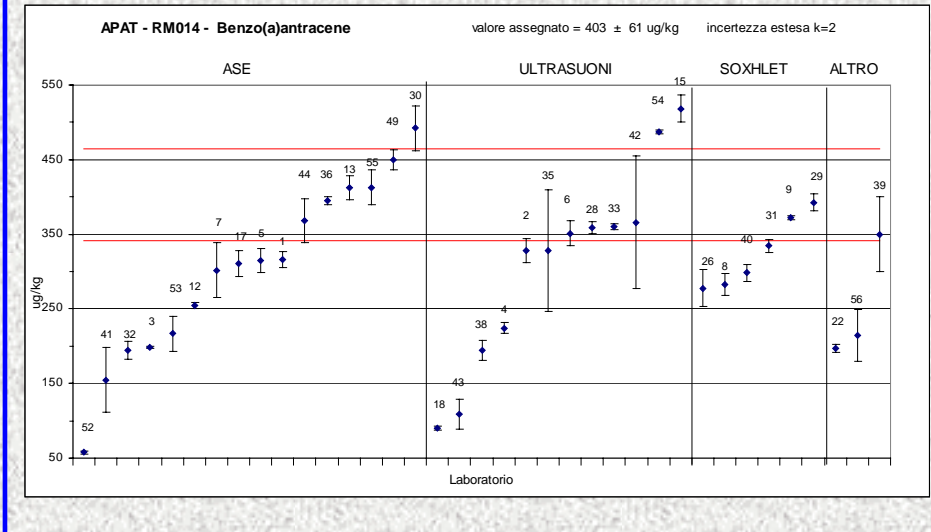
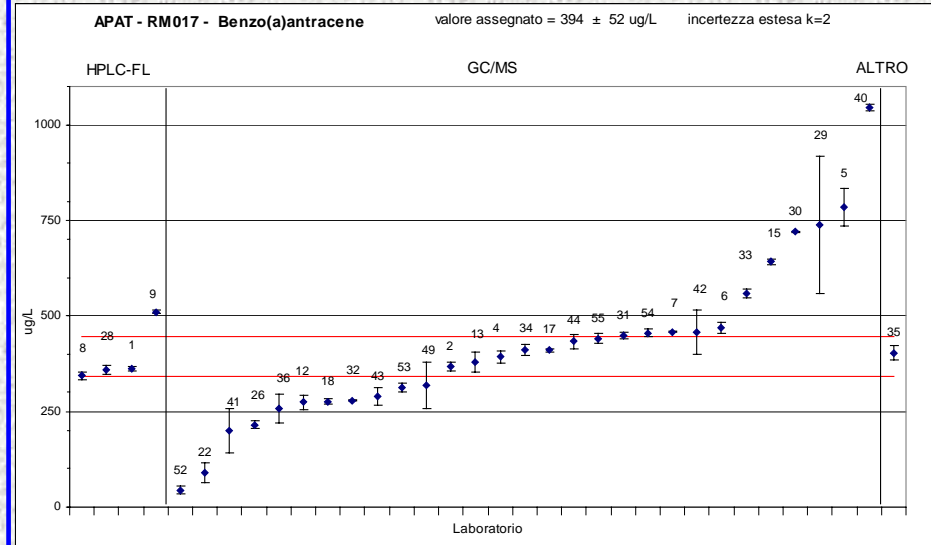
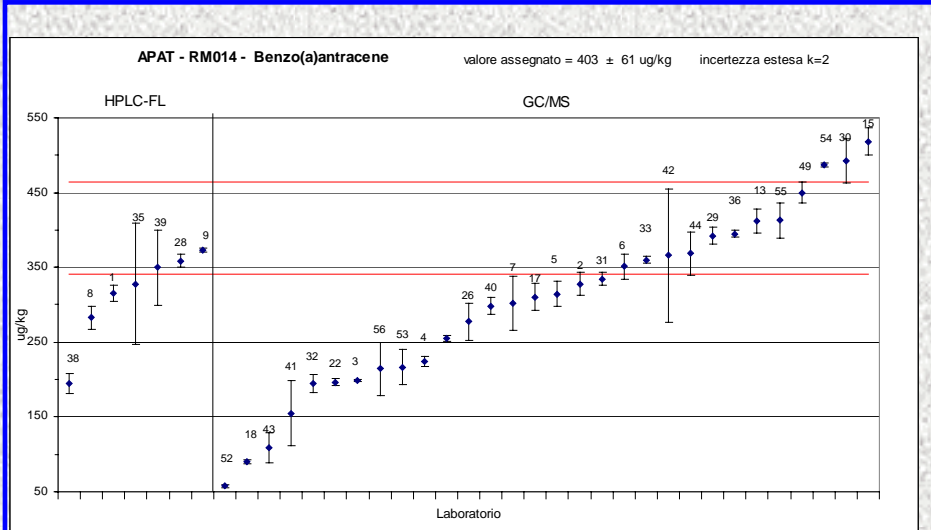
Pirene



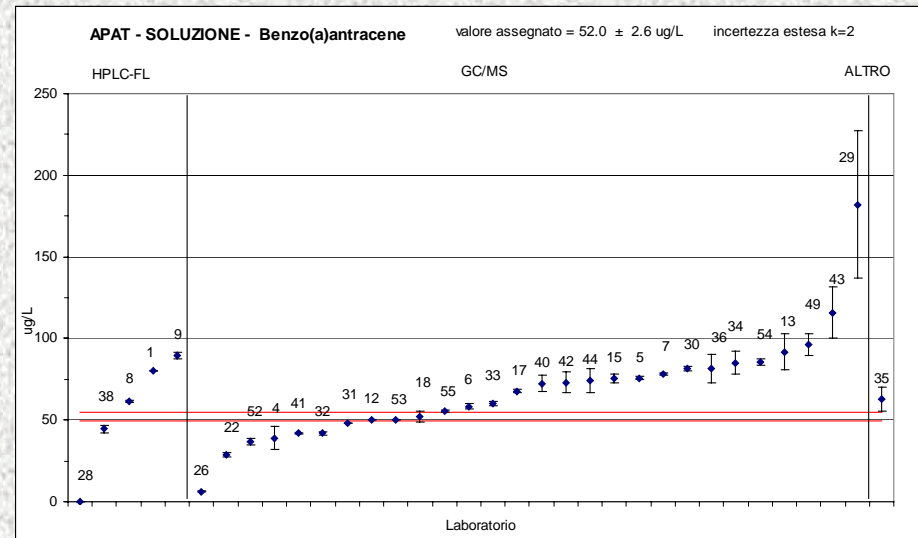
APAT RM014

Benzo[a]antracene

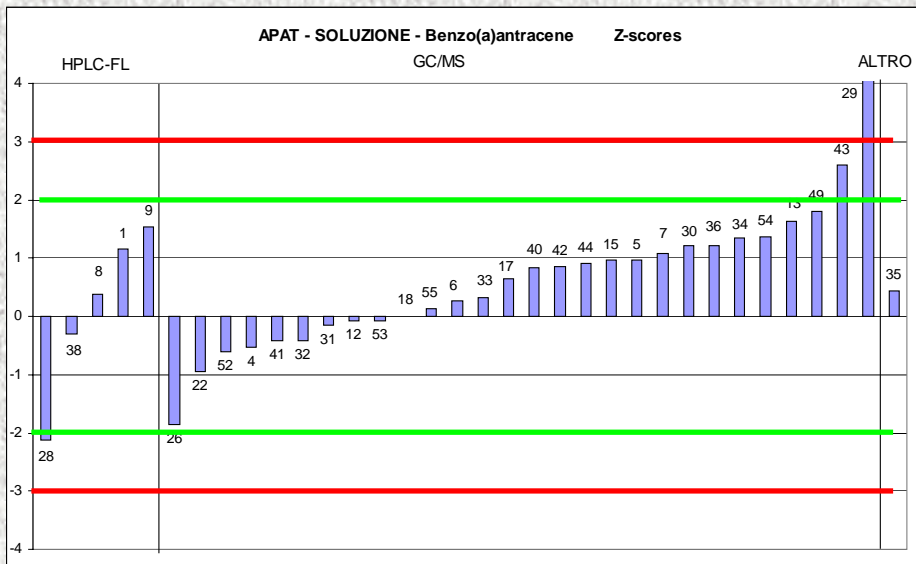
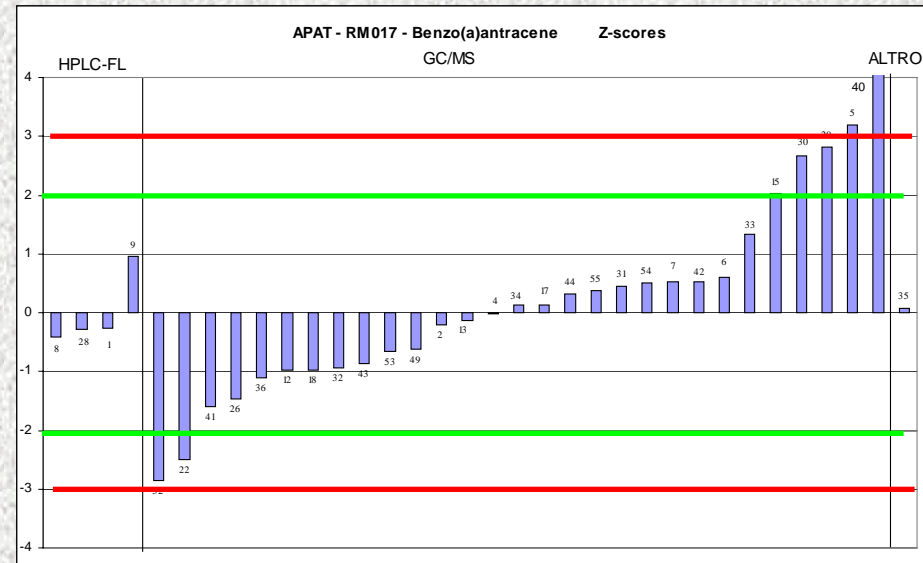
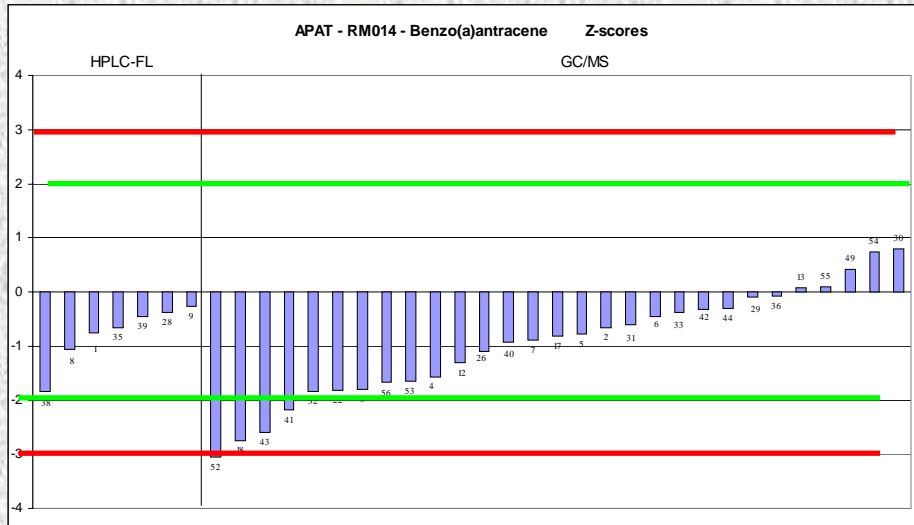
APAT RM017



Soluzione

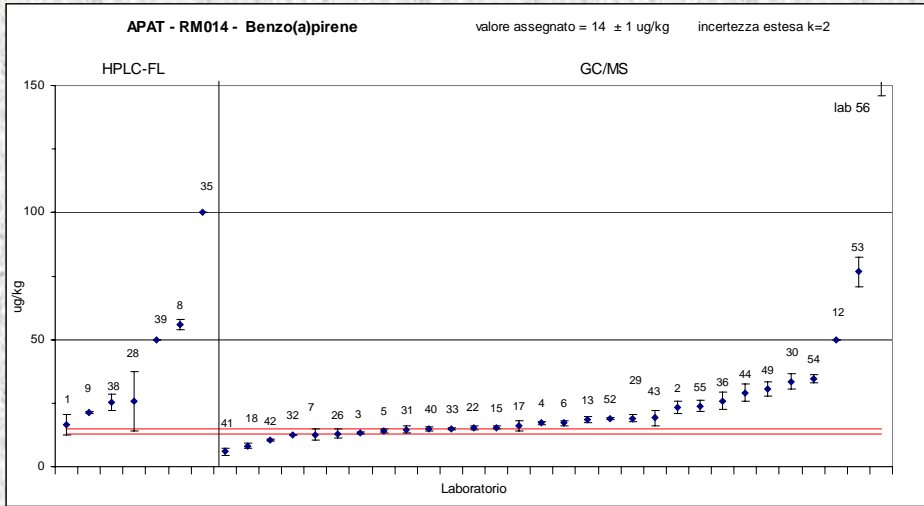


Benzo[a]antracene

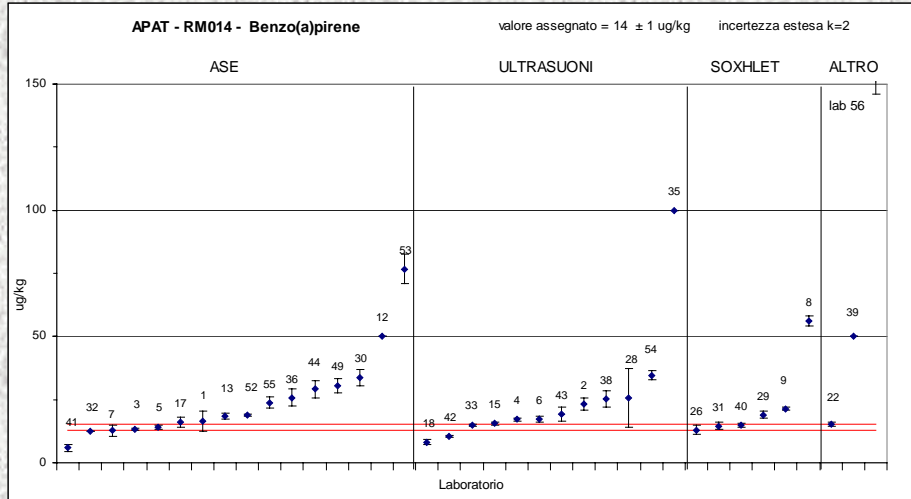
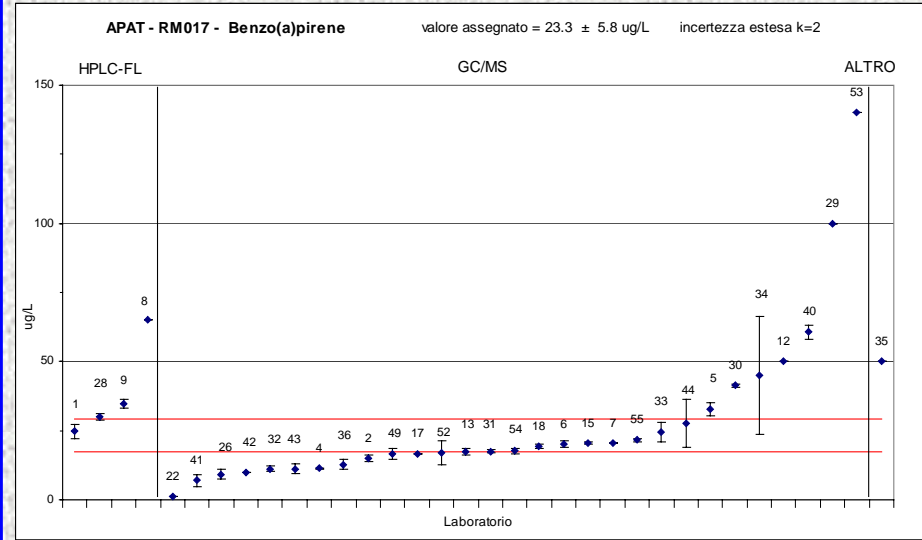


Benzo[a]pirene

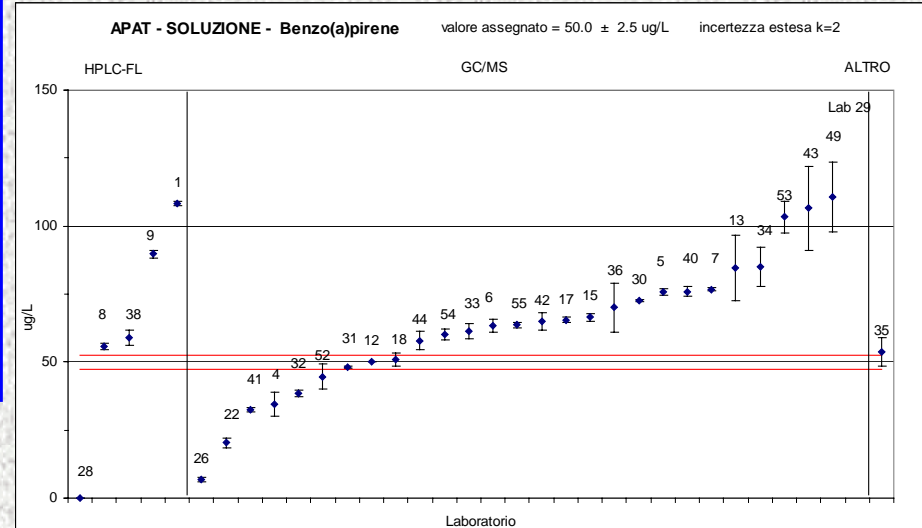
APAT RM014



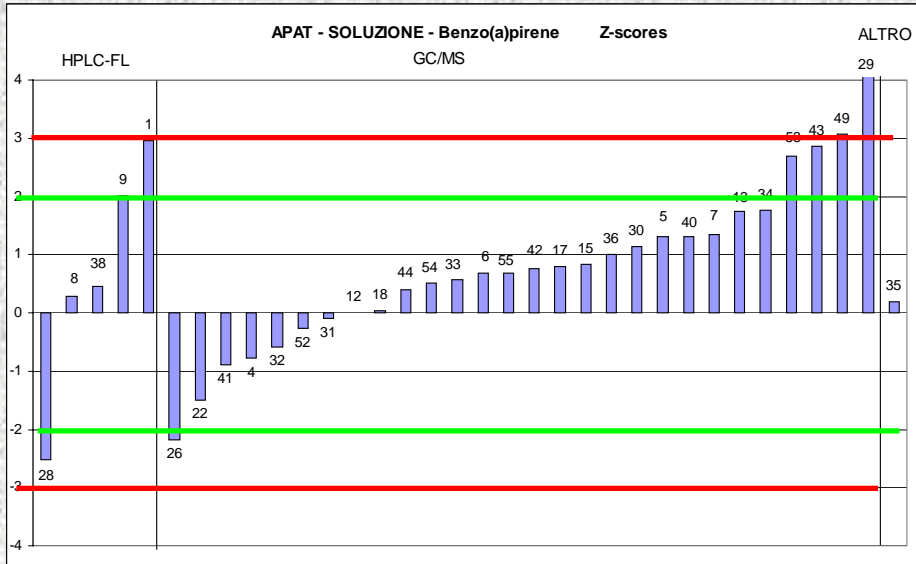
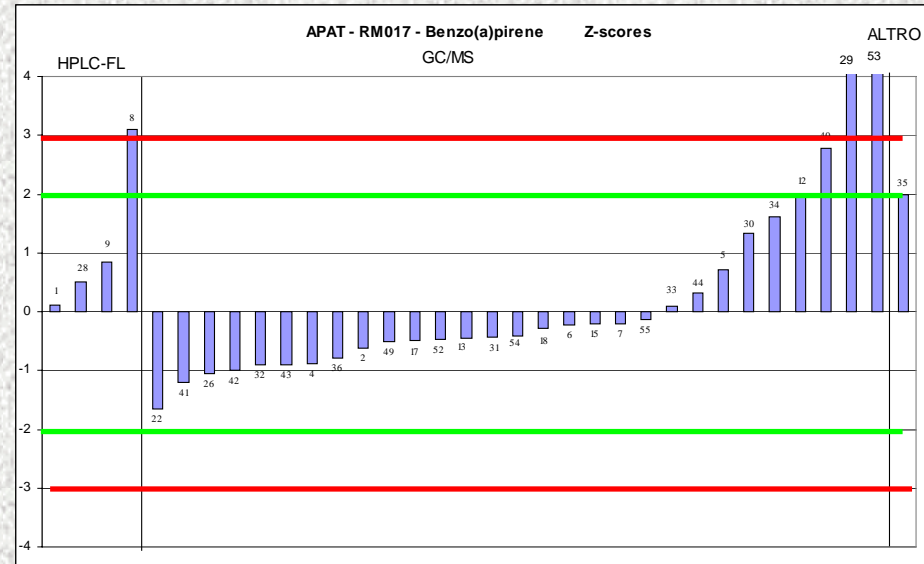
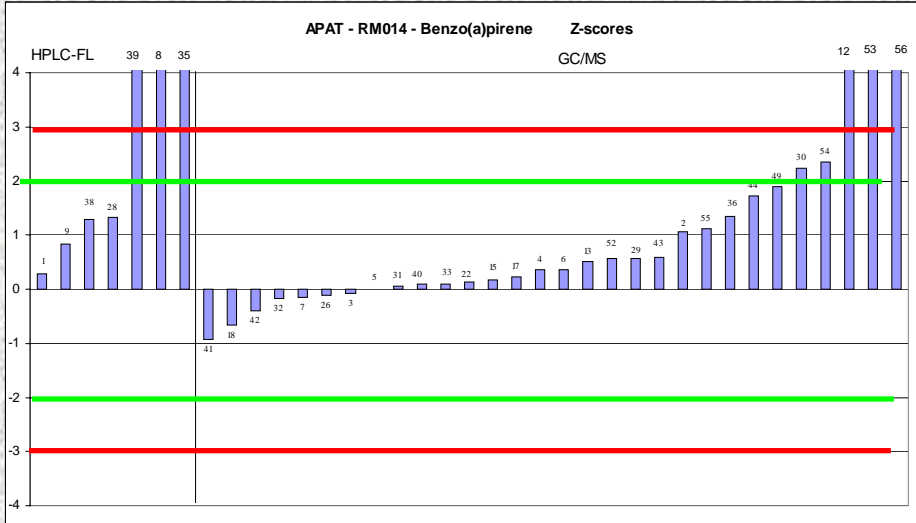
APAT RM017



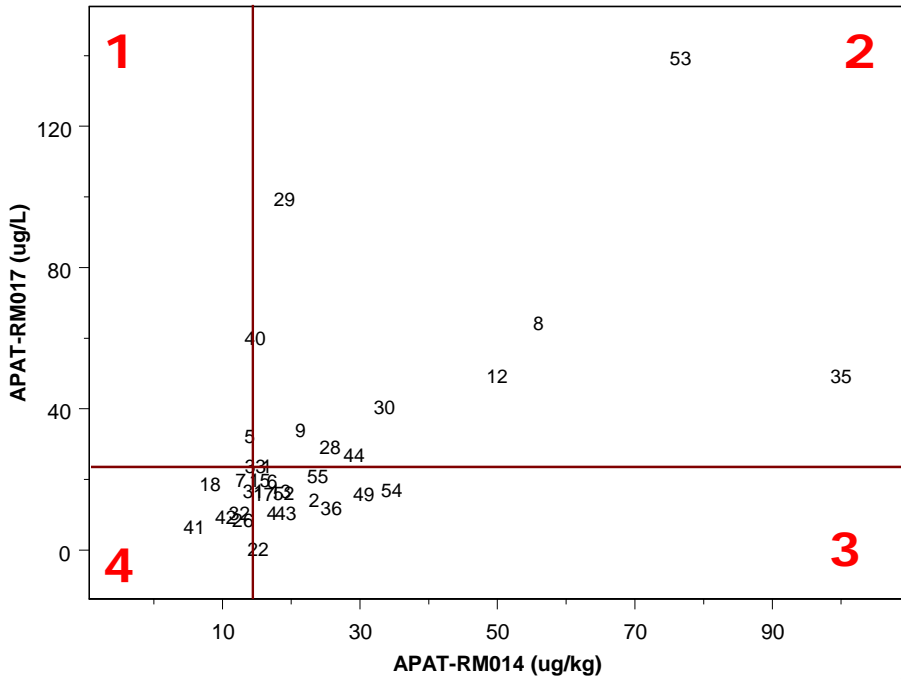
Soluzione



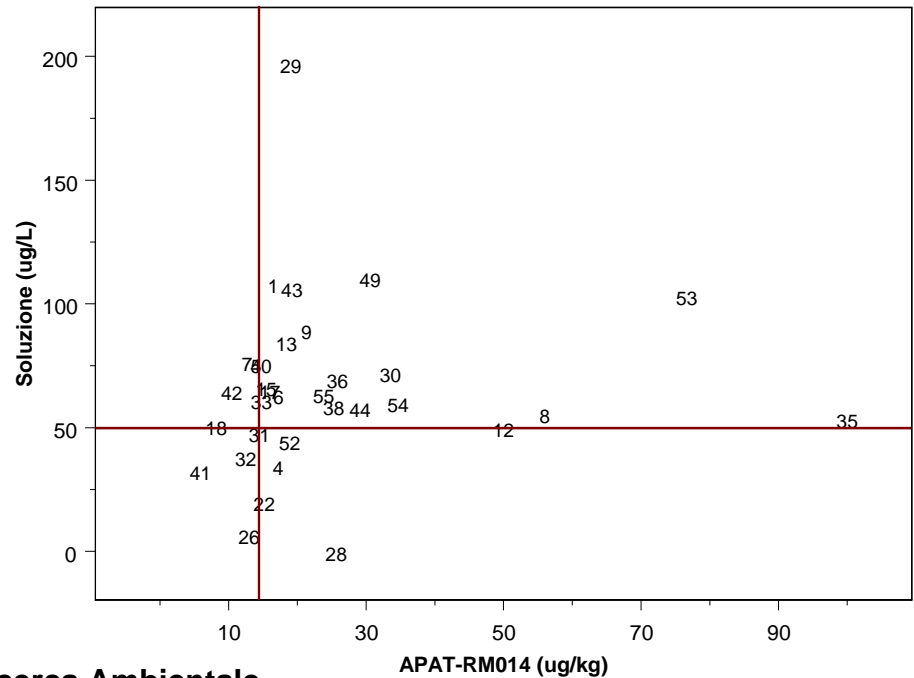
Benzo[a]pirene



Benzo(a)pirene



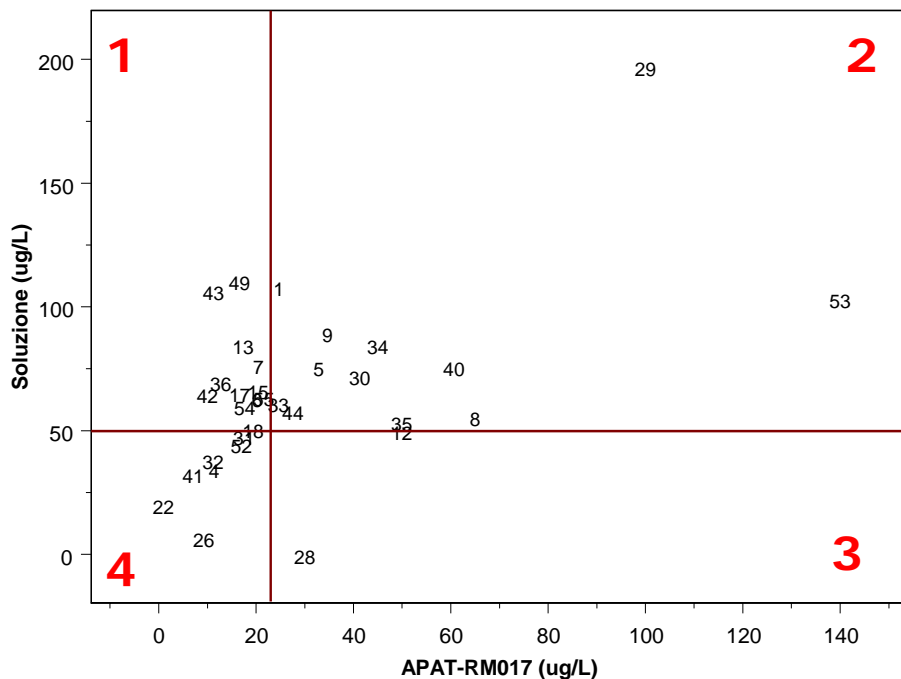
Benzo(a)pirene



Youden plot



Benzo(a)pirene

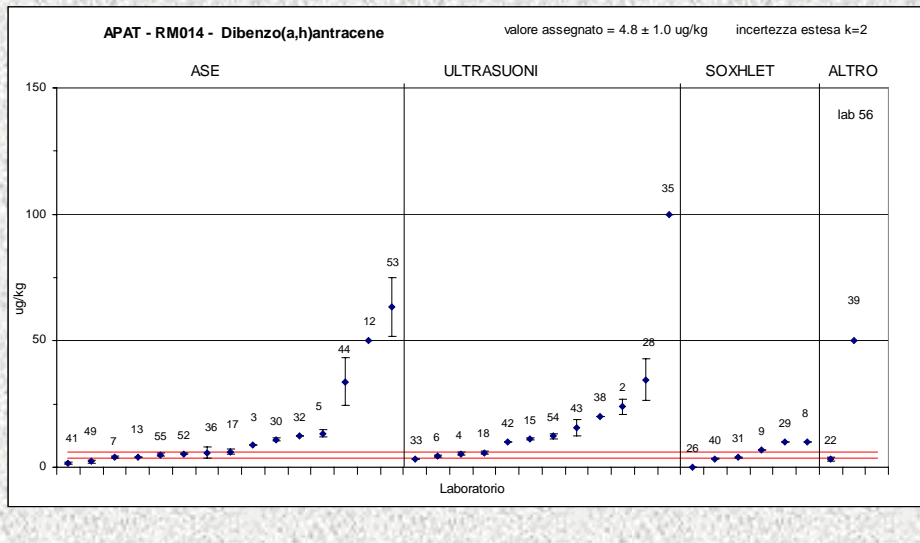
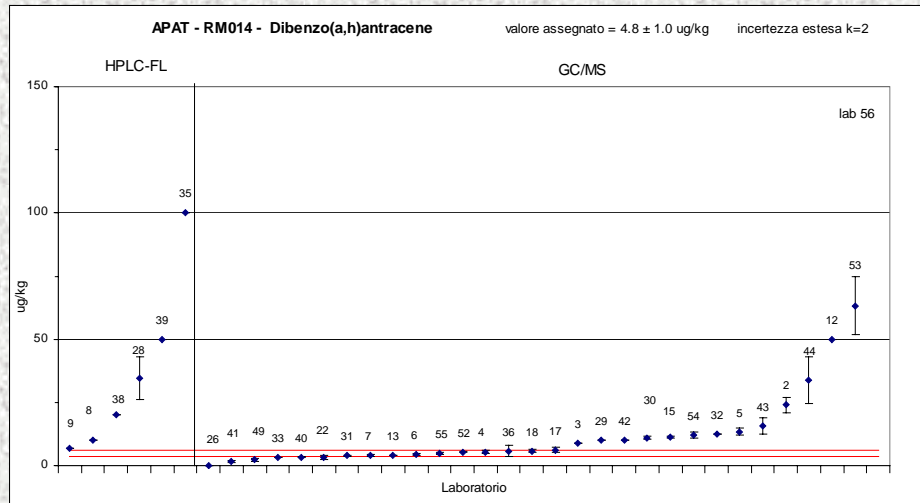


- Dal confronto il laboratorio può apprezzare discrepanze tra le misure eseguite su diversi materiali
- Individuare potenziali problemi nelle diverse fasi analitiche

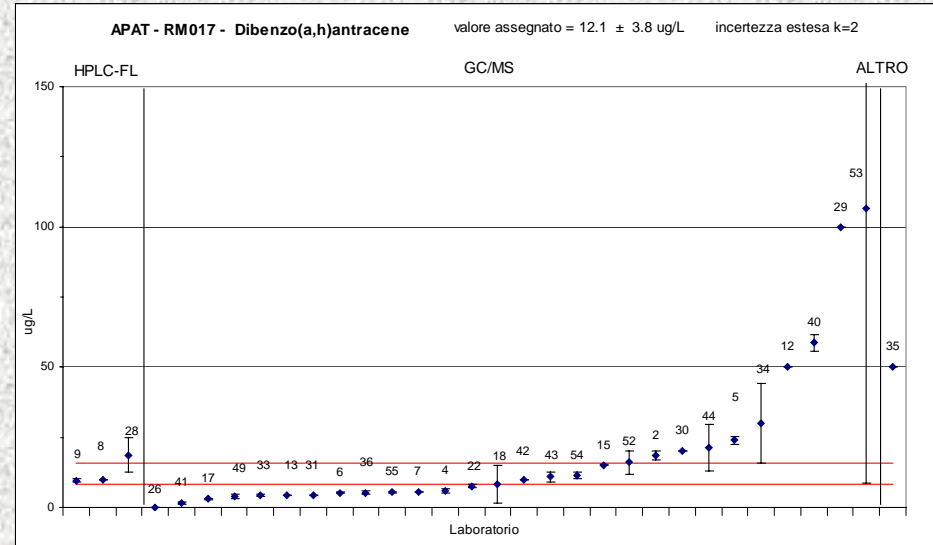
Youden plot

Dibenzo[a,h]antracene

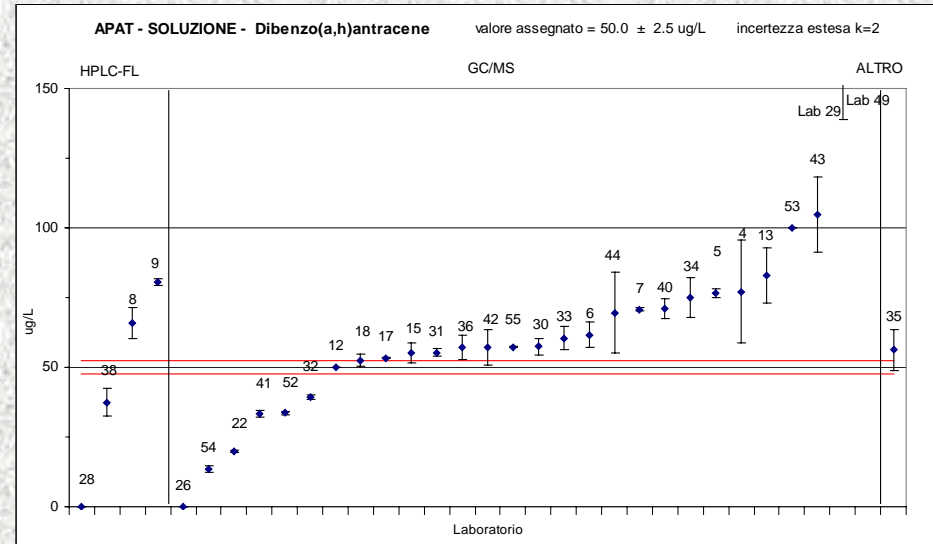
APAT RM014



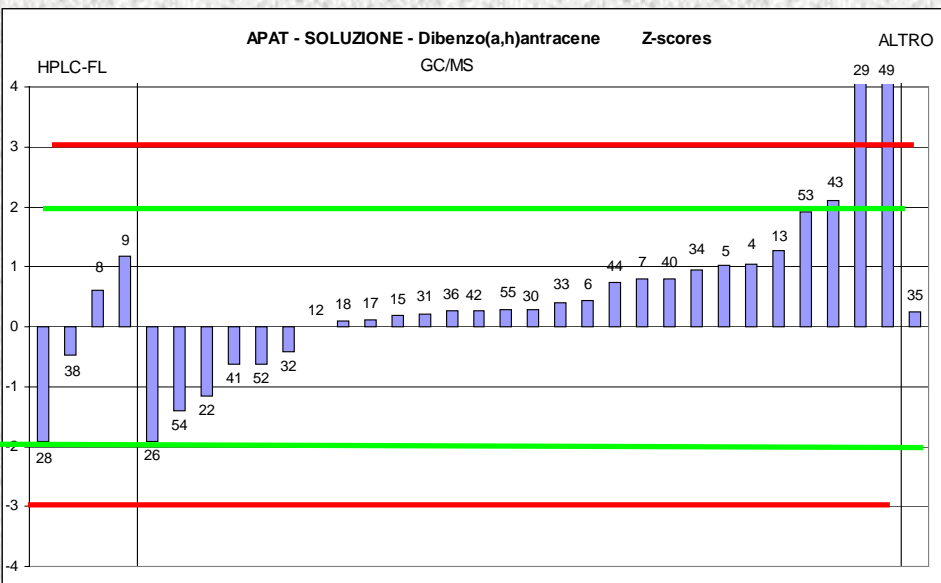
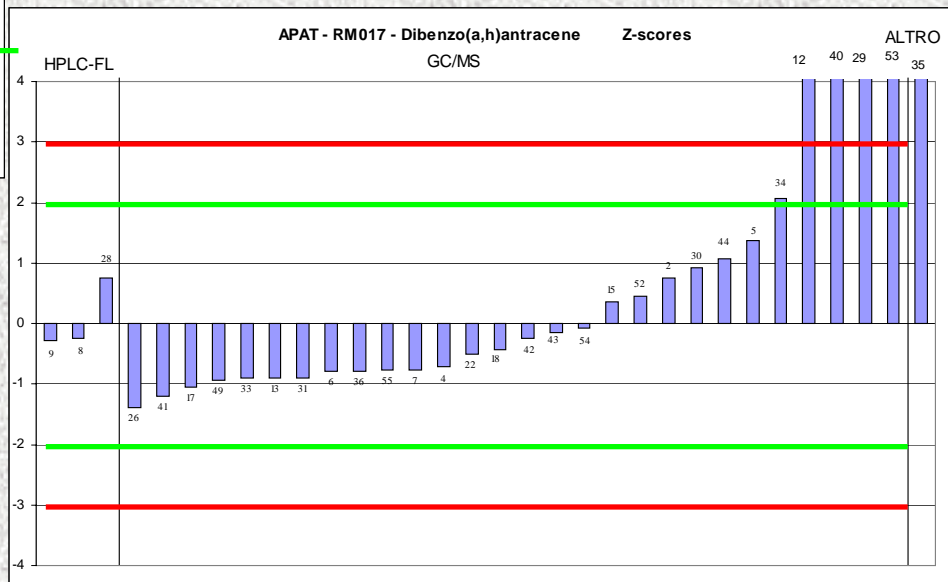
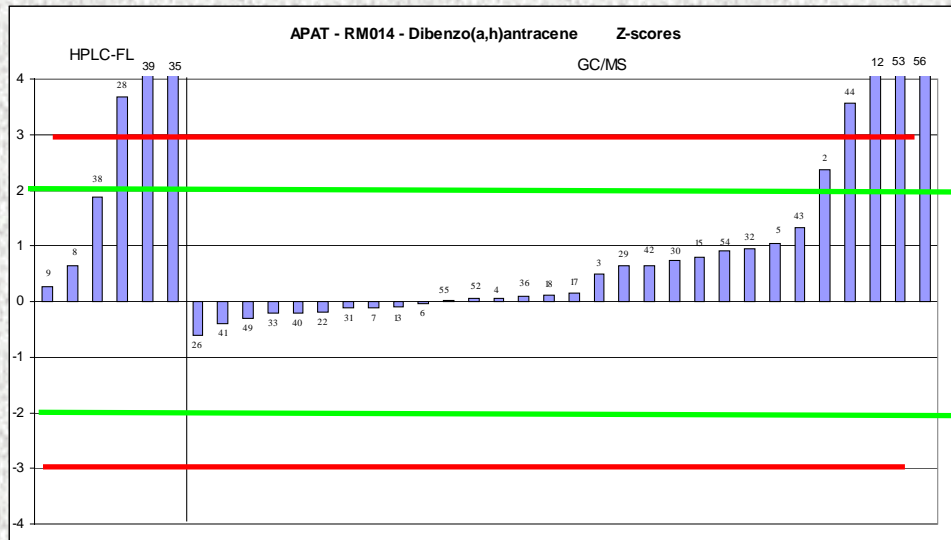
APAT RM017



Soluzione



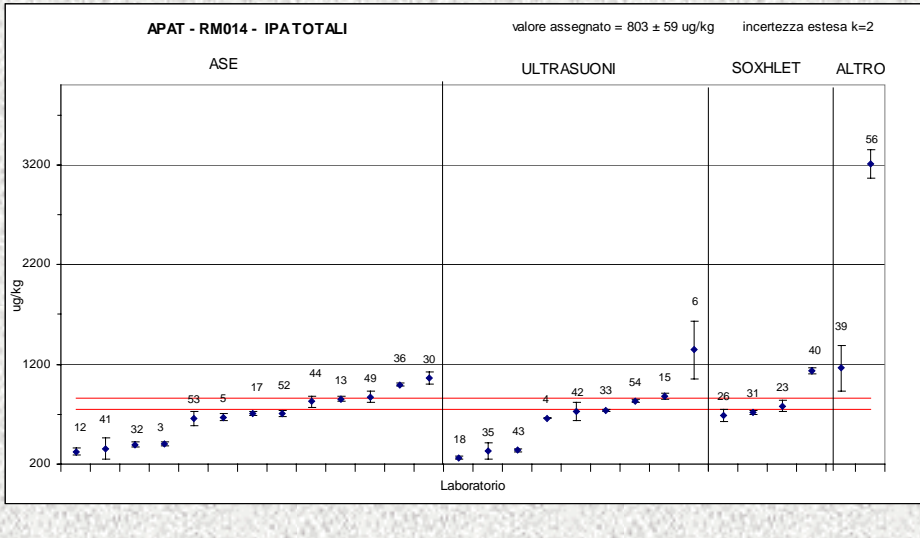
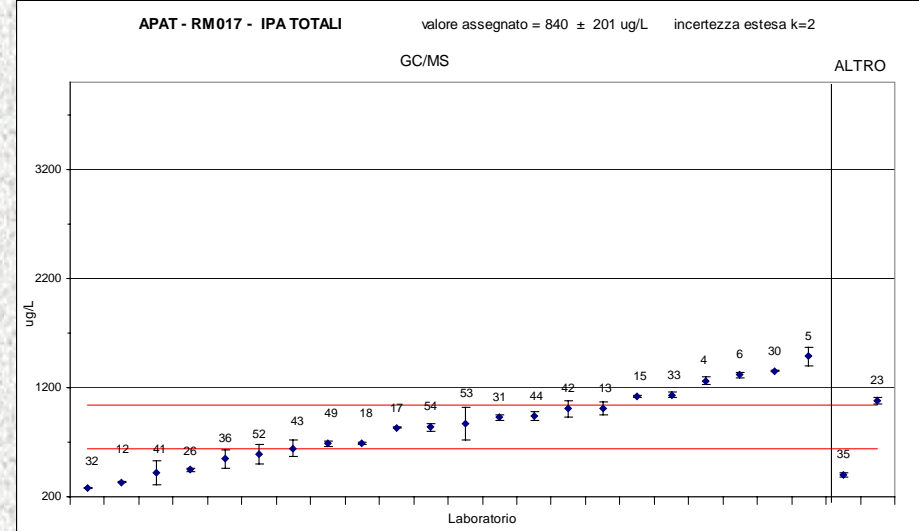
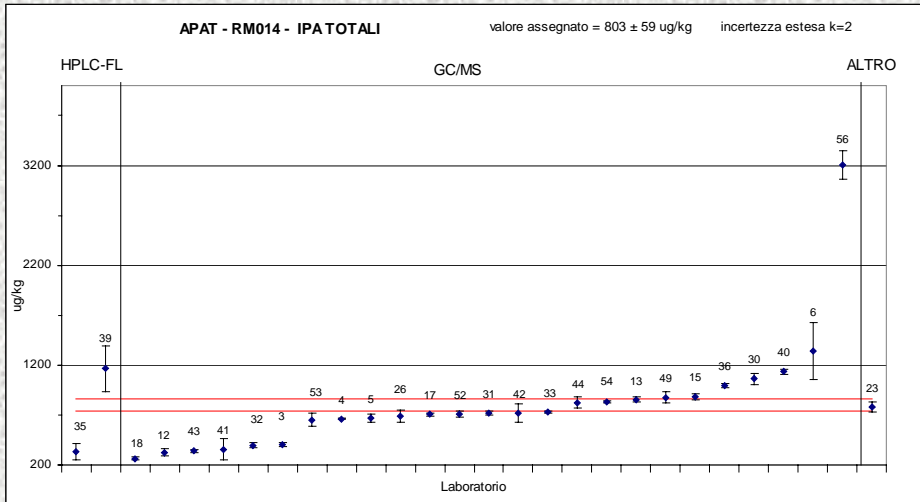
Dibenzo[a,h]antracene



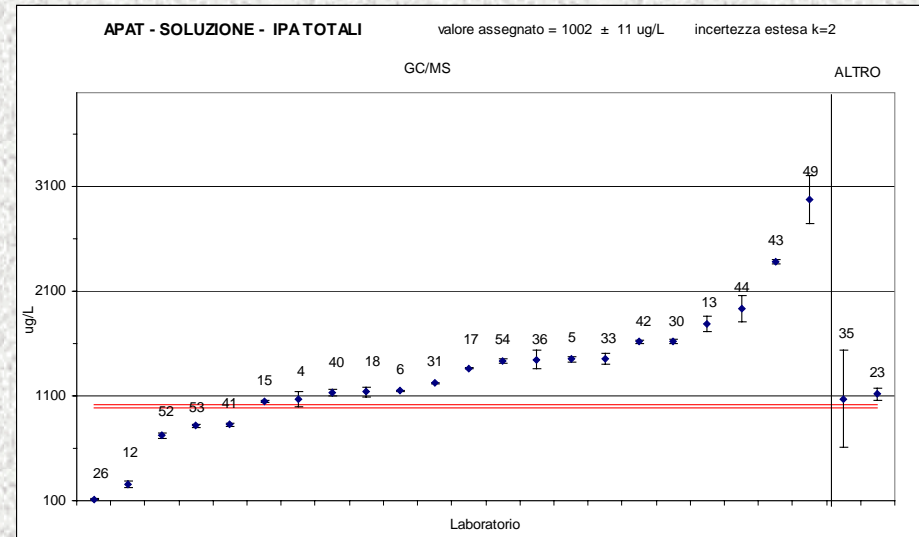
APAT RM014

Somma IPA

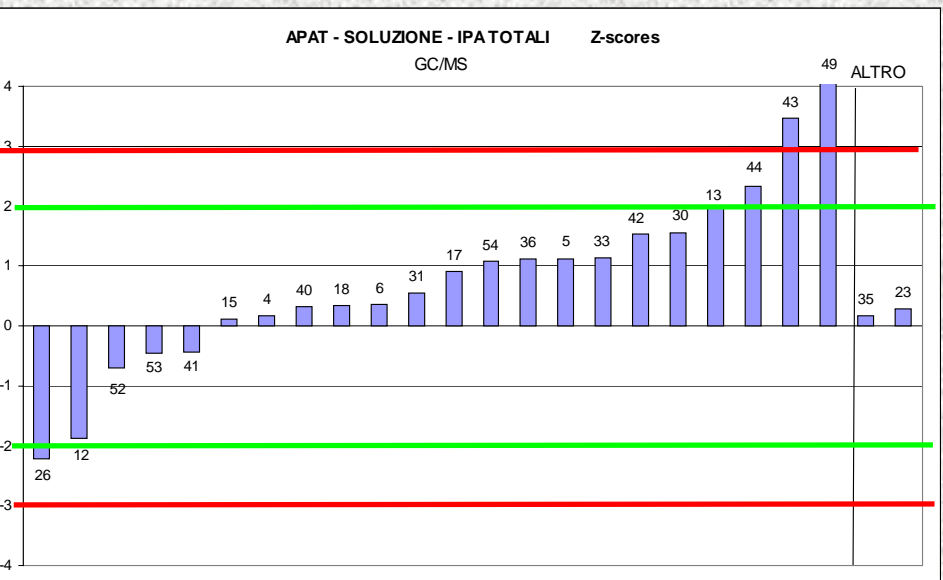
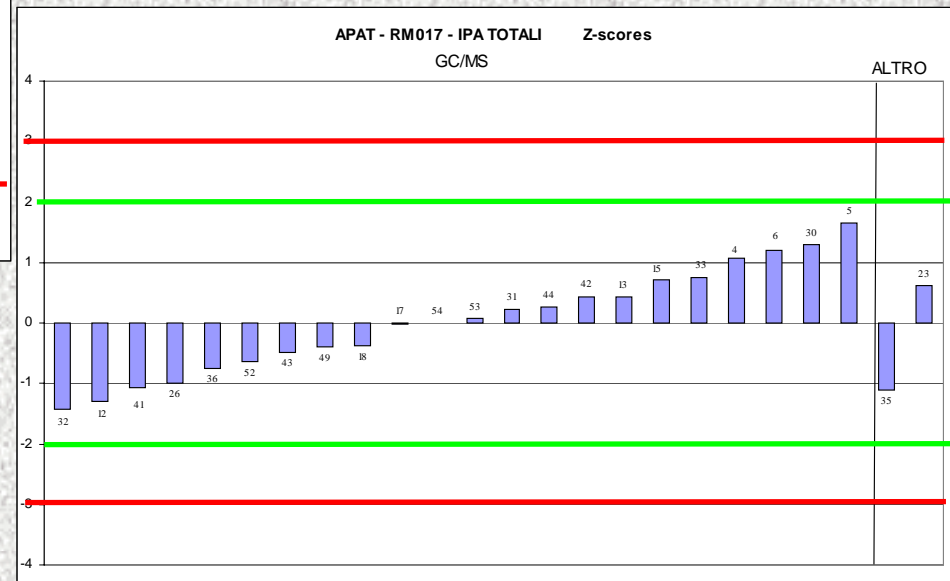
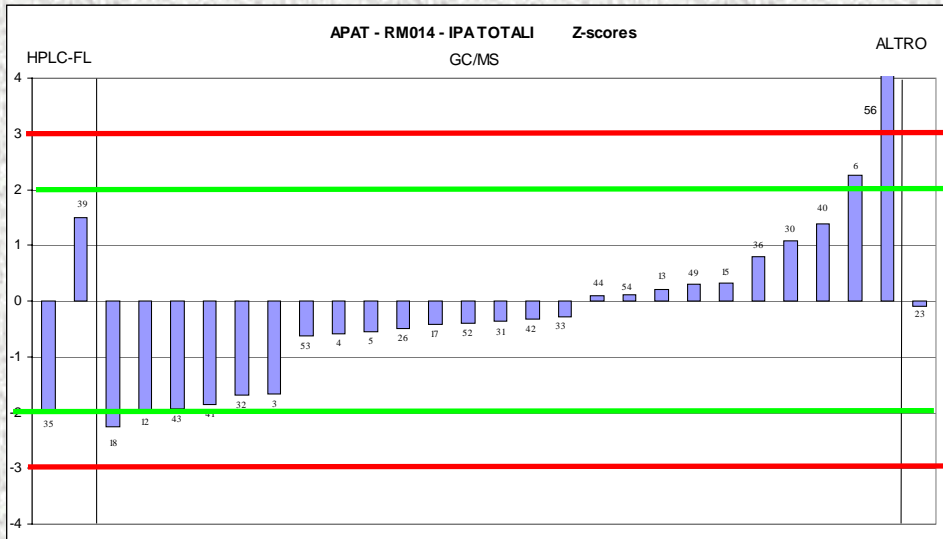
APAT RM017



Soluzione



Somma IPA



APAT RM014 - Consenso: partecipanti vs. caratterizzazione

PARAMETRO	Algoritmo A A15 – sMAD lab APAT-IC011		Algoritmo A A15 – sMAD lab caratterizzazione	
	$\mu\text{g kg}^{-1} \text{ s.s}$		$\mu\text{g kg}^{-1} \text{ s.s}$	
Dibenzo[a,e]pyrene	4,38	2,08	3,46	0,05
Dibenzo[a,h]anthracene	10,49	8,10	4,85	0,52
Benzo[ghi]perylene	15,36	8,21	12,77	1,37
Indeno[1,2,3-cd]pyrene	15,05	4,71	14,08	1,64
Perylene	9,83	2,77	12,61	1,69
Benzo[a]pyrene	20,78	8,77	13,98	0,54
Benzo[e]pyrene	22,90	8,36	21,69	2,90
Benzo[j]fluoranthene	30,03	10,01	36,80	3,74
Benzo[k]fluoranthene	32,99	18,99	21,86	1,78
Benzo[b]fluoranthene	34,96	18,53	24,97	2,37
Crysene	41,79	19,94	41,70	4,02
Benzo[a]anthracene	307,44	113,34	402,61	28,76
Pyrene	43,77	13,78	42,41	2,83
Fluoranthene	54,50	16,96	56,22	6,20
Anthracene	42,58	20,44	53,33	8,90
Phenantrene	35,85	22,59	30,78	1,86
Fluorene	8,02	4,09	3,96	0,71
Acenaphtene	6,06	3,19	4,27	1,67
Acenaphtylene	7,81	4,69	1,40	0,23

Considerazioni [1]

- Criticità nella definizione del valore assegnato in APAT RM014 (Acenaftene, Acenaftilene, IPA totali)
- Utilizzo in taluni casi del valore di consenso dei partecipanti anziché del valore assegnato in caratterizzazione (es. leggeri in APAT RM014)
- Difficoltà nella separazione di Benzo[b,k,j]fluorantene (valore assegnato anche per la somma)
- Valori z-score accettabili per tutti i materiali (≤ 2 80-90 %)
- Non evidenti graficamente effetti associati alle diverse tecniche estrattive
- Dispersioni significative dei risultati per tutti i materiali

GRAZIE
DELL'ATTENZIONE
E DELLA
PARTECIPAZIONE AL
CIRCUITO

