“Capacity Building and Strengthening Institutional Arrangement”

Analysis and sampling of air and air pollution

Emission monitoring

Ms. Maria Belli

APAT

Agency for Environmental Protection and Technical Service

Reasons of stack emission monitoring

- compliance with environmental legislation
- emission-inventory compilation
- environmental impact assessements
- process efficiency and process control
- performance of a pollution-control device
- calibration of continuous emission monitoring systems

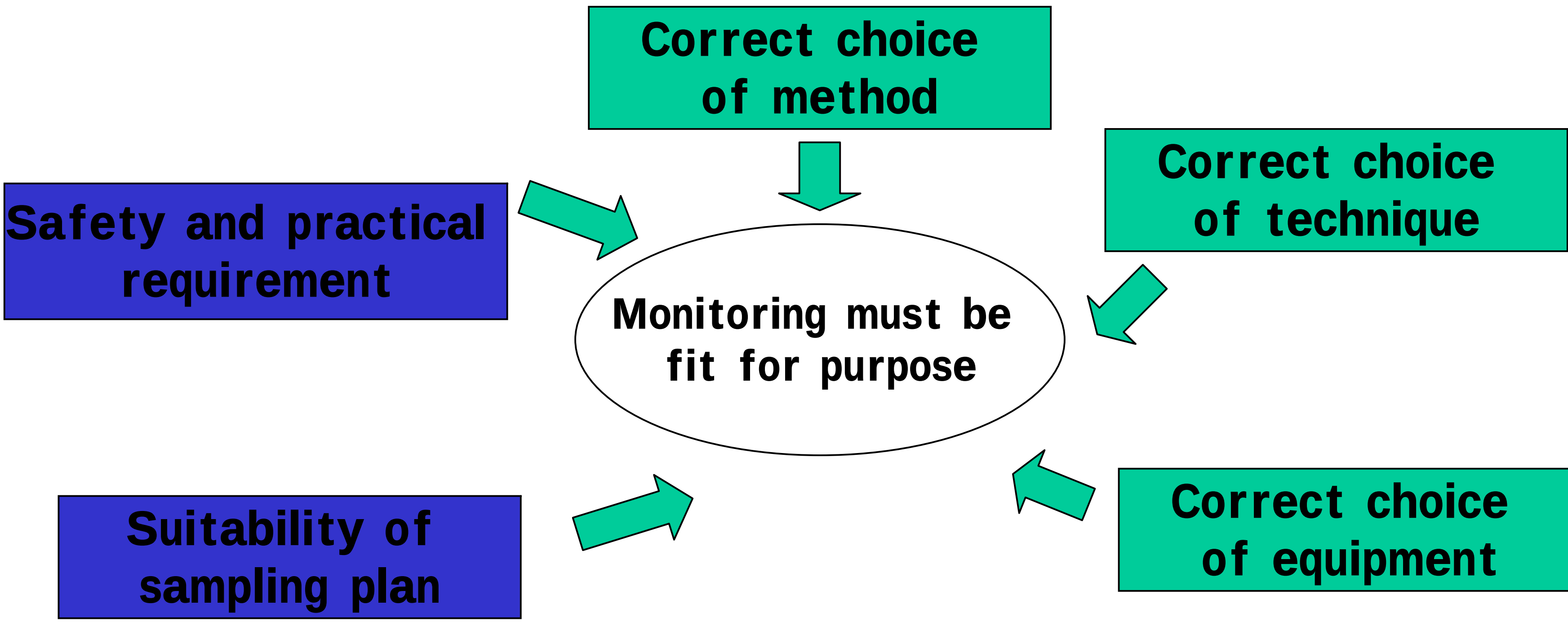
Stack emission monitoring

- Periodic measurements campaign
  - Samples are withdrawn from the stack (sample analysed after in the lab)
  - Instrumental or automated technique are used (sample fed in an on line analyser)
- Sample can be obtained on several hours or may be on “spot” or “grab” collected over a period of second or several minutes

Stack emission monitoring

- Continuous emissions monitoring systems
  - Continuous measurements carried out with automated equipment
    - measurements may be carried out *in situ* in the stack
    - extractive sampling fed in an instrument placed permanently at or near the stack

Monitoring fit for purpose



From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (harmonization of sampling and measurements methods among ARPA/APPA)

- Technical guidance contents
  - Elements for site specific protocol
    - Site review to understand the physical and logistical situation on-site
      - Type of plant
      - State of authorizations
      - Technical elements to specify what, where and when to sample

Manuale operativo per il controllo delle emissioni in atmosfera (legge 93/01 ARPAT, ARPA-Lombardia, ARPA-Liguria

Stack emission monitoring (harmonization of sampling and measurements methods among ARPA/APPA)

- **Technical guidance contents**
  - Choice of monitoring methods
  - Sampling and measurements equipment
  - Guidance for call for tender (equipment acquisition)

Manuale operativo per il controllo delle emissioni in atmosfera (legge 93/01 ARPAT, ARPA-Lombardia, ARPA-Liguria

Stack emission monitoring (harmonization of sampling and measurements methods among ARPA/APPA-choice of methods)

- Standards developed by different organization vary in the degree of validation work carried out as part of their development (CEN, ISO)
- The choice of method could be also dictated by the requirement of national legislation or EU directives
- If the standard is not dictated by mandatory requirements should be used the following order of priority (European IPCC Bureau's Reference Document on the general Principles of monitoring)

Manuale operativo per il controllo delle emissioni in atmosfera (legge 93/01 ARPAT, ARPA-Lombardia, ARPA-Liguria

Stack emission monitoring (harmonization of sampling and measurements methods among ARPA/APPA-choice of methods)

- Comité Européen de Normalisation (CEN)
- International Standardization Organization (ISO)
- American Society for testing and materials (ASTM)
- Association Francaise de Normalisation (AFNOR)
- British Standard Institution (BSI)
- Deutsches Institut fur Normung (DIN)
- United States Environmental Protection Agency (US EPA)
- Verein Deustcher Ingenieure (VDI)

Stack emission monitoring (harmonization of sampling and measurements choice of methods)

- Particulate matter
  - Total
  - Pm10
- Supplementary parameters (physical)
  - Gas velocity and temperature
- Supplementary parameters (chemical)
  - Oxygen
  - Carbon dioxide
  - Moisture

Speciated particulates and phase partitioned species (inorganic)

Stack emission monitoring (harmonization of sampling and measurements choice of methods)

- Speciated particulates and phase partitioned species (inorganic)
  - heavy metals
  - hydrogen chloride
  - asbestos, man made fibres and ceramic fibres
- Speciated particulates and phase partitioned species (organic)
  - dioxin and furan
  - PHAs
  - PCBs
  - Tar and bitume fume
  - Oil mist

Stack emission monitoring (harmonization of sampling and measurements choice of methods)

- Gaseous substances (inorganic)
  - sulphur dioxide, sulphur trioxide and total sulphur
  - nitrogen oxide
  - carbon monoxide
  - ammonia
  - hydrogen cyanide, total cynide
  - hydrogen sulphyde, TRS, carbon disulphide, carbonil sulphide
  - halogens and halides
  - phosphorous and its inorganic compound

Stack emission monitoring (harmonization of sampling and measurements choice of methods)

- Gaseous substances (organic)
  - Total VOCs
  - Speciated VOCs
  - Mercaptans (thiols)
  - Diisocyanates
  - Amines and amides
  - Aldehydes
  - phenols and creosols
  - carboxylic acids
- Odour

Stack emission monitoring (choice of analytical method-total particulate matter)

Monitoring approach	Type of monitoring	Technique/ principle	Standard / method	Strengths/ applications	Limitations
CEMs	In situ/ cross-duct CEMs	Opacity meter or transmissometer	BS ISO 10155	In widespread use. Opacity or smoke density measurements can be related to Ringelmann chart. Some instruments can be calibrated to give dust concentration. mg m^{-3}. Laser opacimeters have LOD down to 1 mg m^{-3}	Concentration calibration factor dependent on particle size, composition, shape, colour and refractive index. Gives a measure of dust concentration, but after calibration against SRM. Typical range about 10 to 3000 mg m^{-3}. Not suitable for low concentration emissions.
		Tribo-electric probe	BS ISO 10155	Can be used simply as an alarm indicator or as quantitative monitor. Claimed to be suitable for low dust concentrations (LOD less than 1 mg m^{-3}).	Tribo-electric response dependent on particle size, composition and moisture. Gives a measure of dust concentration, but after calibration against SRM.
		Light scattering	BS ISO 10155	Reported to be suitable for low dust concentrations (LOD down to 1 mg m^{-3}).	Gives a measure of dust concentration, but only after calibration with SRM.
	Extractive CEMs	Beta attenuation monitor	BS ISO 10155	Can be calibrated to give dust concentration mg m^{-3} directly. Gives successive average readings over set sampling periods. Absorption coefficient is independent of dust composition.	Typical range about 2 to 2,000 mg m^{-3} depending on sampling rate, frequency and integrating time.
		TEOM	BS ISO 10155	Equipment can be installed permanently, as a CEM. Gives continuous gravimetric results but is limited by filter life.	Manufacturer's data: LOD 0.2 mg m^{-3} (2 min sample); typical range 0-50 mg m^{-3} (depending on filter change frequency); precision ±2.5%.
		Extractive light-scattering system	BS ISO 10155	Suitable for low dust concentrations. Extractive part of the system may retain dust.	Manufacturer's data: range 0-1000 mg m^{-3}; LOD 0.02 mg m^{-3}; reproducibility 0.5% FSD.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-particulate)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
Periodic	Periodic manual techniques	Isokinetic sampling and gravimetry	BS EN 13284-1	Developed for low dust concentrations (<50 mg m^{-3}), however the scope states that it can be used for a wide range of concentrations. Primarily developed for hazardous waste incinerators (HWIs), however the scope also indicates that it can be applied more widely.	Reproducibility (worst quoted) ±5.7 mg m^{-3} at 6.4 mg m^{-3} and 30 min sample. Validated at concentrations around 5 mg m^{-3} and 30-minute sampling duration (usually used for concentrations below 50 mg m^{-3}). The overall uncertainty of the method complies with the uncertainty of ±30% required by HWID and WID sites.
			BS ISO 9096	This standard is a reference method for the measurement of particulates in stack gases of concentrations between 20 mg m^{-3} to 1000 mg m^{-3}. It was developed by close co-operation between ISO and CEN. It is similar to EN 13284-1 with additional emphasis given on the use of high-volume sampling techniques.	The overall uncertainty of the method complies with the uncertainty of ±30% required by HWID and WID sites.
	Periodic instrumental techniques	TEOM	BS ISO 10155*	Gives continuous gravimetric results. Technique intended by manufacturers for calibration of CEMs.	Manufacturer's data: LOD 0.2 mg m^{-3} (2 min sample); typical range 0-50 mg m^{-3} (depending on filter change frequency); precision ±2.5%.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-pm10)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
CEMs	In situ/ cross-duct CEMs	Light scattering	BS ISO 10155*	Light scattering systems can be configured to classify particulate numbers into size ranges.	Gives a measure of dust concentration, but after calibration with the SRM.
	Extractive CEMs	Photometric analyser	BS ISO 10155	Low range. Suitable for low-range, large, wet processes.	Range 0 – 40 $mg\ m^{-3}$.
Periodic	Periodic manual techniques	Sampled using cascade impactor or in-stack cyclone and gravimetry	US EPA method 201A	Cascade impactor gives particle-size distribution over 10 size ranges.	Must be operated at constant flow and at one sampling point.
	Periodic instrumental techniques	TEOM when used with PM10 sampling head or cyclone	BS ISO 10155**	Gives continuous gravimetric results. Technique intended for calibration of CEMs.	Manufacturer's data: LOD 0.2 $mg\ m^{-3}$ (2 min sample); typical range 0-50 $mg\ m^{-3}$ (depending on filter change frequency); precision ±2.5%.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-gas velocity and temperature)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
CEMs (gas velocity)	In situ/ cross-duct CEMs	Dynamic pressure technique	BS ISO 14164: 1999*	Uses probe with series of openings and pressure-sensing device.	
		Ultrasonic sensors and receivers	BS ISO 14164: 1999	Gas velocity related to speed of pulsed soundwaves.	Interference from vibrations and turbulence
		Balance technique	None published	Force exerted by flow on probe element measured by strain gauge.	
	In situ CEMs	Triboelectric	None published	Good agreement with Pitot tube demonstrated in combustion plants	Interference from moisture
		Thermal mass	None published	Gas velocity related to energy required to keep a probe at temperature (wind chill effect). Good for low velocities.	Limited temperature range
Periodic (gas velocity and temperature)	Periodic manual techniques	Traverse of sample plane using Pitot probe with manometer and thermocouple	BS EN 13284-1**	An integral part of the standard method for particulates measurement	The lowest gas velocity that can be measured is about $2-3\ m\ s^{-1}$ since the smallest pressure difference that can be practically measured under field conditions is about 5 Pa. Upper temperature limit is about 400°C, unless constructed with high-temperature-resistant material. However, due to the effects of temperature on gas density, the repeatability of Pitot measurements varies with increasing temperature. Type K thermocouple cannot be used above about 1370°C.
	Periodic instrumental techniques	As above, but using digital manometer	BS ISO 9096: 2003	An integral part of the standard method for particulates measurement.	Digital manometer may sometimes allow better LOD to be achieved.
		Vane anemometer	None published	Gas velocity related to number of revolutions of vane. Good for velocities from 0.5 to $5\ m\ s^{-1}$	Limited temperature range. Probe diameter can interfere with reading at small duct diameters.
		Thermal anemometer	None published	Gas velocity related to energy required to keep a probe at temperature (wind chill effect). Good for low velocities, 0.2 to $0.5\ m\ s^{-1}$	Limited temperature range. May not be able to confirm flow direction.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-oxygen)

Monitoring approach	Type of monitoring	Technique/ principle	Standard / method	Strengths/ applications	Limitations
CEMs	In situ CEMs	Zirconium oxide film	ISO 12039		Main interferences: hydrocarbons, CO.
	Extractive CEMs	Paramagnetic analyser	ISO 12039	Range 0-100% with typical resolution of 0.1%	Interferences from high concentrations of NO_2, NO and certain hydrocarbons.
		Electrochemical cell	ISO 12039	Electrochemical cell can also be mounted in the gas stream for an in-situ CEMs measurement.	Interference from SO_2, NO_x and acid gases. Requires appropriate conditioning and purging with clean air for sensor recovery.
Periodic	Periodic instrumental techniques	Zirconium cells	ISO 12039[*]		Interference from CO and hydrocarbons if their concentrations are in the same order as oxygen. Intended for use in the range of up to 25% volume fraction.
		Paramagnetic analyser	ISO 12039	Range 0-100% with typical resolution of 0.1% Typical response time (T_{90}) about 45s.	Interference from high concentrations of NO_2, NO and certain hydrocarbons.
		Electrochemical cell	ISO 12039		As above for CEMs.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-carbon dioxide)

Monitoring approach	Type of monitoring	Technique/ principle	Standard / method	Strengths/ applications	Limitations
CEMs	In situ/ cross-duct CEMs	Cross-duct NDIR	ISO 12039		CO is a positive cross interferant. Methane also interferes.
		DOAS	ISO 12039	Simultaneous monitoring of CO_2 along with many other pollutants.	Range up to 100%, LOD approx. 0.1% by volume.
	Extractive CEMs	NDIR analyser	ISO 12039		Interferences from CO, water, methane and ethane.
		FTIR analyser	ISO 12039 ASTM D6348-03 USEPA-Method 320	Simultaneous monitoring of CO_2 along with many other pollutants. Faster response than NDIR.	Typical range 0 to 35%.
Periodic	Periodic instrumental techniques	NDIR analyser	ISO 12039[a]	As above for CEMs.	As above for CEMs.
		FTIR analyser	ISO 12039 ASTM D6348-03 USEPA-Method 320	As above for CEMs.	As above for CEMs.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-moisture)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
CEMs	In situ/ cross-duct CEMs	NDIR	None published	In widespread use	Interference from other IR absorbing species, e.g. CO, CO_2 hydrocarbons
		DOAS	None published	Simultaneous monitoring of H_2O and other pollutants	Typical range 0-30%, LOD approx. 0.1% volume
	Extractive CEMs	NDIR analyser	None published		Interferences from CO, CO_2, hydrocarbons.
		FTIR analyser	ASTM D6348-03 US EPA Method 320	Simultaneous monitoring of H_2O and other species. Faster response than NDIR	Typical range 0 to 35%
		Paramagnetic analysers	None for H_2O, but oxygen to ISO 12039*	Range 0-100%, typical resolution 0.1%. H_2O calculated from the difference between two analysers, one measuring O_2 wet and other dry.	Not a direct measurement of moisture. Interferences from high concs. of NO_2, NO and hydrocarbons.
Periodic	Periodic manual techniques	Gravimetric or volumetric (impingers)	US EPA Method 4	US EPA method 4 is incorporated into several other periodic manual methods, therefore allowing moisture to be measured as part of another sampling method.	Requires a balance to be taken on site
	Periodic instrumental techniques	Paramagnetic analysers	None published	As above for CEMs.	As above for CEMs.
		NDIR analyser	None published	As above for CEMs.	As above for CEMs.
		FTIR analyser	ASTM D6348-03 US EPA Method 320	As above for CEMs.	As above for CEMs.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-speciated particulate and phase partitioned species-heavy metal)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
CEMs	In situ/ cross-duct CEMs	DOAS	None published	Will measure many other pollutants simultaneously.	For mercury vapour only. Range up to 1000 μg m^{-3}, LOD <3 μg m^{-3}.
	Extractive CEMs	Thermocatalytic reduction then UV absorption	None published	Good LOD (<1 μg m^{-3}).	For mercury vapour only. Range up to 1000 μg m^{-3}
Periodic	Periodic manual techniques	Isokinetic sampling and impingement. Analysis by ICPMS.	BS EN 13211* (covers both sampling and analysis. The analysis refers to EN 14835).	Method for the determination of mercury and its compounds in all phases.	The method was validated on the incineration of waste at a concentration range 0.001 to 0.5 mg m^{-3} of mercury.
		Isokinetic sampling and impingement. Analysis by ICPMS, ICP-OES or AAS.	BS EN 14385	Method for the determination of total emissions of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl, V, and other metals as specified in MID 14385**	
	Periodic instrumental techniques	NDUV	None	Portable mercury vapour analysers available.	Does not measure mercury present in particulate phase.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-speciated particulate and phase partitioned species-hydrogen chloride)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
CEMs	In situ/ cross-duct CEMs	DOAS	None published	Measures HCl, specifically, rather than total chlorides. Simultaneous monitoring of HCl along with many other pollutants.	Measures gas-phase HCl only. Range up to 5000 mg m^{-3}, LOD <1 mg m^{-3}. Not suitable for the measurement of chlorides
		Tuneable diode laser	None published		
		NDIR analyser	None published		
	Extractive CEMs	NDIR analyser	VDI 3480 Blatt 2*	Measures HCl, specifically, rather than total chlorides.	Measures gas phase HCl only. Interferences from particulates, H_2O, CO, CO_2 and any other IR-absorbing components.
		FTIR	ASTM-D6348-03 US EPA-Method 320	Measures HCl, specifically, rather than total chlorides. Simultaneous monitoring of HCl along with many other pollutants. Faster response and fewer interferences than NDIR.	Typical range up to 1000 mg m^{-3}. Measures gas phase HCl only
		Ion mobility spectrometry	None published	LOD down to ppb levels.	
		Continuous-flow analysers, based on IC, ISE, etc.	None published	Simultaneous monitoring of chloride expressed as HCl along with many other halides.	Measures gas phase only. Not specific to HCl (also responds to chlorides). Interferences from particulates, H_2O, CO_2, Cl_2, SO_2, SO_3, NO_2 and NH_3. Slow response time, require consumable reagents.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-speciated particulate and phase partitioned species-hydrogen chloride)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
Periodic	Periodic manual techniques	Isokinetic / non-isokinetic sampling and impingement. Analysis by titration, spectrometry or IC	BS EN 1911 1998 Parts 1 to 3*	Method for particulate and gas-phase chlorides.	Measures total gaseous chlorides, reported as HCl. Typical range 0-1000 mg m^{-3} (can be varied with volume). "External uncertainty" (reproducibility) at 5 mg m^{-3} approx. ±30% Interferents depend on analytical end-method selected"*.
	Periodic instrumental techniques	Extractive sampling and NDIR analyser	VDI 3480 Blatt 2	As above for CEMs.	As above for CEMs.
		Extractive sampling and FTIR analyser	ASTM D6348-03 US EPA-Method 320	As above for CEMs.	As above for CEMs.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-asbestos, man made mineral fibres and ceramic fibres)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
Periodic	Periodic manual techniques	Isokinetic sampling*, followed by counting of fibres on filter using phase-contrast microscopy	BS 6069: Section 4.2: 1991	Method intended for exhausts of asbestos plant and arrestment equipment. Method may also be applied to man-made mineral fibres and ceramic fibres. Gives a quantitative concentration in units of fibres per ml or per m^{-3}.	Other fibrous material interferes: all fibres assumed to be asbestos. Typical uncertainties are ±20% for a count of 100 fibres, and around 35% for a count of ≤40 fibres, in 100 graticule areas. Typical range 0.05 to 10 fibres ml^{-1} (varies with sample volume). LOD 0.01 fibres ml^{-1} (10,000 fibres m^{-3})
		Isokinetic sampling, followed by counting of fibres on filter using scanning electron microscope (SEM)	None covering whole technique. Sampling to BS 6069: Section 4.2: 1991; analysis by custom and practice method	Can distinguish asbestos from other fibres.	Useful for investigative work, but not for routine work.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method- dioxin and furan)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
Continuous sampling	Extractive	Continuous, automatic isokinetic batch sampler	None published	Installed on some processes in Europe. Integrated samples obtained over averaging periods ranging from 1h to 30 days.	Though sample is obtained continuously, results are not instantaneous: the filter and absorption media need to be sent off for analysis.
Periodic	Periodic manual techniques	Isokinetic sampling , extraction, then GC-MS analysis	BS EN 1948: 1997 Parts 1,2 and 3[4]	A standard reference method, validated on HWIs.	Validated at concentrations around 0.1 ng m^{-3} in total particulate concentration range 1-15mg m^{-3}

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Stack emission monitoring (choice of analytical method-PHA)

Monitoring approach	Type of monitoring	Technique/ principle	Standard/ method	Strengths/ applications	Limitations
Continuous sampling	Extractive	Continuous, automatic isokinetic batch sampler	None published	Installed on some processes in Europe. Integrated samples obtained over averaging periods ranging from 1 h to 30 days.	Though sample is obtained continuously, results are not instantaneous: the filter and PUF cartridge still need to be sent off for analysis.
Periodic	Periodic manual techniques	Isokinetic sampling , extraction, then HPLC or GC-MS analysis	BS ISO 11338-1,2.	Will measure 16 main PAHs[14].	Range dependent on spectrometer settings. Range 0.1-1000 ng m^{-3}. A method LOD of less than 1 ng m^{-3} can be obtained from a sample of 6 m^3. Uncertainty ±25%.

From UK environment agency Technical guidance note M2 version 3.1 June 2005

Techniques for continuous or semi-continuous monitoring of gaseous and phase-partitioned species from coal, waste-fired combustion and gasification plant

Analysis Technique	Pollutant					
Extractive Systems	SO_2	NO_x	CO	VOC	HCl	HF
Simple non-dispersive infrared (NDIR)	✓	✓	✓	✓	✓	
Luft detector NDIR	✓	✓	✓	✓		
Photoacoustic detector	✓	✓	✓	✓		
Gas filter correlation (GFC) NDIR	✓	✓	✓	✓	✓	✓
Differential optical absorption spectroscopy (DOAS)	✓	✓	✓	✓	✓	✓
Fourier transform infrared spectroscopy (FTIR)	✓	✓	✓	✓		✓
Non-dispersive ultraviolet (NDUV)	✓	✓				
Ultraviolet fluorescence	✓					
Electrochemical cells	✓	✓	✓	✓		
Flame photometric	✓					
Conductivity (conductometric) analyser	✓				✓	
Chemiluminescence analysers		✓				
Flame ionisation detectors				✓ (Total VOC)		
Photo ionisation detectors				✓ (Total VOC)		
Gas chromatography				✓		
→ Mass spectroscopy				✓		
→ Ion-mobility spectrometry				✓	✓	✓
Potentiometric analysis					✓	✓
***In situ* systems**	SO_2	NO_x	CO	VOC	HCl	HF
Differential optical absorption spectroscopy (DOAS)	✓	✓	✓	✓	✓	✓
Derivative spectroscopy	✓	✓	✓		✓	✓
Gas filter correlation (GFC) NDIR	✓	✓	✓	✓	✓	✓
High temperature electrochemical cells	✓	✓				