



Metodi di laboratorio

| inquinante | metodo | Tecnica analitica |
|-------------------|---|-----------------------------------|
| PM ₁₀ | UNI EN12341:2014 | Gravimetrica |
| PM _{2.5} | UNI EN12341:2014 | Gravimetrica |
| Benzene | EN14662:2005 (1,2,4,5) UNI EN 14662:3-2015 | GC-FID |
| As, Cd, Ni, Pb | UNI EN14902:2005 | ICP-MS or FAAS |
| B(a)P | ISO 16362:2005* UNI EN 15549:2008 | GC-MS or HPLC fluorescenza |
| EC/OC | UNI EN 16909:2017 | Trasmittanza termo ottica |
| IONI in PM | UNI EN 16913: 2017 | Cromatografia ionica |

A Member State may also use any other methods which it can demonstrate give results equivalent to the above method.



Recovery efficiency

The recovery refers to whether or not the methodology measures all of the analyte that is contained in the sample. This is best evaluated by the measurements of reference materials or other samples of known composition. In this absence, spikes or surrogate may be added to the sampled matrix. The recovery is often stated as the percentage measured with respect to what was added.

Recovery in air samples

| pollutant | Range of average recovery rates % | method |
|------------------|--|-----------------|
| Pb | 90 to 110 | EN 14902:2005 |
| Cd | 90 to 110 | EN 14902:2005 |
| As | 85 to 115 | EN 14902:2005 |
| Ni | 85 to 115 | EN 14902:2005 |
| Ba P | 80 to 120 | EN 15549:2008 |
| Benzene | > 90% as desorption efficiency | EN 14662-2:2005 |

blanks

Field blanks are clean samplers taken to the sampling site, handled in every way as the air samples, except that no air is drawn through them. Media blanks are simply unopened, new samplers which are sent with the samples (these blanks are not usually taken to the field).

It is also recommended that additional blind field blanks be sent along with the field samples, labeled as field samples, as a further check on the analysis. Blanks are good insurance to deal with contamination, but the best approach is to avoid sample contamination by being careful.

EN 14662-2 Benzene

Field blanks should be prepared by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the samples except for the actual period of sampling. Label these as blanks.

EN 14902 methals

3.1.6

field filter blank

filter that is taken through the same procedure as a sample, except that no air is drawn through it. It is transported to the sampling site, mounted in the sampling unit, dismantled, returned to the laboratory and worked up in the same way as a sample



Method detection limit

Method detection limit (MDL) is lowest amount of analyte that is detectable using the method as , for example, determined by analysis of laboratory blanks.

Usually MDL shall be less than 10% of the limit value.

$$\text{MDL} = t_{n-1, 0.95} \times S_{lb}$$

$t_{n-1, 0.95}$ is the student factor for n measurements and 95% confidence interval

S_{lb} is the standard deviation of laboratory blanks

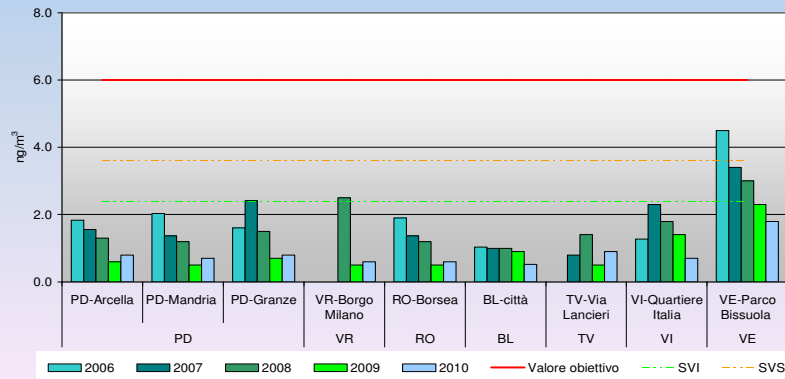
Too high MDLs can give a false overestimation of annual average.

In some analysis is too difficult to lower the analytical MDL, in these cases the sampling volume can be increased using high volume samplers.

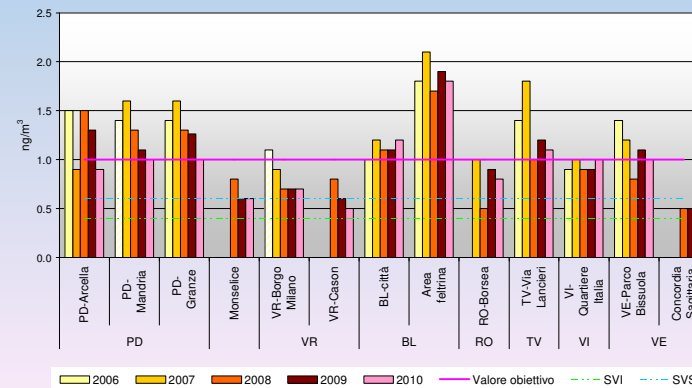
Cosa si determina nel particolato

| Inquinante | Nome limite | Valore |
|------------|---|--|
| Pb | Limite annuale per la protezione della salute umana | 0.5 $\mu\text{g}/\text{m}^3$ |
| BaP | Valore obiettivo | 1.0 ng/m^3 |
| Ni | Valore obiettivo | 20.0 ng/m^3 |
| As | Valore obiettivo | 6.0 ng/m^3 |
| Cd | Valore obiettivo | 5.0 ng/m^3 |

Confronto medie annuali Arsenico
Periodo 2006-2010



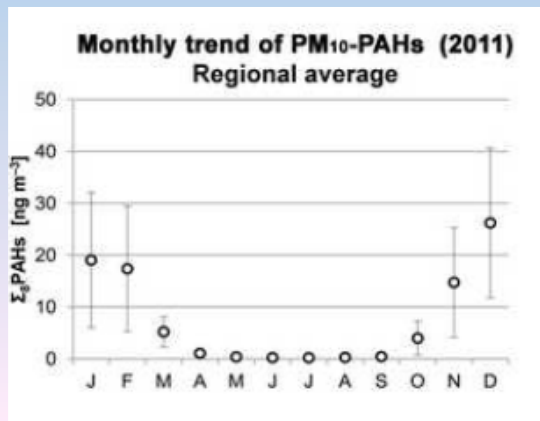
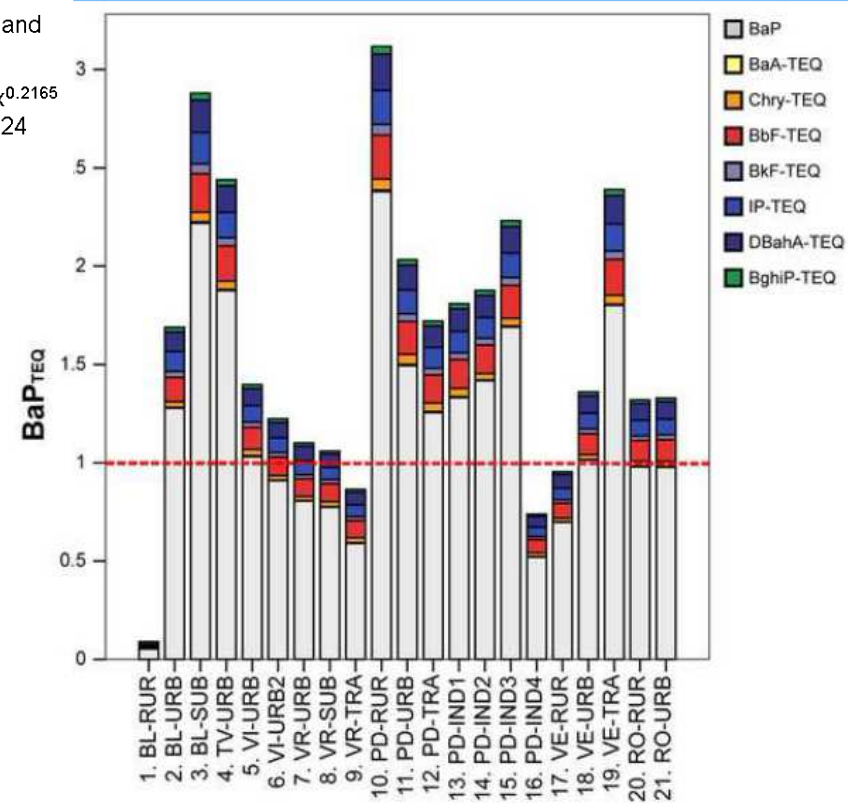
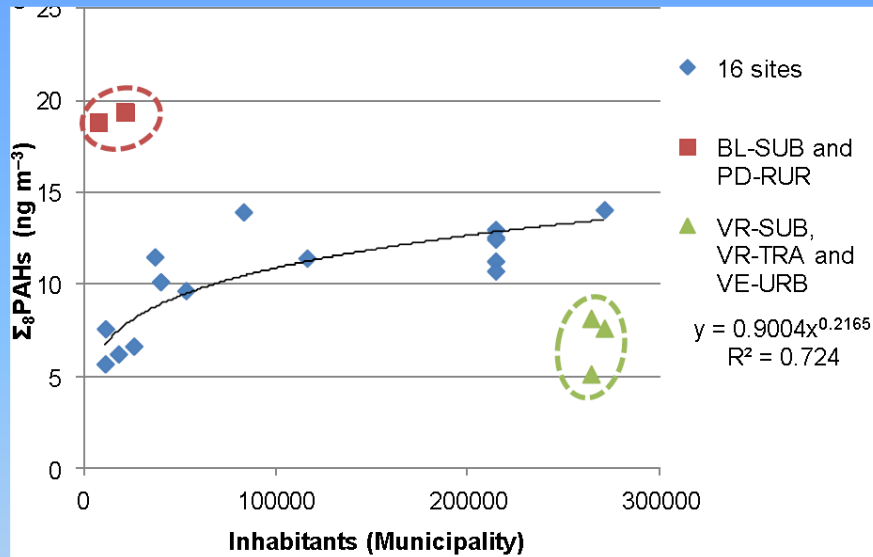
Andamento medie annuali di benzo(a)pirene - Periodo 2006-2010



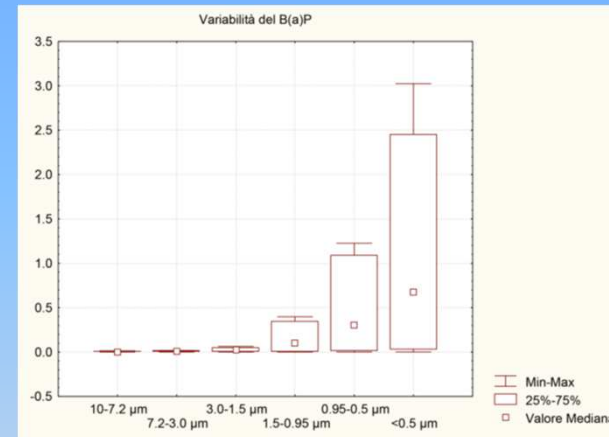
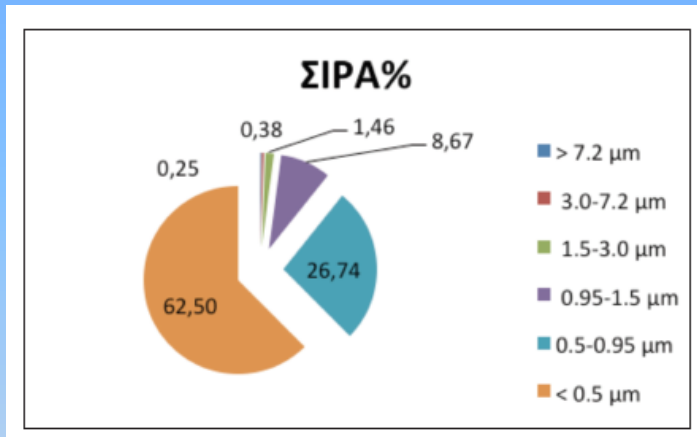
Caratterizzazione del PM

- HPLC per la determinazione degli IPA in particolare del B(a)P
UNI EN 15549:2008
- ICP-MS o GAAS: per i metalli As, Ni, Cd, Pb; UNI EN 14902:2005
- Non ci sono limiti per il Hg, la percentuale più alta di questo metallo si trova in forma gassosa
- Cromatografia ionica per la determinazione degli ioni solubili in acqua PM_{2.5};
- Carbonio organico e carbonio elementare su PM_{2.5}
- Analisi di specie marker es. Levoglucosano

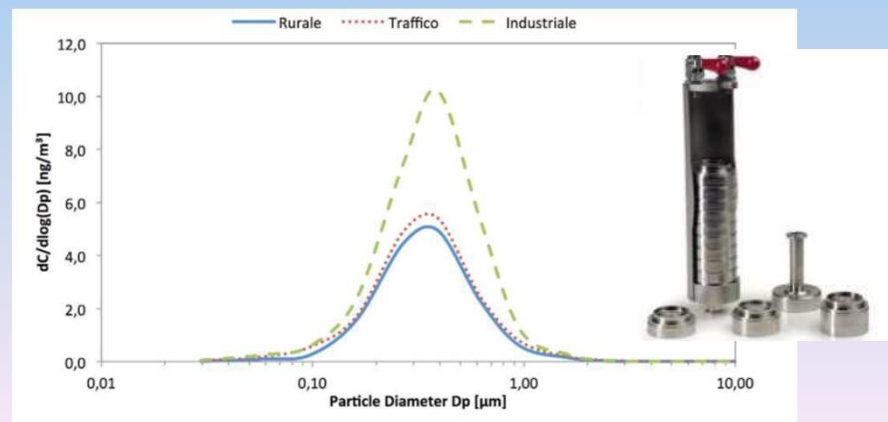
Gli IPA 2011



Ipa distribuzione dimensionale



La distribuzione dimensionale della concentrazione degli IPA analizzati è monomodale, centrata su 0,4 μm

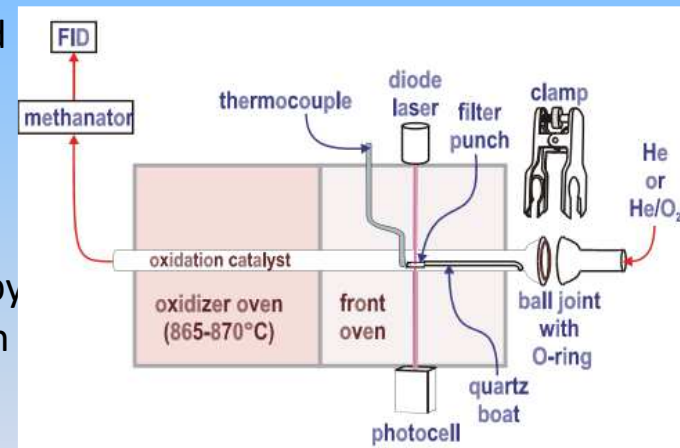


EUSAAR2 NIOSH Method: EC, OC, CC, TC

Thermal Optical transmittance:

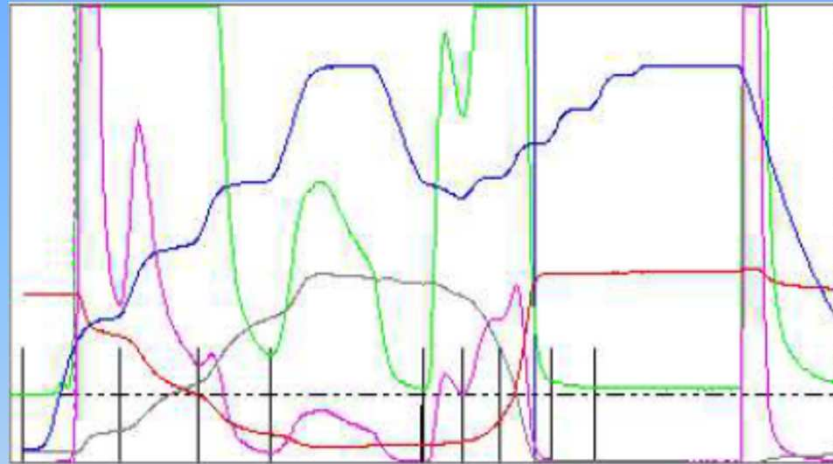
All carbon evolving from the filter is oxidized to carbon dioxide, the carbon dioxide is reduced to methane, and the methane is measured using a flame ionization detector (FID). A red-light laser and photocell are used to monitor transmittance of the filter, which typically darkens as refractory OC chars during a non-oxidizing heat ramp and then lightens as the char burns off during an oxidizing heat ramp. The calculation software divides TC into OC and EC by setting the split time between the two as the time in the analysis when the transmittance of the filter returns (after darkening then lightening) to its original value at the beginning of the analysis.

UNI EN 16909:2017



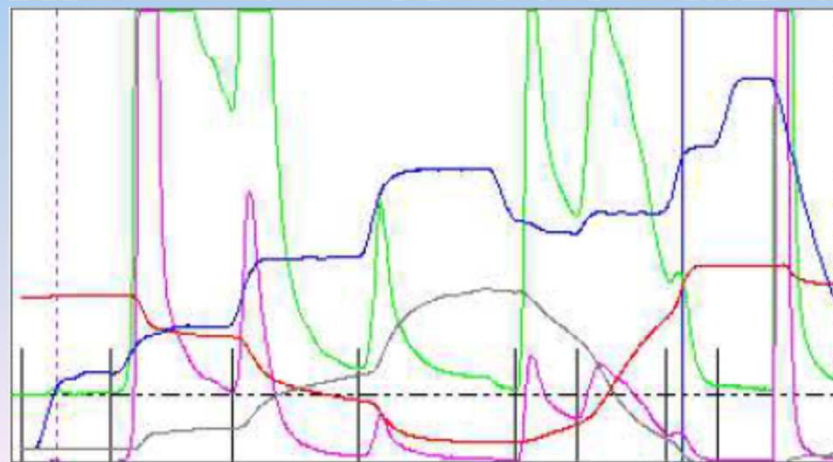
Output strumentale

NIOSH



| Peak | ugC/sqcm | Fraction |
|----------|----------|----------|
| OC1 | 26.3 | 0.568 |
| OC2 | 9.5 | 0.192 |
| OC3 | 2.2 | 0.045 |
| OC4 | 2.7 | 0.054 |
| OC5..... | | |
| OC6..... | | |
| EC1 | 1.4 | 0.028 |
| EC2 | 2.6 | 0.052 |
| EC3 | 2.9 | 0.038 |
| EC4 | 0.1 | 0.001 |
| EC5 | 0.0 | 0.001 |
| EC6 | 0.1 | 0.002 |

EUSAAR



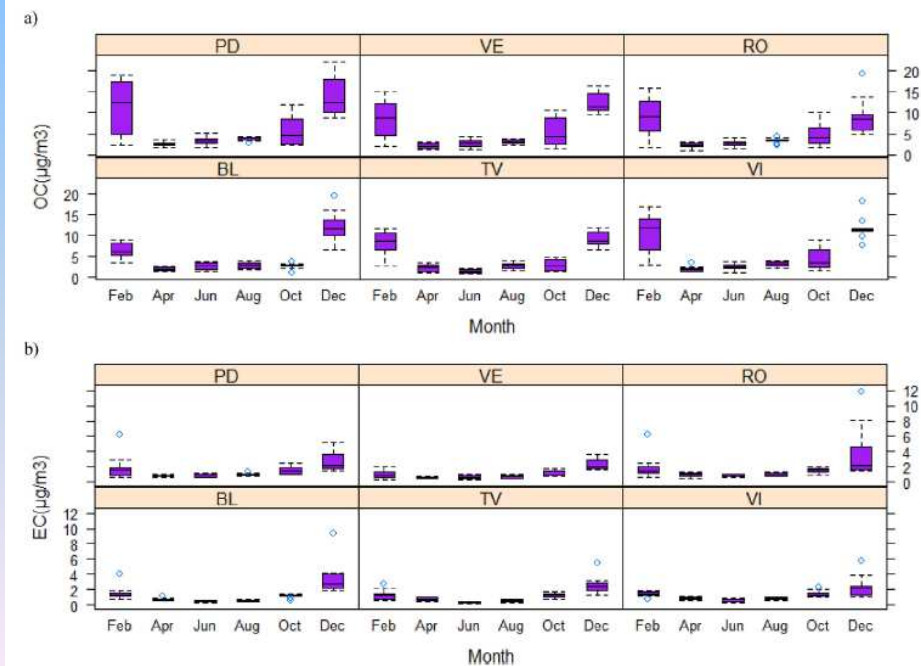
| Peak | ugC/sqcm | Fraction |
|----------|----------|----------|
| OC1 | 0.0 | 0.001 |
| OC2 | 33.6 | 0.659 |
| OC3 | 7.0 | 0.138 |
| OC4 | 1.4 | 0.028 |
| OC5..... | | |
| OC6..... | | |
| EC1 | 3.0 | 0.060 |
| EC2 | 5.1 | 0.100 |
| EC3 | 0.7 | 0.013 |
| EC4 | 0.1 | 0.002 |
| EC5..... | | |
| EC6..... | | |

EC/OC Alcuni dati

| City | OC | EC |
|---------------|---------|---------|
| Helsinki | 3 | 1.2 |
| Budapest | 6.8 | 3.3 |
| Amsterdam | 3.9-6.7 | 1.7-1.9 |
| Barcelona | 3.6-6.9 | 1.5-2.6 |
| Birmingham | | |
| Winter | 3.7 | 1.2 |
| Spring | 2.8 | 0.6 |
| Oslo | 1.7 | 1 |
| Athens | 3.5 | 1.6 |
| Paris | 2.2 | 1.8 |
| London/Oxford | 1.4 | 1.3 |
| Rome | 3.7 | 2.3 |
| Munich | 2.7 | 0.5 |

OC EC in Veneto su PM2.5
2012/2013

| Month | | | |
|----------|--------------------------------|--------------------------------|-------|
| Month | OC ($\mu\text{g m}^{-3}$) | EC ($\mu\text{g m}^{-3}$) | OC/EC |
| February | 9.1 | 1.5 | 6.8 |
| April | 2.2 | 0.8 | 3.0 |
| June | 2.6 | 0.6 | 4.4 |
| August | 3.2 | 0.8 | 4.5 |
| October | 4.4 | 1.3 | 3.5 |
| December | 11.4 | 2.9 | 5.1 |
| Annual | 5.5 | 1.3 | 4.5 |



| Province | | | |
|-----------|----------------------------|----------------------------|-------|
| Province | OC $\mu\text{g m}^{-3}$ | EC $\mu\text{g m}^{-3}$ | OC/EC |
| Belluno | 4.9 | 1.3 | 4.4 |
| Treviso | 4.5 | 1.1 | 4.5 |
| Vicenza | 5.8 | 1.3 | 4.6 |
| Padova | 6.8 | 1.5 | 4.7 |
| Venice | 5.7 | 1.1 | 5.4 |
| RO | 5.2 | 1.7 | 3.7 |
| Provinces | 5.5 | 1.3 | 4.5 |

POC-SOC

$$OC_{sec} = OC_{tot} - POC$$

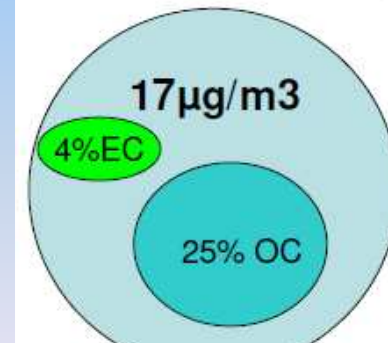
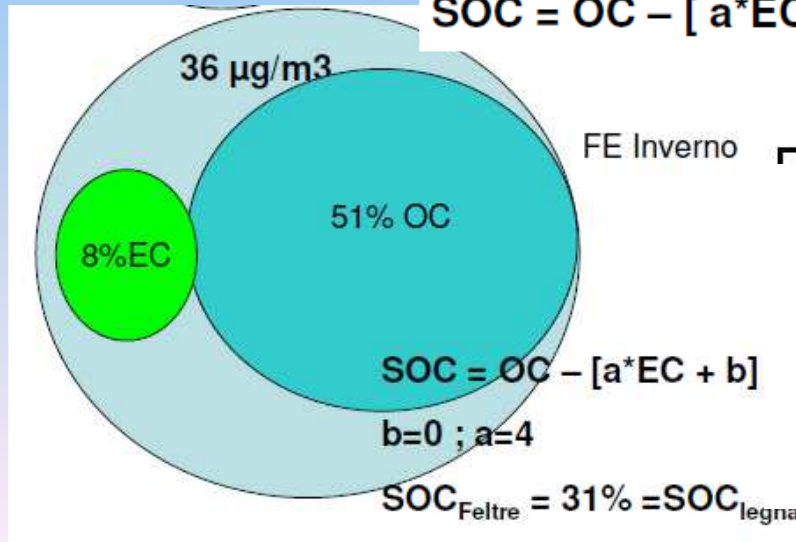
$$POC = \sum_i a_i * EC_i + b$$

Dove a è il rapporto di ciascuna sorgente tra il POC ed EC, b è il carbonio non dovuto alla combustione e biogenico o di risospensione



$$TC = SOC + POC + EC$$

$$SOC = OC - [a * EC + b]$$



RN Estate

COV: definizioni

OMS

| Descrizione | Abbreviazione | Intervallo di ebollizione |
|--|---------------|---------------------------|
| | | (°C) |
| Composti organici molto volatili (gassosi) | VVOC | da < 50-100 |
| Composti organici volatili | VOC | da 50- 240-260 |
| Composti organici semivolatili | SVOC | da 240- 380-400 |
| Composti organici associati al particolato | POM | >380 |

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ii) composto organico: qualsiasi composto contenente almeno l'elemento carbonio e uno o più degli elementi seguenti: idrogeno, alogeni, ossigeno, zolfo, fosforo, silicio o azoto, ad eccezione degli ossidi di carbonio e dei carbonati e bicarbonati inorganici;

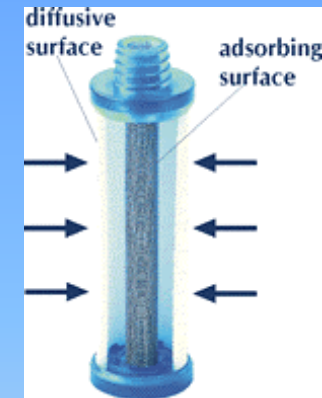
ll) composto organico volatile (COV): qualsiasi composto organico che abbia a 293,15 K una pressione di vapore di 0,01 kPa o superiore, oppure che abbia una volatilità corrispondente in condizioni particolari di uso. Ai fini della parte quinta del presente decreto, è considerata come COV la frazione di creosoto che alla temperatura di 293,15 K ha una pressione di vapore superiore a 0,01 kPa;

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pp) composti organici volatili: tutti i composti organici diversi dal metano provenienti da fonti antropogeniche e biogeniche, i quali possono produrre ossidanti fotochimici reagendo con gli ossidi di azoto in presenza di luce solare;

Passive sampling

Section of radiello. Diffusive and adsorbing surfaces are cylindrical and coaxial: a large diffusive surface faces, at a fixed distance, the small surface of a little concentric cartridge.



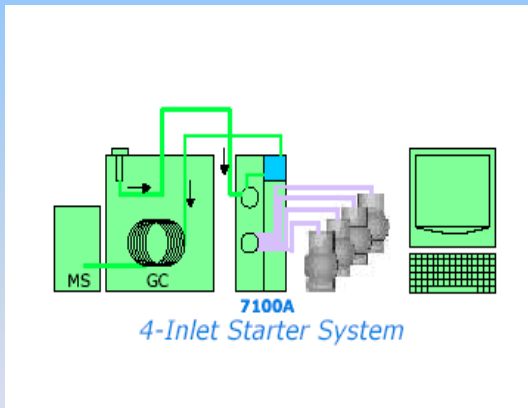
Outdoor Shelter for
Environmental/Ambient Air sampling

Radiello can be used to sample...

- VOCs – over 70 different volatile organic compounds, BTEX – benzene, toluene, ethylbenzene, o-xylene, m,p-xylene,
- O₃ – ozone
- Aldehydes – acetaldehyde, acrolein, benzaldehyde, butanal, hexanal, formaldehyde, glutaric aldehyde, isopentenal, pentenal, and propanal
- NH₃ – ammonia
- HCl and HF – hydrochloric acid and hydrofluoric acid
- NO₂ and SO₂ – nitrogen and sulfur dioxides
- H₂S – hydrogen sulfide
- Phenols – phenol, methylphenol, and dimethylphenol

VOC captured by canister

Method TO-15 documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10 Torr at 25°C and 760 mm Hg.



The use of canister:

- Emergencies
- Industrial hygienist monitoring
- Odour
- Traffic pollution
-

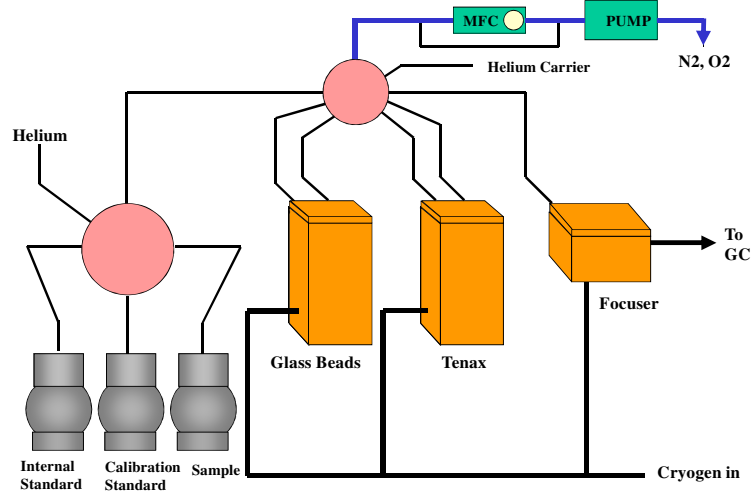


Sostanze riconosciute

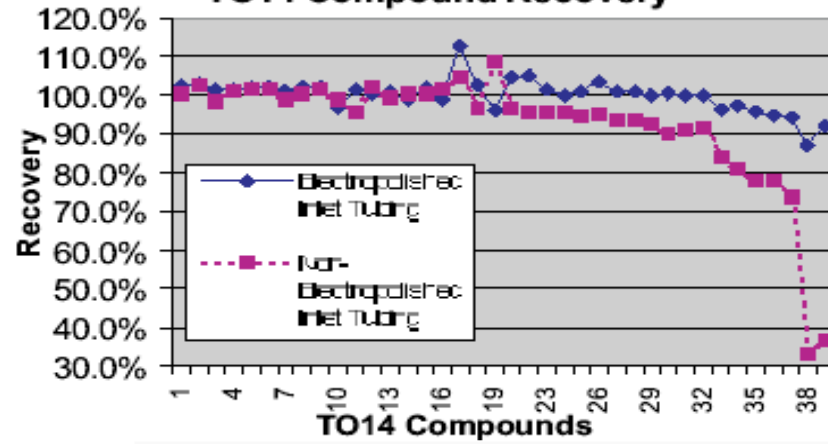
| | |
|-----------------------------------|---------------------------------|
| 1,1,2,2-Tetracloroetano | Clorobenzene |
| 1,1,1-Tricloroetano | Cloroformio |
| 1,1,2-Tricloroetano | Clorometano |
| 1,1-Dicloroetilene | Cloruro di benzile |
| 1,2,4-Triclorobenzene | Cloruro di etile |
| 1,2,4-Trimetilbenzene | Cloruro di metilene |
| 1,2-Diclorobenzene | Cloruro di vinile |
| 1,2-Dicloroetano | Diclorodifluorometano |
| 1,2-Dicloropropano | Diclorotetrafluoroetano |
| 1,3,5-Trimetilbenzene | Etilbenzene |
| 1,3-Butadiene | Isoottano |
| 1,3-Diclorobenzene | m,p-Xilene |
| 1,3-Dicloropropilene cis | Metiletilchetone |
| 1,3-Dicloropropilene trans | Metilisobutilchetone |
| 1,3-Esaclorobutadiene | n-Esano |
| Acetato di vinile | o-Xilene |
| Acetonitrile | Percloroetilene |
| Acrilonitrile | Stirene |
| Benzene | Tetracloruro di carbonio |
| Bromuro di etile | Toluene |
| Bromuro di metile | Tricloroetilene |
| | Triclorofluorometano |
| | Trifluorotricloroetano |

EPA TO15

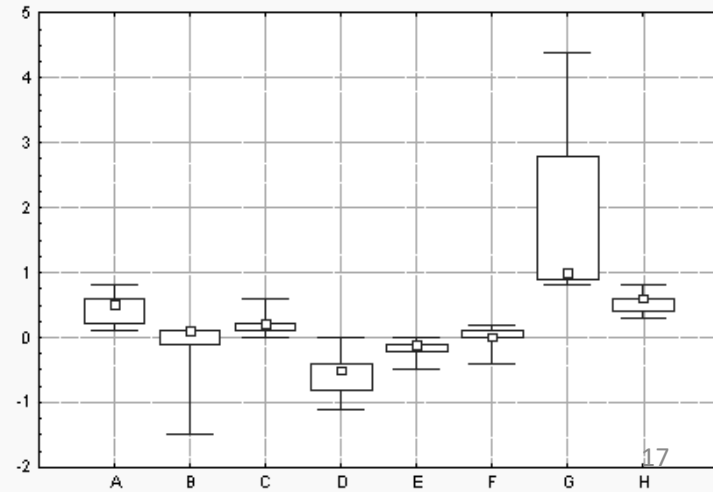
7100 Water and CO2 Management Techniques



Inlet Electropolishing Effects on TO14 Compound Recovery



Zscore round 3



Deposition

The Sixth Community Environment Action Programme establishes the need to reduce pollution... to improve the monitoring and assessment of air quality including the **deposition** of pollutants...

Bulk samplers are polymer structures formed of a cylindrical container and a protection ring to avoid damage by birds and animals. The structure is clamped to a 60 mm pole. A Pyrex bottle with a funnel properly silanised (treated with dimethyldichlorosilane 5% in toluene) for dioxin or PE bottle for metals is placed in the support. Bulk sampling is extensively used, since these samplers are easier to operate than wet and dry ones, and can also be located at sites with no electrical power supply



UNI EN 15853: 2010 Standard method for the determination of **mercury** deposition

UNI EN 15841:2010 Standard method for the determination of **As, Cd, Pb Ni** deposition

UNI EN 15980:2011 Standard method for **PAH** deposition

Alto volume: Diossine

In caso di incendio i processi di combustione sia controllati (inceneritori), sia incontrollati (incendi) sono indicati come una delle più rilevanti fonti di emissione di PCDD/F, qualora ci siano i precursori (fonti di carbonio e di cloro).

In caso di evento incidentale - in quasi tutti i processi industriali in cui si fa uso di cloro, le diossine possono rappresentare degli indesiderati prodotti di scarto, o altri settori industriali con produzione di pesticidi, coloranti, solventi clorurati...



Altri metodi

| PFAS | Molecular formula |
|------------|------------------------|
| PFOA | $C_8H_9F_{15}O_2$ |
| PFHxA | $C_6H_7F_{11}O_2$ |
| 4:2 FTOH | $C_6H_5F_9O$ |
| 6:2 FTOH | $C_8H_5F_{13}O$ |
| PFDA | $C_{10}H_7F_{19}O_2$ |
| 10:2 FTOH | $C_{12}H_5F_{21}O$ |
| 7:2 sFTOH | $C_9H_5F_{15}O$ |
| PFHpA | $C_7H_7F_{13}O_2$ |
| PFTeDA | $C_{14}H_9F_{27}O_2$ |
| PFPeA | $C_5H_7F_9O_2$ |
| PFNA | $C_9H_7F_{17}O_2$ |
| PFDoA | $C_{12}H_9F_{23}O_2$ |
| PFHxDA | $C_{16}H_9F_{31}O_2$ |
| 5:2 sFTOH | $C_7H_5F_{14}O$ |
| PFTrDA | $C_{13}H_9F_{25}O_2$ |
| PFUdA | $C_{11}H_7F_{21}O_2$ |
| N-MeFOSA-M | $C_9H_4F_{17}NO_2S$ |
| N-EtFOSA-M | $C_{10}H_6F_{17}NO_2S$ |
| N-MeFOSE-M | $C_{11}H_8F_{17}NO_3S$ |
| PFODA | $C_{18}H_9F_{35}O_2$ |
| 8:2 FTOH | $C_{10}H_5F_{17}O$ |

TD:

Sorbent tubes: Universal tubes (C3-AAXX-5266)
 TD instrument: TD100-xr™ (Markes International)
 Flow path: 180°C
 Tube desorption: 300°C (8 minutes) at 75 mL/min
 Focusing trap: 'Air Toxics' (U-T15ATA-2S)
 Trap low: 25°C
 Trap desorption: 300°C (4 minutes)
 Trap outlet split flow: 6 mL/min

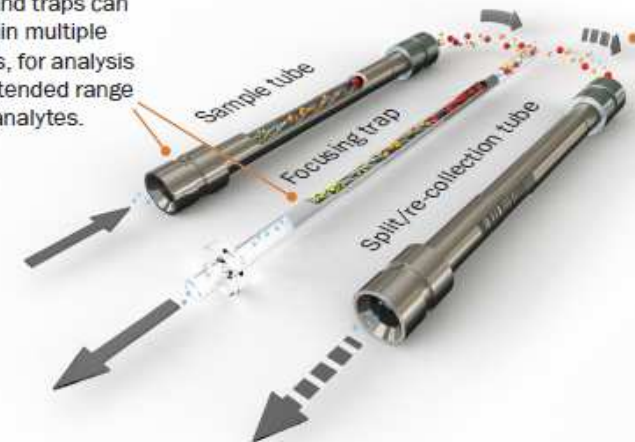
GC:

Column: DB-VRX (Agilent Technologies)
 60 m x 0.25 mm x 1.4 µm
 Column flow: 1.2 mL/min, helium
 Oven: 35°C (5 min), 10°C/min, 230°C (15 min)

Quadrupole MS:

Scan mode: m/z 35-350

Tubes and traps can contain multiple sorbents, for analysis of an extended range of analytes.



Analisi degli Odori: tecniche

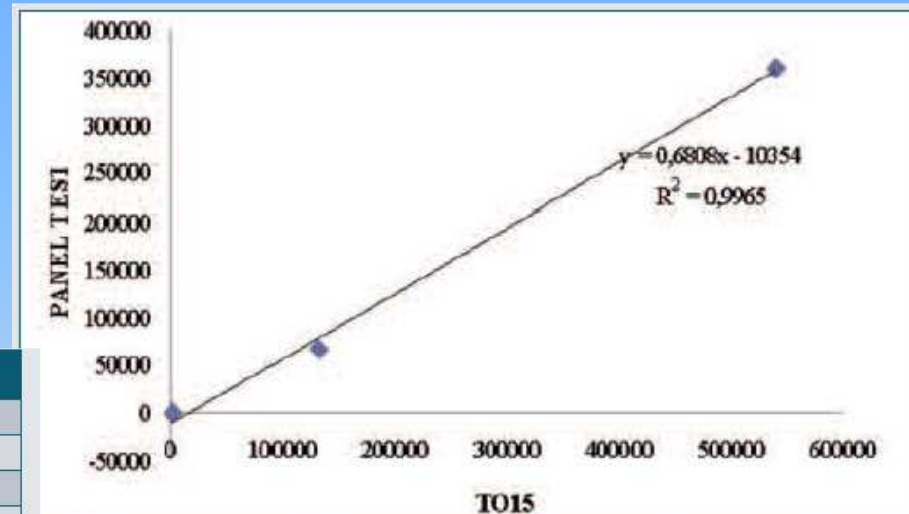
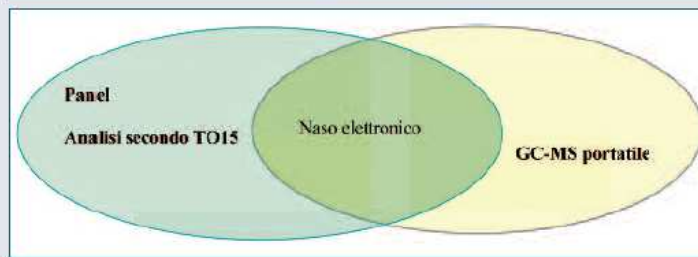


Fig. 1 - In ascissa è riportata la sommatoria delle sostanze ritrovate con il metodo PA TO15 moltiplicate per il fattore che tiene conto della soglia olfattiva, in ordinata il valore odorigeno degli stessi campioni esaminati mediante N 13725:2003

| | SENSIBILITA' ¹ | MISURA EFFETTO OLFATTIVO ² | SELETTIVITA' ³ | TEMPO DI ANALISI |
|------------------|---------------------------|---------------------------------------|---------------------------|------------------|
| Analisi TO15 | Buona | Scarsa | Buona | Medio |
| GC MS portatile | Media | Scarsa | Buona | Buono |
| Panel | Buona | Buona | Nulla | Medio |
| Naso elettronico | Buona | Buona | Nulla | Buono |

¹Sensibilità: capacità d'individuare composti a bassissima concentrazione
²Misura effetto olfattivo: capacità di rilevare composti responsabili dell'effetto odorigeno od osmogeno
³Selettività: facoltà di discriminare i singoli analiti



Odori: norme tecniche

EN 16841-1:2016 describes the grid method for the determination of the level of odour exposure in ambient air within a defined assessment area. The method relies on qualified human panel members to determine the distribution of the frequency of odour exposure over a sufficiently long period (6 or 12 months) to be representative of the meteorological conditions of that location. The sources of the odorant under study may be located within or outside the assessment area.

EN 16841-2:2016 describes the plume method for determining the extent of recognisable odours from a specific source using direct observations in the field by human panel members under specific meteorological conditions (i.e. specific wind direction, wind speed and boundary layer turbulence) The results are typically used to determine a plausible extent of potential exposure to recognisable odours or to estimate the total emission rate using reverse dispersion modelling.

| Standard | Title |
|-----------------|--|
| EN 13725:2003 | Air quality - Determination of odour concentration by dynamic olfactometry |
| EN 16841-1:2016 | Ambient air - Determination of odour in ambient air by using field inspection - Part 1: Grid method |
| EN 16841-2:2016 | Ambient air - Determination of odour in ambient air by using field inspection - Part 2: Plume method |

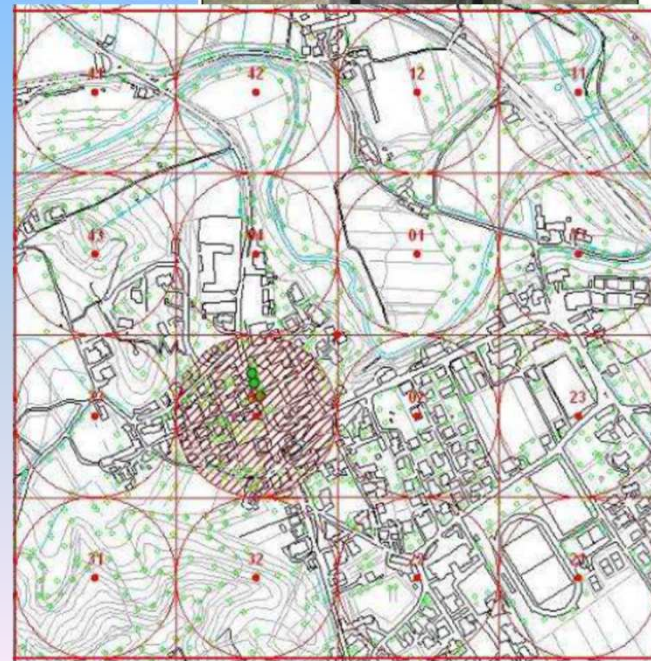
Biomonitoraggio

- le tecniche di bioindicazione che stimano le alterazioni morfologiche, fisiologiche o genetiche a livello di organismi o le modificazioni nella composizione delle comunità animali o vegetali, indotte dalle variazioni ambientali;
- le tecniche di bioaccumulo che si avvalgono di organismi in grado di assorbire ed accumulare, con alto livello di tolleranza, sostanze più o meno tossiche (es. metallipesanti) le cui concentrazioni vengono misurate.



Licheni come bioindicatori

- Assenza di cuticola: contatto diretto con l'atmosfera
- Attivi tutto l'anno in particolare dopo ogni pioggia
- Dipendono dall'aria per il nutrimento
- Assenza di sistemi di regolazione degli scambi
- Riproduzione mediante strutture aerodiffuse (soradi, isisidi, spore).
- Contatto diretto con gli inquinanti
- Crescita lenta





Metodi strumentazione automatica

| inquinante | metodo | Tecnica analitica |
|-----------------|-------------------|---------------------------------------|
| SO ₂ | UNI EN 14212:2012 | Ultraviolet fluorescence |
| NO ₂ | UNI EN 14211:2012 | chemiluminescence |
| CO | UNI EN14626:2012 | non-dispersive IR spectroscopy |
| O ₃ | UNI EN14625:2012 | Ultraviolet photometry |

A Member State may also use any other methods which it can demonstrate give results equivalent to the above method.