SOFTWARE and USER GUIDE DOWNLOAD

- Go to www.ecochem.biz
- From the left-hand menu select "User's Area – PAS-DC Monitors"
- Enter "user" as user name and "pas2000" as the password (no quotes, all lower-case)
- Download the appropriate manuals

If you have any questions, please send an email info@ecochem.biz

Thank you!

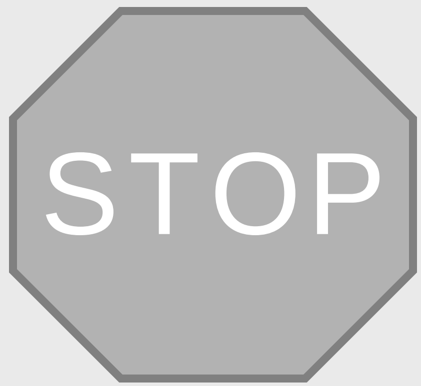
Introduction to the Handheld Photoelectric Aerosol Sensor and the Diffusion Charger

EcoChem Analytics

Presentation Outline

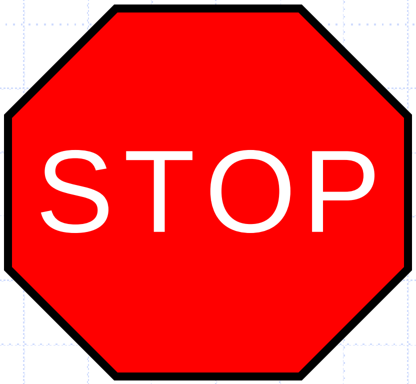
- Safety Warnings & Precautions
- Working Principle
- Health Risk Perspective
- Analyzer Operations
  - Description of Instrument
  - Software
- Service and Maintenance
- Applications

Safety Warnings and Precautions



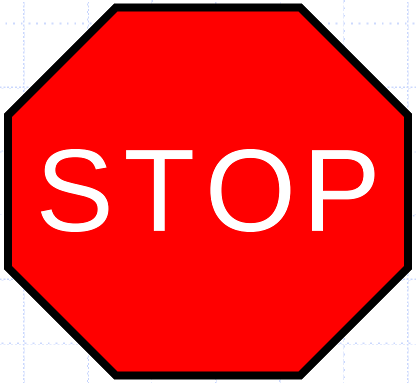
Safety Warnings & Precautions!

1. Never operate the instrument if the cover is removed.
2. Maintenance and repair work should only be done by trained personnel.
3. Care should be taken under extremely humid conditions! The monitor should be prevented from becoming wet. (If the sensor got wet and is not working properly, it should be placed into a dry place and left there for 1-2 days. This may restore the proper functioning.)

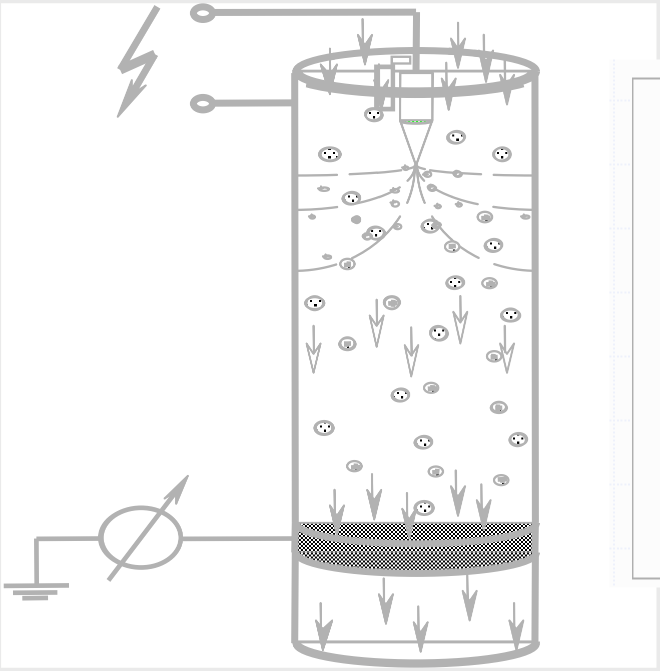


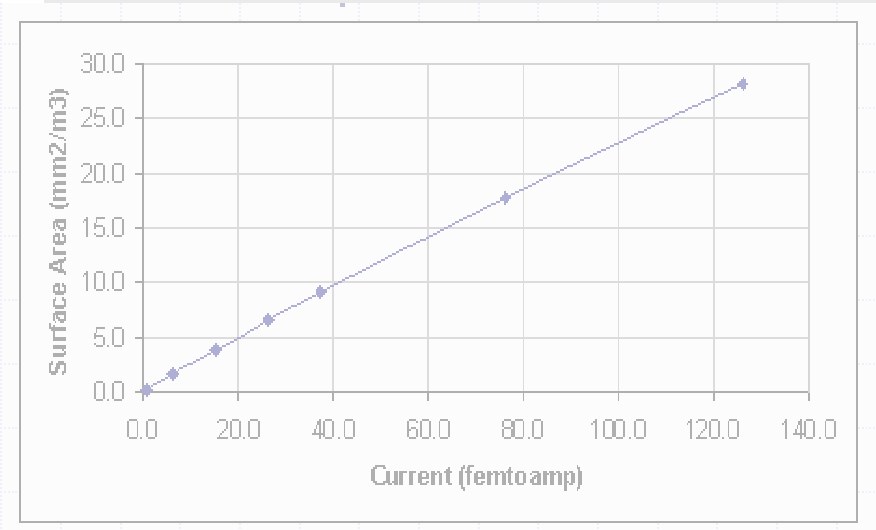
Safety Warnings & Precautions (Contd.)

4. Do not expose the instrument directly to rain or snow!
5. Always use the original serial cable supplied with the analyzer for downloading data.
6. Do not substitute the analyzer power supply with a standard laptop power supply (though they may look similar). You will seriously damage the analyzer by using an incompatible power supply unit.



Working Principle





Focus of Attention...

DC 2000CE measures
PARTICLE SURFACE AREA

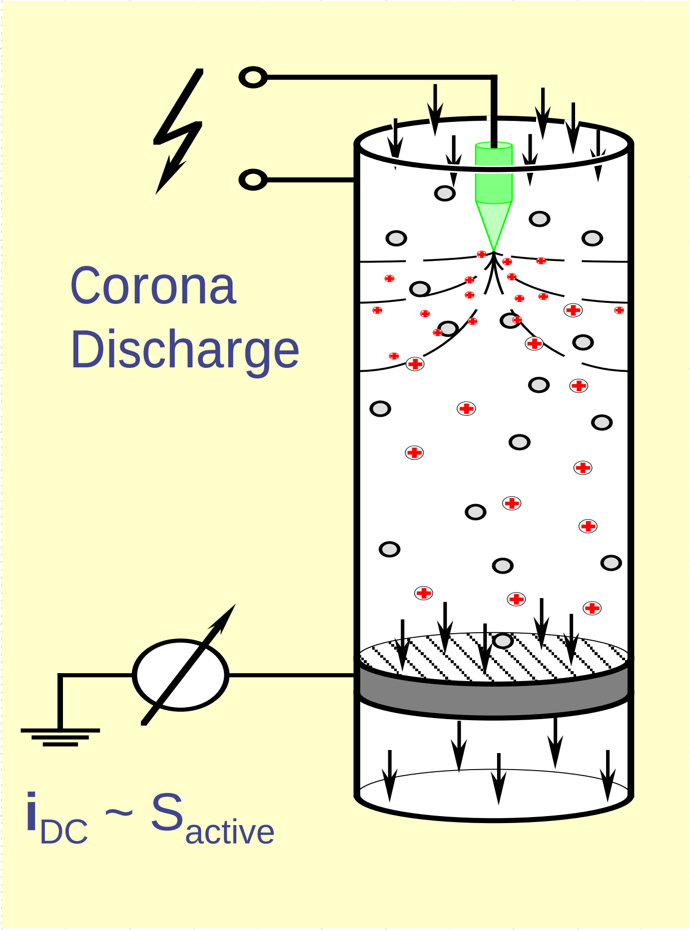
PAS 2000CE measures
PARTICLE PAH / SOOT

Diffusion Charger (DC 2000CE)

- Particle surface area
- Large particle size range
- Fast response, high sensitivity
- Compact, rugged and user-friendly

Principle of the Diffusion Charger (DC)

- Corona discharge is used to produce ions in the carrier gas
- Ions attach to particle surface by diffusion
- Collect particles in an electrically insulated filter
- Measure electric current flowing from filter (resolution ~1 femtoamp)

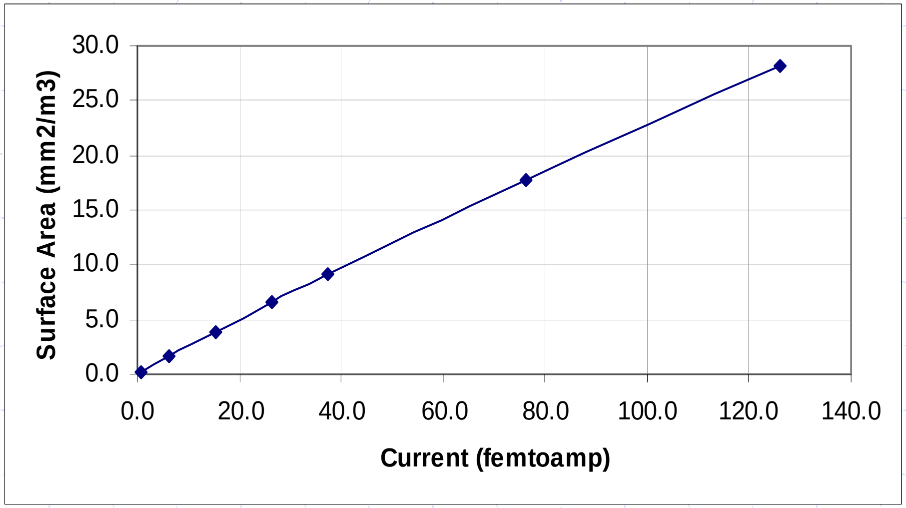


i_{DC} = DC Current
S_{active} = Particle active surface area

Working Principle

What does the DC measure...

- The diffusion chargers measures the particle Active Surface Area (mm2/m3)
- The Active Surface Area is defined as the particle area accessible for impinging molecules of the carrier gas. It is surface upon which transfer of momentum, energy and mass from the gas to the particle takes place.

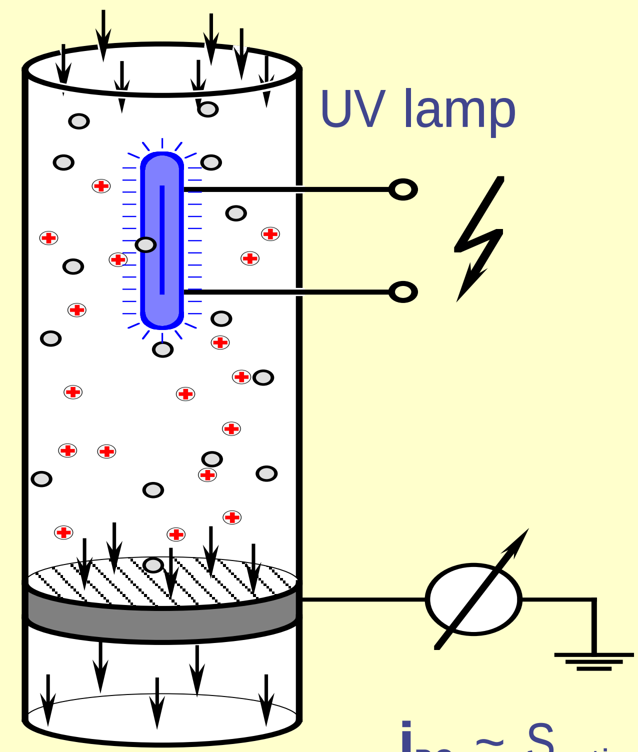


Photoelectric Aerosol Sensor -- PAS 2000CE

- Sensitive to surface chemistry
- Responds to ultrafine carbon particles
- High sensitivity, large measurement range
- Light, compact and field-ruggedized

Principle of the Photoelectric Aerosol Sensor (PAS)

- Excimer lamp used to produce UV radiation
- Photoionization of carbonaceous particles
- Collect particles in an electrically insulated filter
- Measure electric current flowing from filter (resolution ~1 femtoamp)



$i_{PC} \sim S_{active} \times F$

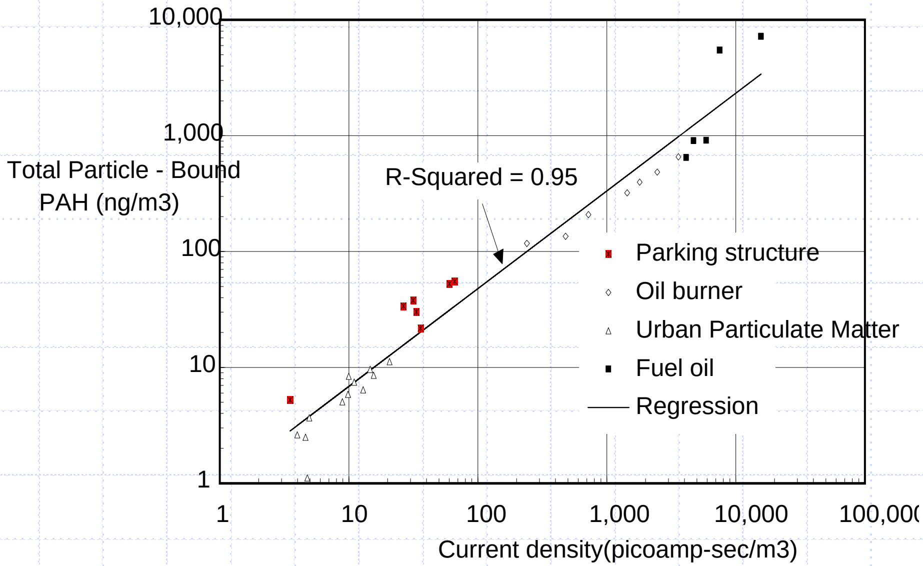
I_{PAS} = PAS Current
S_{active} = Particle active surface area
F = Surface chemistry factor

Working Principle

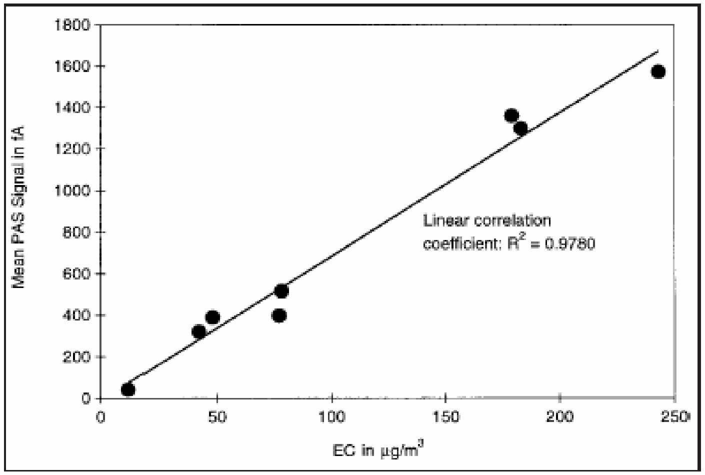
What does the PAS measure...

The PAS analyzer estimates TOTAL PARTICLE BOUND PAH. The analyzer signal has also been correlated to other related compounds like Soot, Elemental Carbon and Black Carbon.

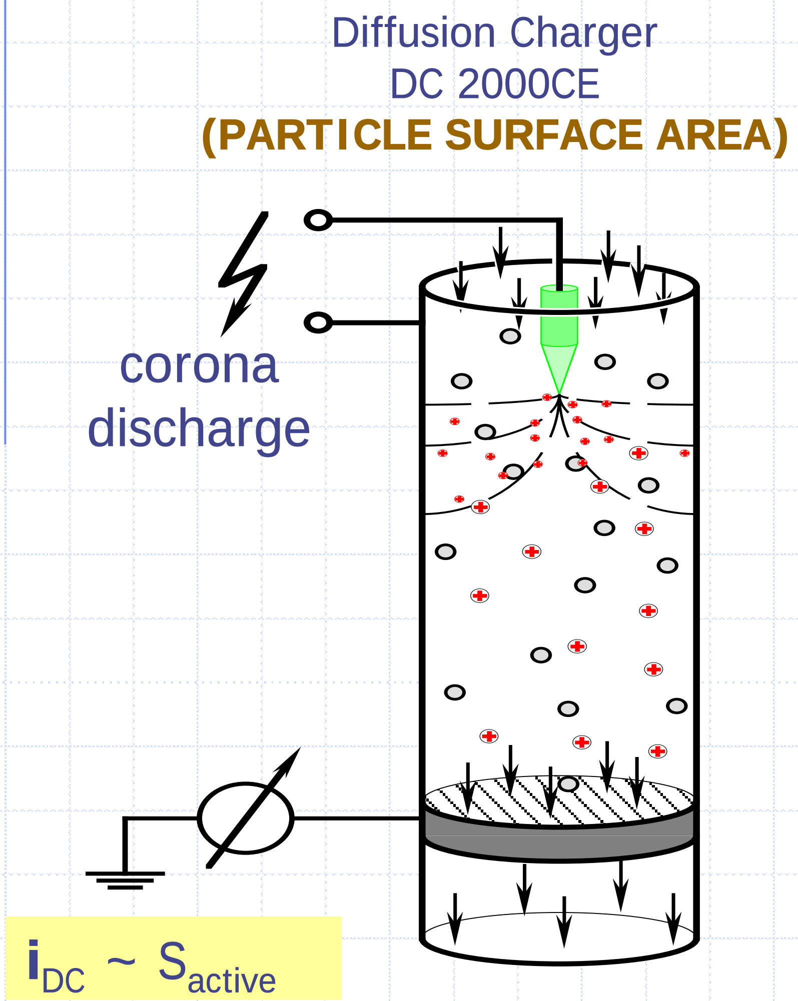
PAH

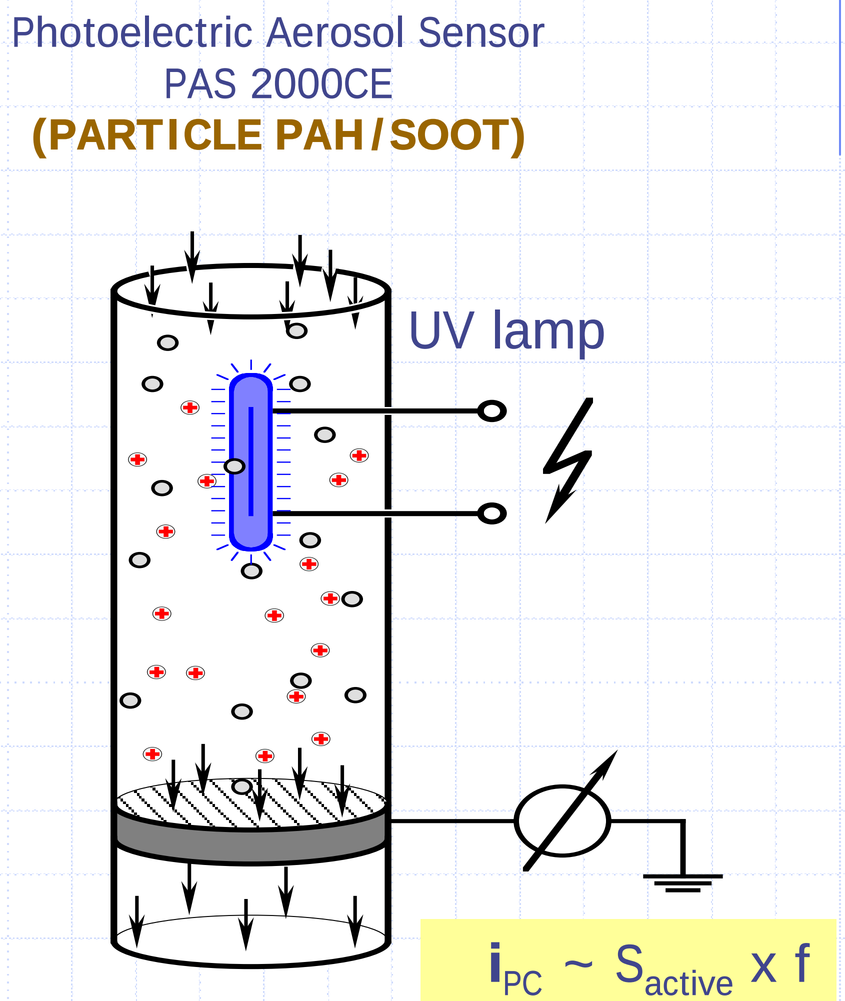


Elemental Carbon

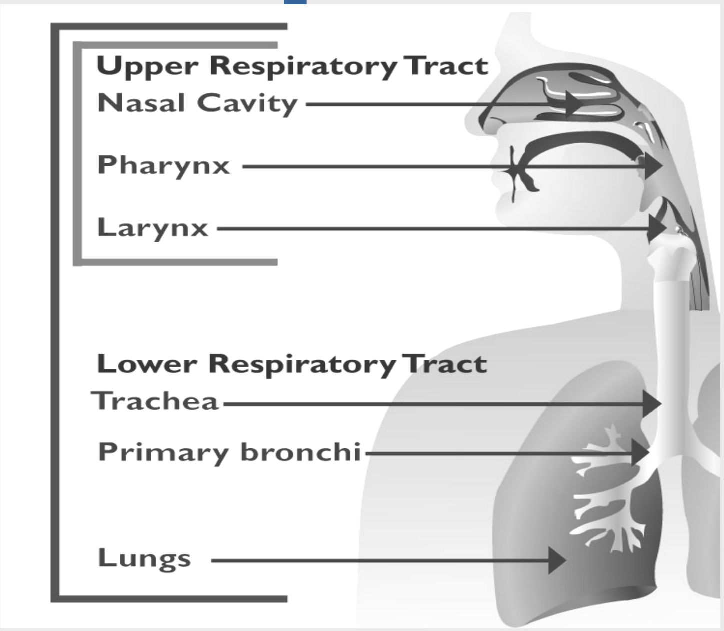


Complementary Measurements





Health Risk Perspective

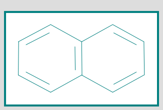


What are PAH

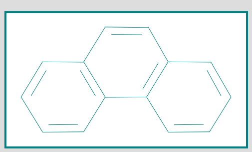
- PAH – are POLYCYCLIC AROMATIC HYDROCARBONS … also frequently referred to as Polynuclear Aromatic Compounds (PNA)
- PAH are primarily products of incomplete combustion

TYPICAL PAH COMPOUNDS

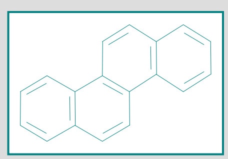
Naphthalene



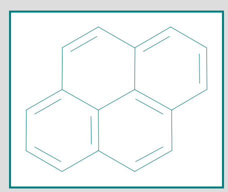
Phenanthrene



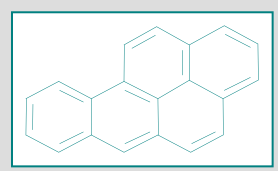
Chrysene



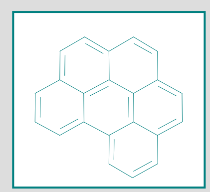
Pyrene



Benzo(a)pyrene

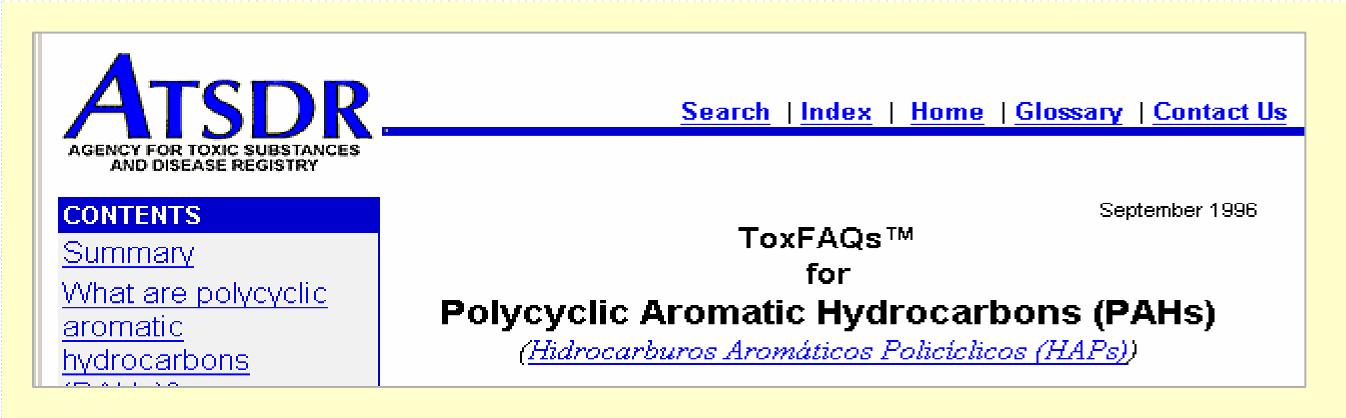


Benzo(g,h,i)perylene



Why measure PAH Compounds

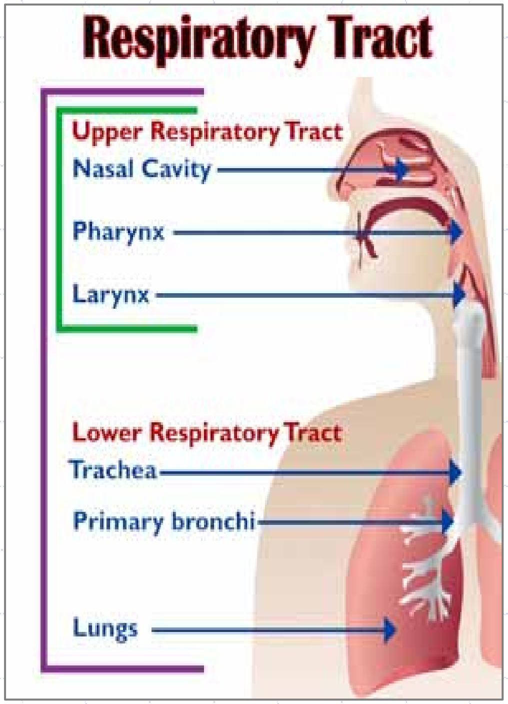
- The U.S. Department of Health and Human Services has determined that PAHs may reasonably be anticipated to be carcinogens.
- Several of the PAHs, including benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, have caused tumors in laboratory animals when they ate them, when they were applied to their skin, or when they breathed them in the air for long periods of time.
- Reports in humans show that individuals exposed by breathing or skin contact for long periods of time to mixtures of other compounds and PAHs can also develop cancer.



http://www.atsdr.cdc.gov/tfacts69.html

Why measure Particle Surface Area

- Ultrafine particles act as carriers of toxic compounds (like PAH) and are transported to the lower respiratory tract.
- Ultrafine particles have an extremely large surface area which is not adequately reflected by taking a particle weight measurement (traditional method for estimating particle concentration).
- Health risk posed by ultrafine particles is more related to measurement of the Particle surface area since the particle surface is a better measure of estimating the amount of toxic compounds that can be transported by the ultrafine particles.



Health Risk Perspective

Why use a combination of Instruments

The combination of the Photoelectric Aerosol Sensor (PAS 2000CE) which measures particle chemistry (PAH) and the Diffusion Charger (DC2000CE) which measures particle surface area provides an approximate estimate of the health risk posed by exposure to ultrafine particles.

Surface Area

+

Surface Chemistry

=

Estimate of ultrafine particulate health risk

Health Risk Perspective

Analyzer Operations

Front Panel

Digital Display (LCD)

Power Supply (LED)

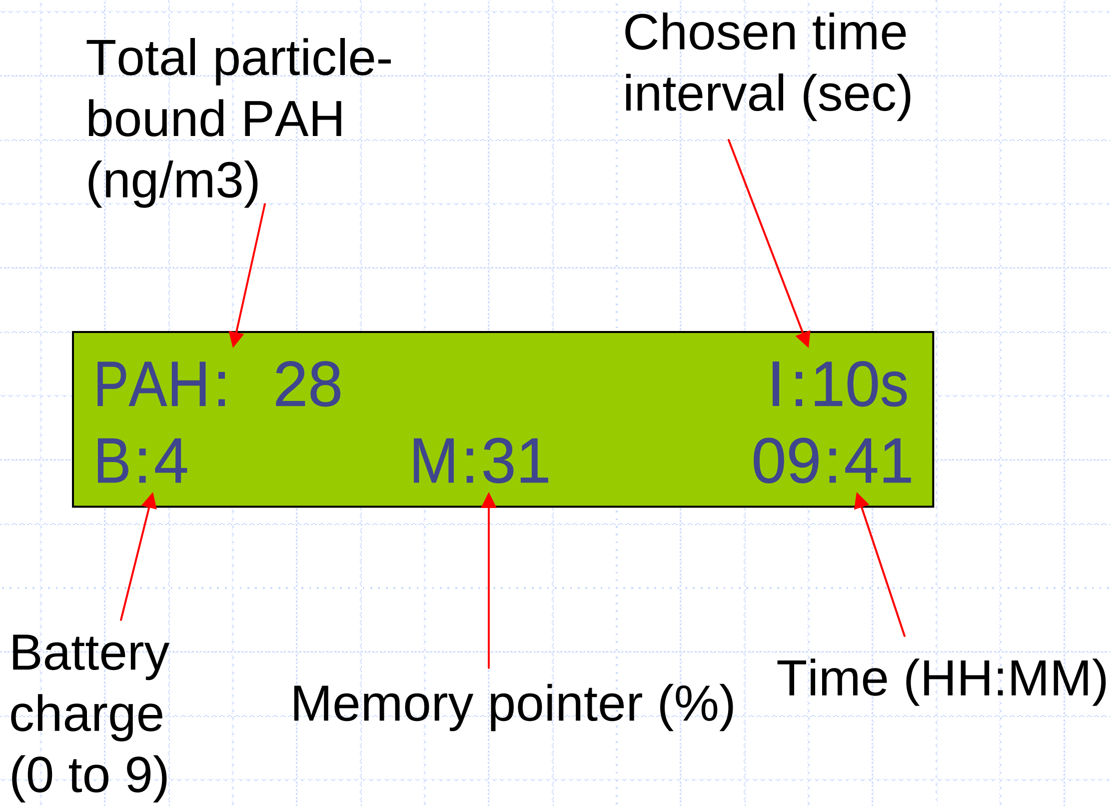
Operation Status (LED)

Air Intake

OFF switch

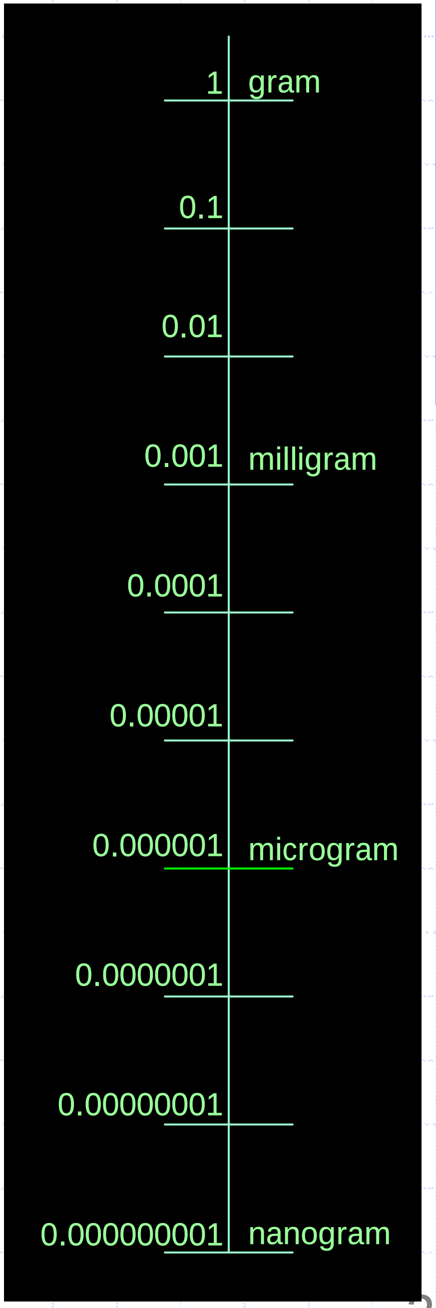
ON switch along with Illumination of digital display

LCD on Front Panel



Instrument Readings

- Measurements made by the PAS 2000CE are ng/m3 (nanogm per cubic meter) of PPAH (particle-bound PAH)
- Measurements made by the DC 2000CE represent mm2/m3 (millimeter squared per cubic meter) of particle surface area



Front Panel Diagnostic Messages

A exclamation mark "!" next to the memory number indicates that the memory is filled and new data values are overwriting old ones.

The battery charge level is a "normalized" number between 10 ("fully charged") and 0 ("no charge")

```
PAH:  28                I:10s
B:4          M:31!      09:41
```

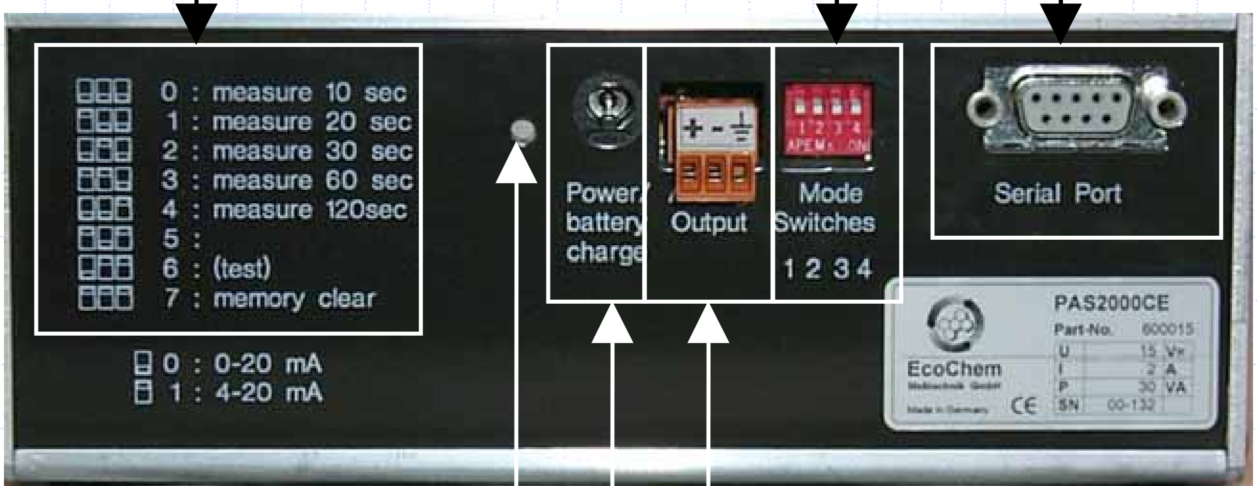
Back Panel

Related functionality

Table for different operation modes

Switches for choosing operation modes

Digital output RS-232 port



Reset button

Analog output (voltage or current)

Battery and Power

Measurement Modes

Mode	Storage time interval	Measurement and display time interval	Resolution of measurement
0	10 sec.	5 sec.	30 sec.
1	20 sec.	5 sec.	30 sec.
2	30 sec.	5 sec.	30 sec.
3	60 sec.	10 sec.	60 sec.
4	120 sec.	20 sec.	120 sec.

Back Panel of Instrument

Analyzer Operations

Choice of Measurement Mode

Mode	Storage time interval	Measurement and display time interval	Resolution of measurement
0	10 sec.	5 sec.	30 sec.
1	20 sec.	5 sec.	30 sec.
2	30 sec.	5 sec.	30 sec.
3	60 sec.	10 sec.	60 sec.
4	120 sec.	20 sec.	120 sec.

- Modes 0 - 2 offer high time resolution data
- Modes 3 – 4 increase the total time interval that can be stored in the internal memory of the instrument
- Choose a mode that is optimum for your application!

Starting and Terminating a Measurement

Press ON/L button for Starting

ON – for starting a measurement

L – "Light" digital display is lit when switch is pressed

Press OFF button for Terminating

There maybe a slight time delay in shutdown after the OFF switch is pressed

Recording a Measurement

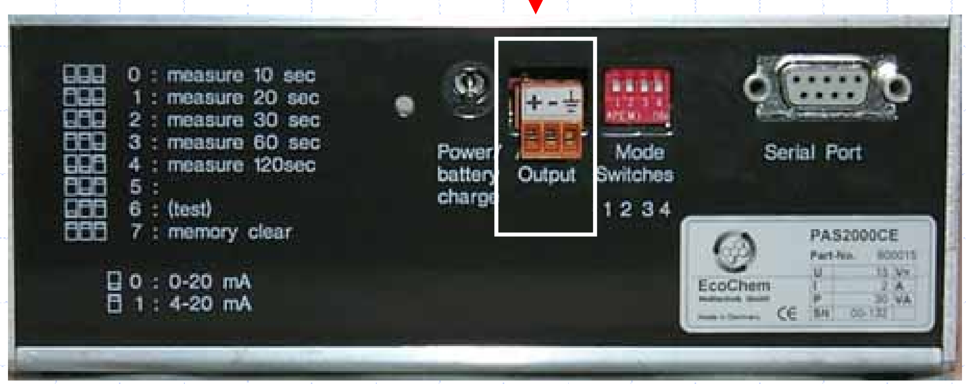
- Values are automatically written in the internal memory of the instrument. The internal memory is approximately 8000 data points

- If you wish to collect real-time data using the analog outputs (current or voltage) you have to connect the instrument to external power.

Analog Output Scaling

PAS 2000CE: 0-4000 ng/m3 corresponds to 0-10 volts or 0-20 mA
DC 2000CE: 0-1000 mm2/m3 corresponds to 0-10 volts or 0-20 mA

Back Panel of Instrument



Software Installation

- Move software from CD-ROM to PC
- No installation program – simply **COPY** files from CD-ROM to hard disk
- Establish a shortcut to the **AIRQUAL** program

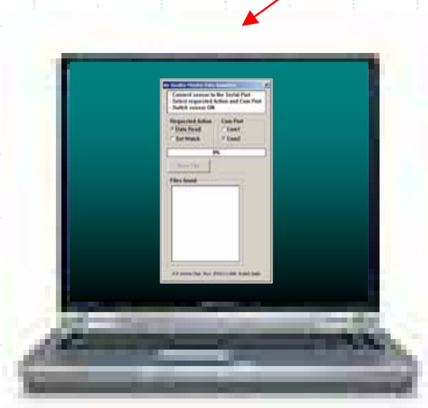
Airqual.exe

Airqual.exe

Communicating with the Instrument

- Use the serial cable provided with instrument to connect PC to analyzer

Serial cable

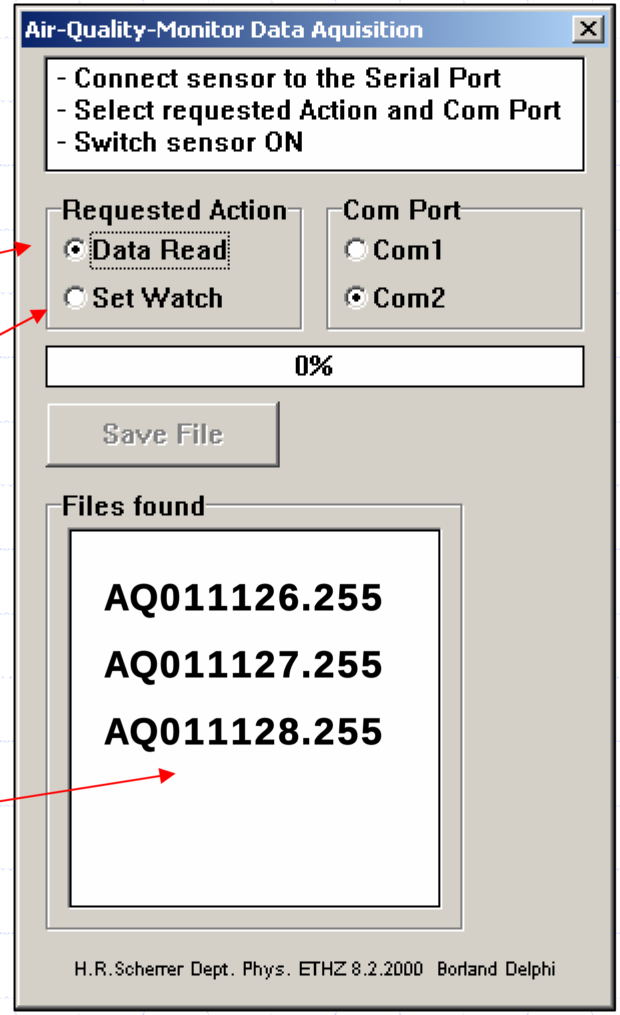


Computer

Back Panel of Instrument

Software Overview

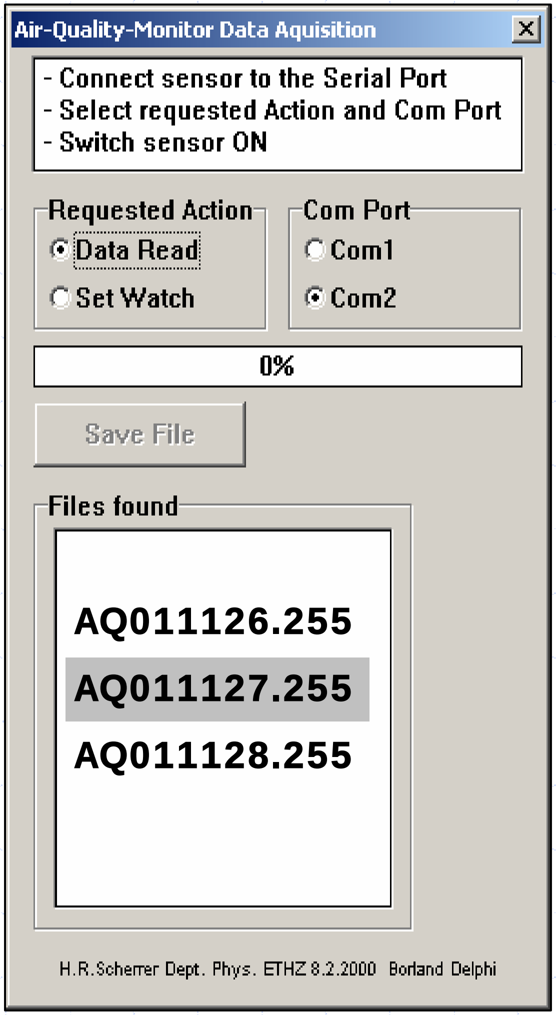
- Run AIRQUAL
- Use program to DOWNLOAD DATA
- Use to set TIME and DATE



This box will contain data file names that exist on your analyzer

Detailed Download Sequence

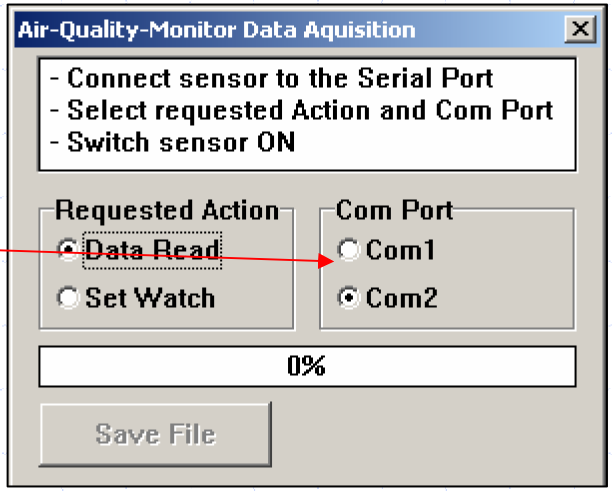
1. Put OFF the analyzer
2. Connect analyzer to computer with serial cable
3. Start AIRQUAL program
4. Select "Data Read" as the Requested Action
5. Select correct COM Port
6. Switch ON the analyzer
7. Wait for the analyzer to start the download mode
8. Select the file to be downloaded
9. Press the "Save File" button to save the file on the computer



Analyzer Operations

Communication Port

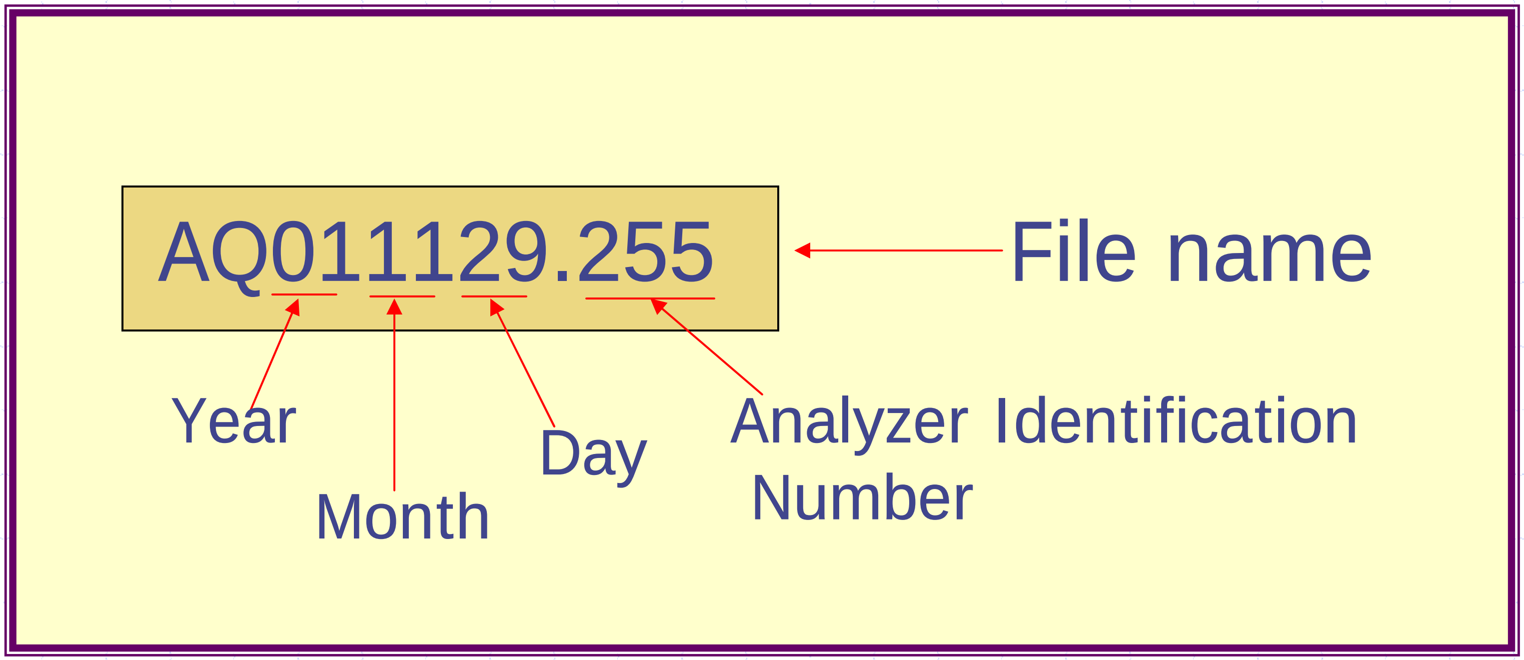
- Select correct COM port (used by RS-232 serial cable)
- If you have a computer without an RS-232 serial port you need a USB to Serial port converter (commonly available at computer stores)



Typical USB/Serial Adapter
Made by Belkin

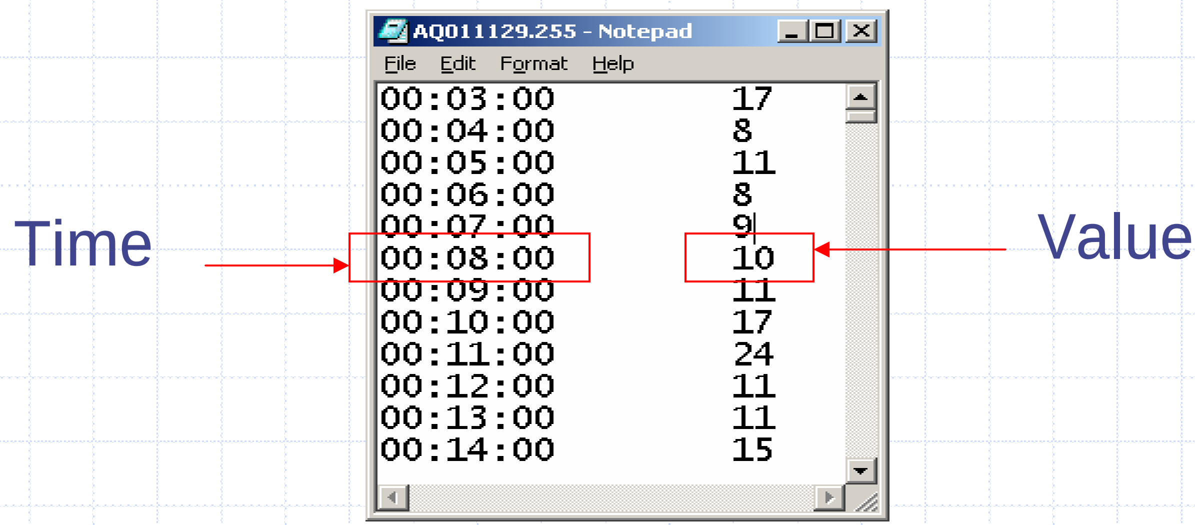
Analyzer Operations

Data File Name Assignment



Data File Contents

- Plain text file
- Time and Value on each line
- Open with Notepad, Word, Excel etc



Software Download Troubleshooting Tips

1. Make sure that you are using the correct serial cable.
2. The serial cable should be connected to the right serial port on the computer (make sure you know whether it is COM1 or COM2).
3. In order to download a file, you have to first select the file by highlighting it.
4. Follow the right sequence to ensure a smooth download.
5. Once you connect the analyzer and the computer, power OFF and ON the analyzer to begin communication

Power for Instruments

1. In the battery-mode the analyzers can be used continuously for 4-6 hours.
2. When connected to the recharger/power supply unit it can be run continuously without interruption while the battery is being charged at the same time.
3. It takes approximately 8 hours to fully recharge the batteries. It is not possible to overcharge the batteries, i.e. when they are left on the power supply while the monitor is switched off.

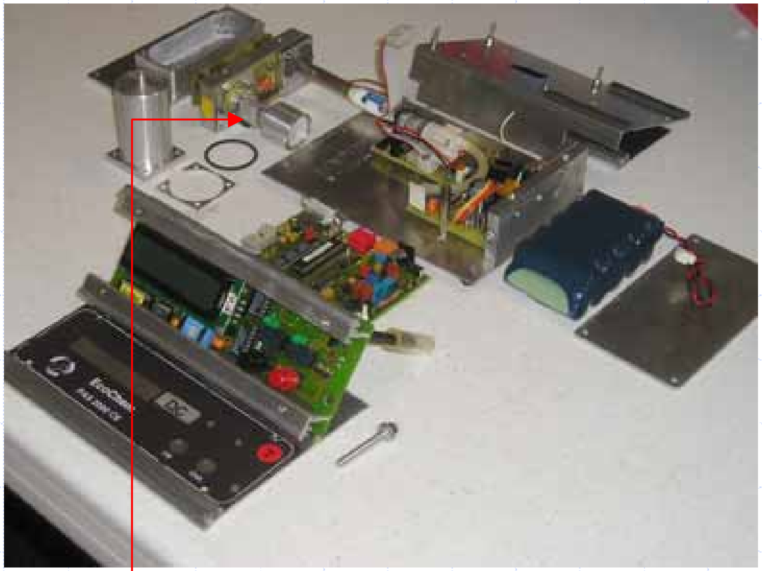

Internal Battery Pack


External power supply unit

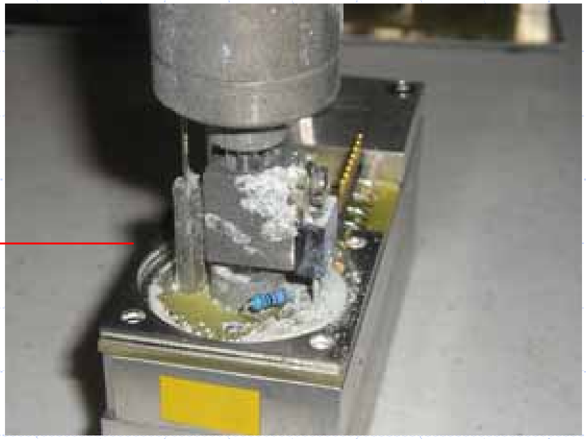
Service and Maintenance

Training and Maintenance Interval

- Both instruments are sensitive electronic devices and should be serviced only by appropriately trained personnel.
- Depending upon usage of the instruments, it is typically recommended that the instrument be sent back to the factory for service and maintenance every 12 to 24 months.



Analyzer components during service



Service needed for an Electrometer

Precision Components

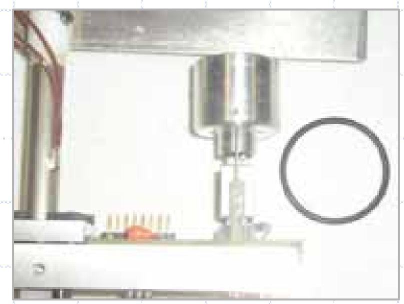

Pump


UV Lamp

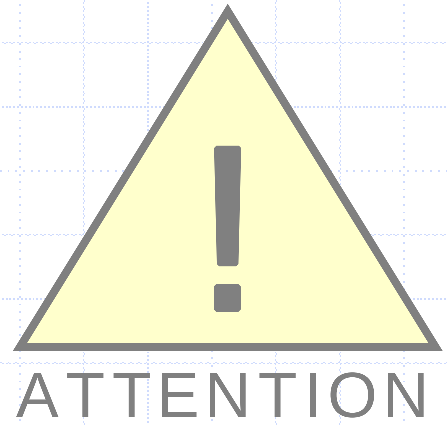

Corona Discharge


Circuit Board


Assembly


Electrometer

Other Activities…



Call for assistance before doing these activities!

- Software is provided for re-setting the analyzer identification number and the calibration factor
- Sometimes you may have to open the analyzer to disconnect the internal battery or to replace an internal fuse

Call for assistance before doing these activities!

When in doubt...

- Refer to the User's Guide
- Contact EcoChem by sending email to info@ecochem.biz

User's Guide...

Photoelectric Aerosol Sensor
(PAS 2000CE)

Diffusion Charger
(DC 2000CE)

EcoChem Analytics

Analyzer Applications

Exploratory study of particle-bound polycyclic aromatic hydrocarbons in different environments of Mexico City

Erik Velasco[a,*], Philip Siegmann[b], Hans C. Siegmann[c]

[a] *Laboratory for Atmospheric Research, Department of Civil and Environmental Engineering, Washington State University, Pullman, WA 99164-2910, USA*

[b] *Department*

[c] *S*

Rec

Abstract

Fine Particulate Matter and Polycyclic Aromatic Hydrocarbon Concentration Patterns in Roxbury, Massachusetts: A Community-Based GIS Analysis

Jonathan I. Levy,[1] E. Andres Houseman,[2] John D. Spengler,[1] Penn Loh,[3] and Louise Ryan[2]

[1]Department of Environmental Health, Harvard School of Public Health, Boston, Massachusetts, USA; [2]Department of Biostatstics, Harvard School of Public Health, Boston, Massachusetts, USA; [3]Alternatives for Community and Environment, Roxbury, Massachusetts, USA

Given an elevated prevalence of respiratory disease and density of pollution sources, residents of Roxbury, Massachusetts, have been interested in better understanding their exposures to air pollution. To determine whether local transportation sources contribute significantly to exposures, we conducted a community-based pilot investigation to measure concentrations of fine particulate matter (particulate matter < 2.5 µm; $PM_{2.5}$) and particle-bound polycyclic aromatic hydrocarbons (PAHs) in Roxbury in the summer of 1999. Community members carried portable monitors on the streets in a 1-mile radius around a large bus terminal to create a geographic information system (GIS) map of concentrations and gathered data on site characteristics that could predict ambient concentrations. Both $PM_{2.5}$ and PAH concentrations were greater during morning rush hours and on weekdays. In linear mixed-effects regressions controlling for temporal autocorrela-

visibility of the pollution sources. Dudley Square once housed an elevated train station, but this station was converted to a major bus terminal and transportation hub when the train was rerouted and the elevated tracks were removed in the 1980s. A recent survey by Alternatives for Community and Environment (ACE) found that 15 bus and truck depots are located within a 1.5-mile radius of Dudley Square, garaging more than 1,150 diesel vehicles, including approxi-

Example Application Paper

Environ. Sci. Technol. **2004**, 38, 2584−2592

Vehicle Traffic as a Source of Particulate Polycyclic Aromatic Hydrocarbon Exposure in the Mexico City Metropolitan Area

LINSEY C. MARR, LISA A. GROGAN, HENRY WÖHRNSCHIMMEL, LUISA T. MOLINA, AND MARIO J. MOLINA*

Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

THOMAS J. SMITH

Department of Environmental Health, Harvard School of Public Health, Boston, Massachusetts 02115

ERIC GARSHICK

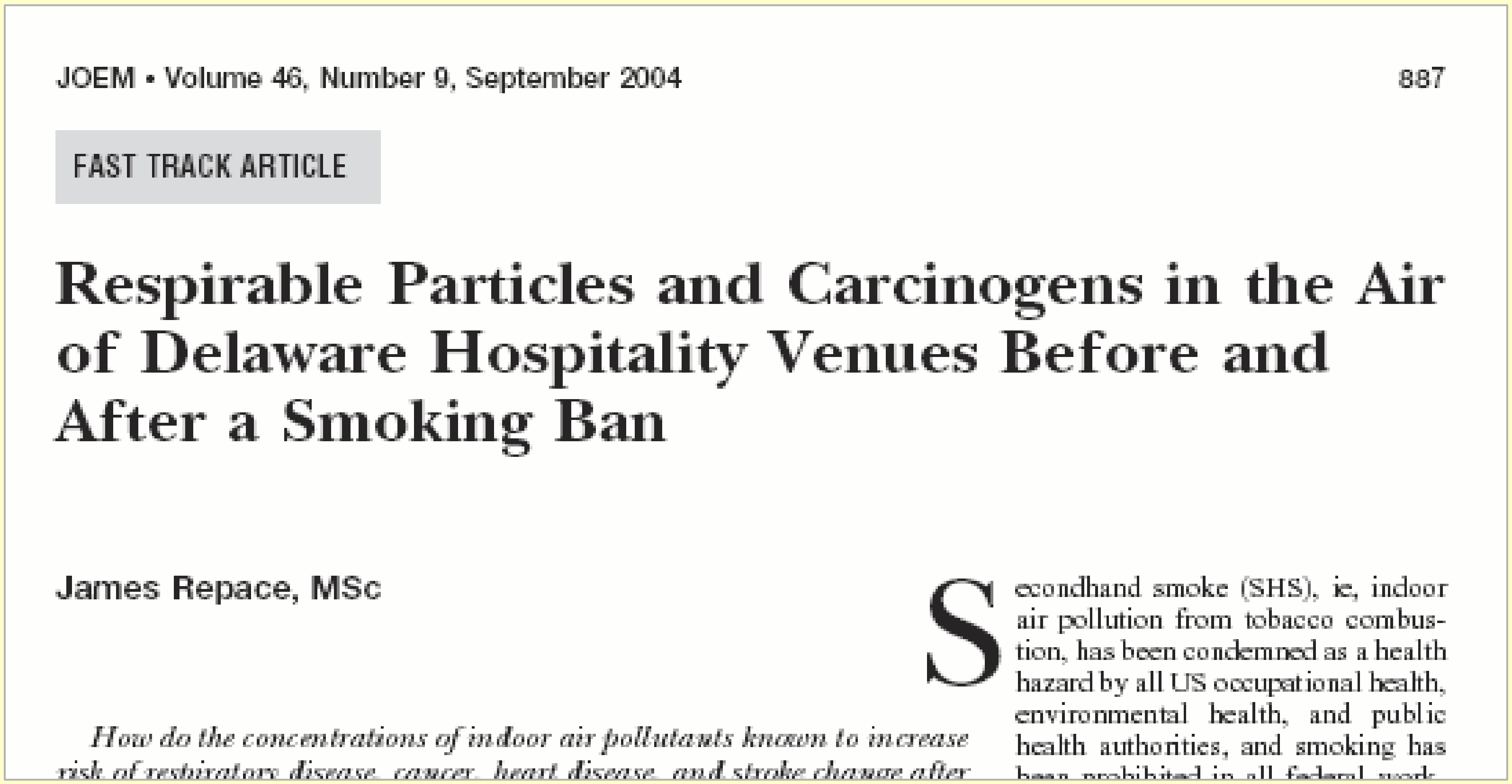
Pulmonary and Critical Care Medicine Section, VA Boston Healthcare System, Boston, Massachusetts 02132, and Channing Laboratory, Department of Medicine

air pollution (*1*). Due to methodological constraints, the quantification of particulate matter has focused mainly on mass and number properties. However, surface properties of particles may be at least as important as mass in assessing their health effects (*2, 3*). Surface properties also affect hygroscopicity (*4, 5*) and heterogeneous chemistry—gas–particle reactions that could alter their chemical composition. New methods allow fast, continuous characterization of aerosol photoemission activity and active surface area using portable, battery-powered instruments. Particulate polycyclic aromatic hydrocarbons (PAHs)—combustion byproducts which include some potent carcinogens and mutagens—can be detected by photoemission induced by exposure to ultraviolet light (*6*).

The Mexico City metropolitan area (MCMA) is making progress in improving its air quality, but the city's nearly 20 million inhabitants, 3.5 million vehicles, 35000 industries, semitropical latitude, ring of mountains, and 2200 m altitude all contribute to a challenging air quality problem. Ozone levels exceed the health-based standard, which is equivalent to the U.S. standard, on approximately 80% of all days; concentrations of particulate matter of diameter 10 μm and less (PM_{10}) exceed the standard on more than 40% of all days in most years (*7*). While the literature on particulate matter

Contact info@ecochem.biz for other studies

Example Application Paper (Contd.)



JOEM • Volume 46, Number 9, September 2004 887

FAST TRACK ARTICLE

Respirable Particles and Carcinogens in the Air of Delaware Hospitality Venues Before and After a Smoking Ban

James Repace, MSc

How do the concentrations of indoor air pollutants known to increase risk of respiratory disease, cancer, heart disease, and stroke change after

Secondhand smoke (SHS), ie, indoor air pollution from tobacco combustion, has been condemned as a health hazard by all US occupational health, environmental health, and public health authorities, and smoking has been prohibited in all federal work-

Contact info@ecochem.biz for other studies

THANK YOU

Questions & Answers ?

For more information…

EcoChem Analytics

Email: info@ecochem.biz

User's Guide...

Photoelectric Aerosol Sensor
(PAS 2000CE)

Diffusion Charger
(DC 2000CE)

EcoChem Analytics

Disclaimer

Certain products mentioned in this User's Guide may be trademarks. These products have been mentioned for identification purposes only.

Version Number

Edition	Month / Year	Valid for Software Version
2.0	May 2012	1.1

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202 Reynolds
League City, TX 77573
USA

Part No: PAS2000-006, DC2000-006

Edition 2.0

Release 6.15

Acknowledgement

This User's Guide uses some documentation text originally written by Dr. Reinhold Wasserkort, MIT and Leo Scherrer, Swiss Federal Institute of Technology, Zurich. Their contributions are kindly acknowledged.

Table of Contents

CUSTOMER SERVICE

We at EcoChem want to provide you with the very best customer service possible. If you have any questions, problems or comments about the PAS 2000CE or DC 2000CE, we would like to hear from you.

The PAS 2000CE and DC 2000CE are sensitive electronic instruments. It is recommended that all maintenance and repair work on the PAS 2000CE and DC 2000CE should only be done by customer service or appropriately trained personnel.

You can reach us at:

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SAFETY INSTRUCTIONS

In this User's Guide we will try to indicate explicitly hazardous situations that may result in potential personal injury or damage to the instrument.

Please read this User's Guide carefully before installing and using the instrument. In particular, please pay attention to paragraphs that refer to possible hazardous situations.

Warnings and references are presented as follows:

Warning	Indicates that non-compliance with the instructions can lead to potential personal injury.

Attention	Indicates that the instructions must be followed explicitly to avoid damage to the instrument.

Warning

Voltage

Danger of potential injury

- Always run the instrument with a ground connection (earthing).
- Under no circumstances remove or open the internal ground connection.
- If the instrument is switched on, the electrical connections are charged. Hence do not attempt to touch internal components when the instrument is switched on. Internal components should only be touched or removed when the monitor has been switched off.
- **The power supply is operated at high voltage. Do not attempt to touch the power supply when the instrument is switched on.**

The following general guidance should be followed during operation of the PAS 2000CE or DC 2000CE instruments:

- Do not touch the interior components of the instrument when it is switched on.
- Never operate the instrument if the cover or any other parts the instruments are removed.
- Customer service or appropriately trained personnel should only do maintenance and repair work.
- If you observe that the instrument has insufficient grounding or that the grounding connection is damaged, please take the instrument out of operation and prevent unauthorized use of the instrument.

Some situations leading to insufficient instrument grounding include:

- Instrument has visible physical damage.
- Instrument was stored for a long time under unfavorable conditions (e.g. high humidity environments).
- Instrument was handled improperly during transportation and shipping.

! **Warning**	Explosive gases in the operating environment The instrument should never be operated in an explosive environment.

Some other environments that can lead to operating problems and should be avoided include:

- Outdoor environments where the instrument is not appropriately protected from nature's elements (sun, rain and snow).
- Excessively high humidity environments.

1 INTRODUCTION

This User's Guide describes the PAS 2000CE and DC 2000CE instruments. These instruments are very similar in functionality and either measure particle-bound PAH (PAS 2000CE) or particle surface area (DC 2000CE).

Chapter 2 provides information regarding the **Measuring Principle** of the instruments. Chapter 3 describes **Operating Procedures** for the Instruments. Chapter 4 discusses **Service and Maintenance**. Chapter 5 presents the **Technical Specifications**.

Appendix A provides a **Discussion on Polycyclic Aromatic Hydrocarbons**. It contains a discussion of PAH compounds, their formation, sources of PAHs, human exposure, toxicity and associated regulations.

Appendix B provides a Discussion on **Particle Surface Area and Related Concepts.** Active surface area definition and measurements are discussed in this Appendix.

Attention

This User's Guide does not contain instructions for doing Service and Maintenance of the PAS 2000CE and DC 2000CE instruments. Both instruments are sensitive electronic devices and should be serviced only by appropriately trained personnel. Depending upon usage of the instruments, it is typically recommended that the instrument be sent back to the factory for service and maintenance every 12 to 24 months.

Attention

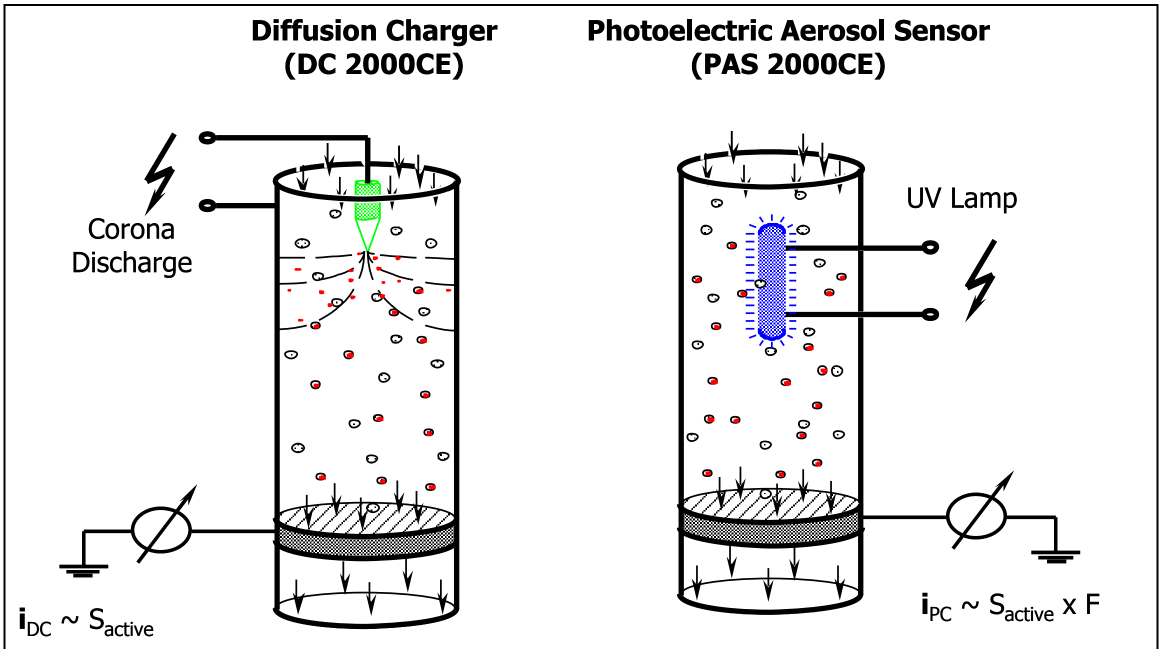
The units for readings of the PAS 2000CE are ng/m^3 (nanogram per cubic meter).
The units for readings of the DC 2000CE are mm^2/m^3 (millimeter squared per cubic meter)

Attention

Measurement of particle-bound PAH and active surface area is an evolving field. Hence the PAS 2000CE and DC 2000CE results must be interpreted within the right context. The instruments are provided with approximate general calibration factors. However every particle system has its own characteristic (physical and chemical properties, size distribution, surface area, morphology etc). In order to get accurate site-specific or source-specific readings you can establish a calibration factor for your own instrument by comparing the PAS 2000CE readings to chemically analyzed samples and the DC2000CE readings to other particle measuring instruments.

2 MEASURING PRINCIPLE

The DC 2000CE and the PAS 2000CE are very similar instruments. The basic difference between the two instruments is the charging mechanism employed by the instruments. The DC 2000CE uses a corona discharge for diffusion charging while the PAS 2000CE uses a UV lamp for photoionization. The DC 2000CE signal is a measure of the particle active surface area while the PAS 2000CE signal is a measure of the particle-bound Polycyclic aromatic hydrocarbons (PAH).



S_{active} – Particle active surface area

F – Factor associated with the chemical composition of the particle surface

i_{DC} – Current measured due to Diffusion Charging

i_{PC} – Current measured due to Photoelectric Charging

Fig. 1: Comparison of the Measurement Principle for the Diffusion Charger and the the Photoelectric Aerosol Sensor

2.1 Photoelectric Aerosol Sensor

The photoelectric aerosol sensor is based on the photoelectric ionization of particles. If one irradiates ultrafine particles with light having energy hν and if this energy is larger than the photoelectric threshold function, the particle emits a photoelectron. After photoemission, the original donor particle becomes a positively charged particle.

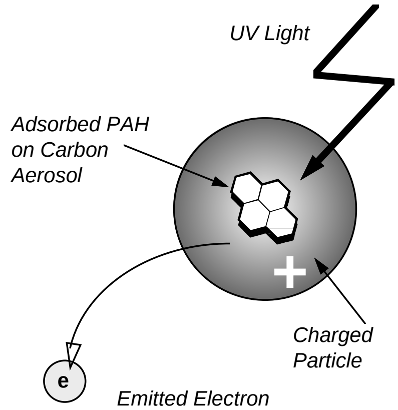


Fig. 2: Principle of the Photoelectric Aerosol Sensor

By themselves, the particles are not capable of photoemission. However the particles frequently have a layer of PAH, which are condensed or adsorbed on the surface. These surface bound PAH molecules can be easily photoionized.

A free gas molecule or another charged particle can capture the photoelectron emitted from a particle. The recapture probability (i.e. chance that the photoelectron meets a charged particle or encounters a neutral gas molecule) is high for large particles. From this it follows that photoemission is especially effective for small particles in the ultrafine region. This group of ultrafine particles is however of particular interest, because these particles are capable of reaching the lower respiratory tract and pose maximum health risk concerns.

The charge created by photoemission can be modeled as:

$$dN^+ / dt = f \{ \Phi_{UV}, \pi(rp)^2, Y(h\nu), F, N \}$$

where

N^+	= Number of positive charged particles
t	= Time
Φ_{UV}	= Light intensity
$\pi(rp)^2$	= Illuminated cross section of the particles
$Y(h\nu)$	= Photoelectric yield (depending on the light energy)
F	= Fraction of particle surface capable of photoemission
N	= Number of particles

With Φ_{UV}, $\pi(rp)^2$, $Y(h\nu)$, N being constant, the charge rate is a direct measure of the PAH concentration. This charge is measured by the PAH sensor. For a reproducible measurement it is most important that the lamp energy, particle geometry and chemical composition remain essentially constant. From previous scientific studies, it has been observed that most combustion sources have a unique “PAH-signature“, i.e. within a specific operating range, a combustion source will consistently produce similar PAH along with a specific particle size distribution.

The dependence of the charge production on the lamp intensity is non-linear and varies between different applications. Therefore all instruments are delivered with normalized lamp intensity. The lamp intensity is automatically controlled internally to avoid a drift of the sensitivity during the lifetime of the lamp. In addition the flowrate of the instrument is also controlled at a constant value of 1 liter/min.

2.1.1 Measuring Principle for Photoelectric Aerosol Sensor

The measuring principle of the instrument is illustrated in Fig. 3. The particle-loaded flow is passed through a quartz tube. Around the quartz tube an excimer lamp is mounted. The excimer lamp is a hollow double-wall quartz tube. The hollow space (2 mm thickness) between the concentric walls is filled with Krypton (approx. 300 mbar) and traces of Bromine. The electrodes are external to the lamp. The outer electrode of the lamp is a metallic reflecting tube. The inner electrode is transparent to the light. The lamp is operated at high frequency and at high voltage. The lamp radiation occurs at 207 nm with an approximate half-bandwidth of 2%. A silicon detector measures the intensity of the fluorescence radiation in a quartz tube. This signal is used for monitoring the intensity of the lamp.

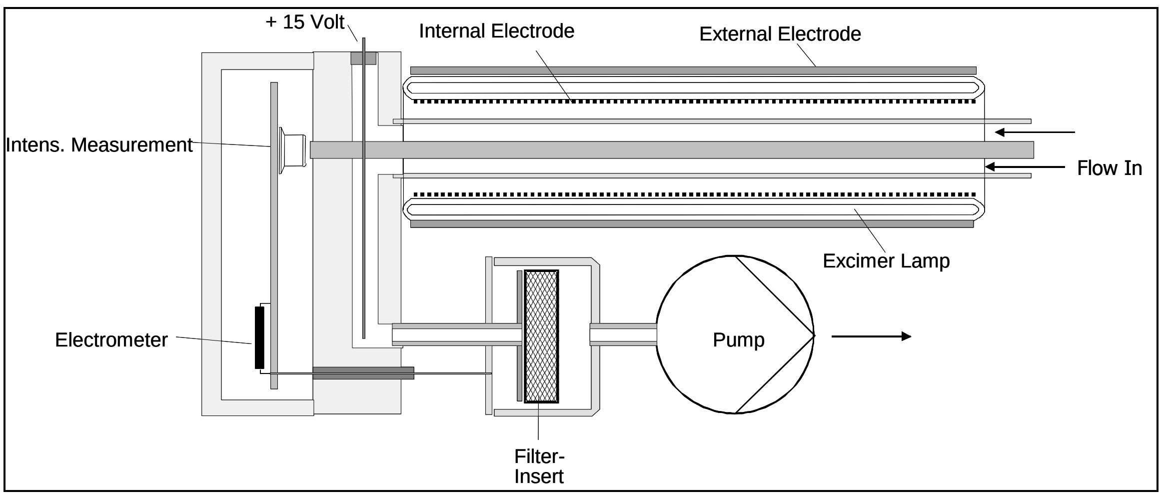


Fig. 3: Process Schematic for the Photoelectric Aerosol Sensor

The charged particles then flow through a short tube before entering a filter component. Within this tube a small voltage is applied to remove all negatively charged particles safely. Subsequently the charged particles are collected on a filter element, which is mounted in a Faraday cage. The electrical current associated with the ion current is shunted over an electrometer and measured. The flowrate of the pump is 1 liter/min approx.

PAH-sensors manufactured in the past used a mercury lamp, which was operated on a continuous basis. The mercury lamp requires a warm-up time and hence always had to be switched on. The advantage of the excimer lamps is that they can be switched on and off without any delay. The use of the excimer lamp in a pulsed mode suggests itself. The measurement signal is obtained by integration over the current pulse produced during the time of exposure. The advantage of this pulsed-mode operation is that any background interference of the signal by precharged particles is avoided. In addition any drift of the baseline is suppressed.

2.1.2 Correlation between Photoemission and Particle-Bound PAH

In principle, aerosol photoemission is possible with solids of very diverse materials such as metals, carbon, salt or others. The efficiency with which they can be charged depends on the work function of each of these different materials, i.e. on the required ionization energy. More important, however, is the composition of the exposed particle surface. Trace amounts of adsorbants on the surface can greatly alter the work function and thus reduce or increase the probability of the emission of an electron (Burtscher and Schmidt-Ott, 1984). If the adsorbant is electropositive compared to the core particle the ionization energy required for photoemission is lowered while the opposite is true for electronegative adsorbates.

In the case of combustion particles the carbonaceous core is covered by a mixture of different organic chemicals. However, experimental evidence suggests that among the different classes present in the organic fraction, only the polycyclic aromatic hydrocarbons reduce the photoelectric workfunction and thus the ionization energy required to induce photoemission.

A direct comparison of aerosol photoemission and the analytical quantification of PAH by means of gas chromatography on different combustion aerosols revealed a good correlation between the photoelectric signal and the total amount of 15 different PAH which were extracted from the organic phase of collected particles (McDow et al., 1990, and Hart et al., 1993). Because of the importance of this finding for the interpretation of the photoemission signal, these data are summarized in Fig. 4. On the x-axis we plot the chemically determined total particle-bound PAH. On the y-axis we plot the raw PAH monitor signal in ampere (A) divided by the monitor flow rate in m^3/s. It is observed that for a wide variety of sources (cigarette smoke, urban air, burners etc.) and for a large range of values (several log cycles) the correlation is very high.

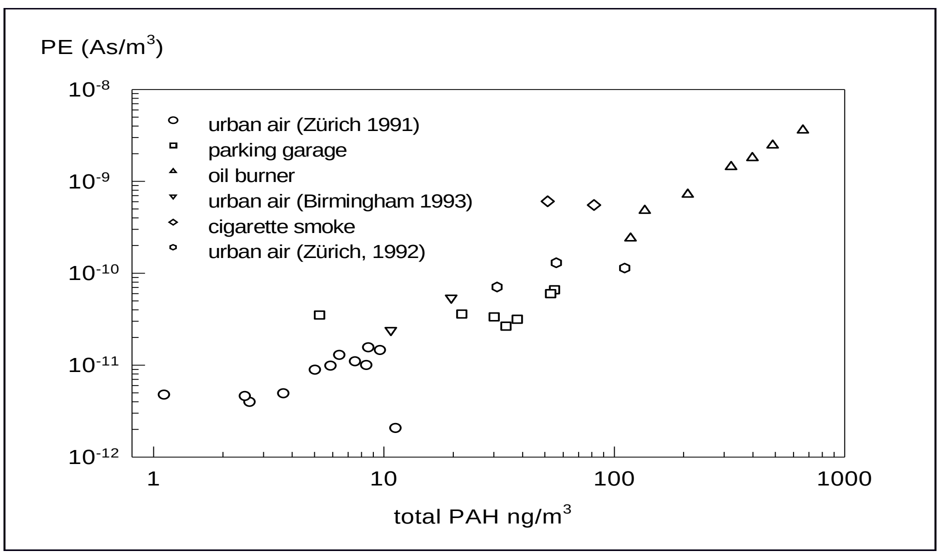


Fig 4. Correlation between chemical analysis of PAH and aerosol photoemission

The irradiation energy and the wavelength of the uv-excimer lamp in the PAS2000CE are adjusted such that only particles with adsorbed PAH will emit photoelectrons while particles, even if in the same size range, without PAH (like dust, tirewear, salt particles, bioaerosols etc.) will not contribute to the charges measured. This defines the specificity of the monitor to combustion particles. The contribution of PAH derivatives, such as nitro- or oxy-PAH, to the photoemission signal is minimal.

The PAS2000CE features a so called lock-in technique which is mainly responsible for the reliable performance with respect to background noise and zero drift. After the excimer lamp emitted uv-light for about 0.3 sec the generated charge-cloud appears at the particle filter. This causes the signal of the amplifier to rise (in proportion to the number of charges) and drop back again quickly to zero level. This takes about 1.0 sec. The operating processor scans this signal 60 times and creates the sum of this. Subsequently the processor scans the recent zero level also 60 times and calculates the sum. The difference between both sums is the background corrected reading of the instrument which is converted into a value that corresponds approximately to the PAH concentration in ng/m^3. The value appearing in the display is the averaged value of the last six measurements. The PAH concentration is obtained by multiplying the actual PAS2000CE measurements with a factor derived from the comparison of this monitor with a similar but calibrated photoemission monitor. The calibration of the latter is based on experimentally determined correlations such as the one shown in Fig. 4.

Current experience with this technical design shows that the monitor can be operated at ambient particle concentrations without the need to clean the filter or other maintenance duties for long periods of time. However, after operating the instrument for over 1 year proper maintenance procedures are recommended.

2.2 Diffusion Charger

The DC 2000CE instrument has a design which is very similar to the PAS 2000CE instrument described previously. The measuring principle is illustrated in Fig. 5 (compare with Fig. 3). Instead of using a UV lamp for photoionization as used in the PAS 2000CE, the DC 2000CE uses a corona discharge for doing diffusion charging of all particles. A detailed explanation of the issues associated with measurement of the particle surface area is presented in Appendix B.

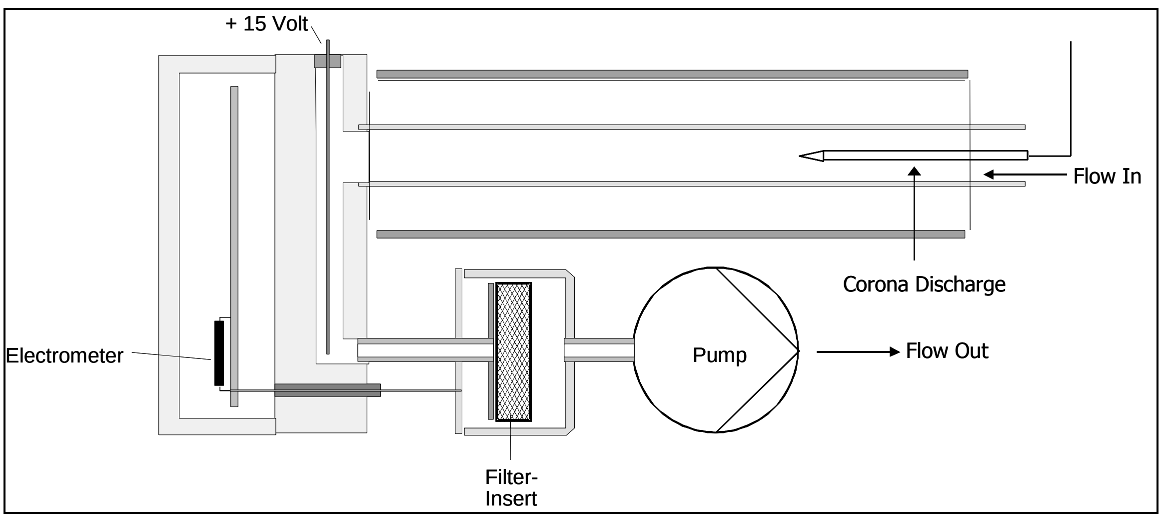


Fig. 5: Process Schematic for the Diffusion Charger

The corona discharge produces a negative oxygen ions by applying a voltage to a thin metallic wire. The negative oxygen ions (more precisely cluster ions with oxygen ion in the center) diffuse in the gas carrying the particles and when they come in contact with the particles they transfer the electrical charge. This is called “diffusion charging“ and depends solely upon the active particle surface area (as opposed to the photoelectric charging which depends upon the chemistry of the surface). The remaining oxygen cluster ions are removed and the current is measured by a Farady cup electrometer (similar to the PAS 2000CE).

Calibration of the DC 2000CE is carried out by comparison to a master/standard instrument. The standard instrument has been calibrated by comparing the DC 2000CE readings with a commercially available differential mobility analyzer to generate particles of specific mobility and measuring them with a condensation nucleus counter. By changing the particle mobility and measuring the diffusion charge the master instrument has been calibrated.

2.4 Calibration Guidance

Attention

Measurement of particle-bound PAH and active surface area is an evolving field. Hence the PAS 2000CE and DC 2000CE results must be interpreted within the right context. The instruments are provided with approximate general calibration factors. However every particle system has its own characteristic (physical and chemical properties, size distribution, surface area, morphology etc). In order to get accurate site-specific or source-specific readings you can establish a calibration factor for your own instrument by comparing the PAS 2000CE readings to chemically analyzed samples and the DC2000CE readings to other particle measuring instruments.

2.5 References

1. Burtscher, H.; Scherrer, L.; Siegmann, H.C.; Schmidt-Ott, A. and Federer, B. (1982) Probing aerosols by photoelectric charging; Journal of Applied Physics, 53, 3787-3791.

2. Burtscher and Schmidt-Ott (1984) In-situ measurement of adsorption and condensation of a polycyclic aromatic hydrocarbon on ultrafine particles by means of photoemission. Journal of Aerosol Science, 17, 699-703

3. Burtscher, H. (1992) Measurement and characterization of combustion aerosols with special consideration of photoelectric charging and charging by flame ions; Journal of Aerosol Science, 23 (6), 549-595.

4. McDow, S.R.; Giger, W.; Burtscher, H.; Schmidt-Ott, A.; Siegmann, H.C. (1990) Polycyclic aromatic hydrocarbons and combustion aerosol photoemission. Atmospheric Environment, 24A, 2911-2916.

5. Hart, K.M.; McDow, S.R.; Giger, W.; Steiner, D.; Burtscher, H.(1993) The correlation between in-situ, real-time aerosol photoemission and particulate polycyclic aromatic hydrocarbon concentration in combustion aerosols. Water, Air and Soil Pollution, 68, 75-90.

6. Keller, A.; Fierz, M.; Siegmann, K.; Siegmann, H. C.; Filippov., A.(2001) Surface Science with nanosized particles in a carrier gas. J. Vac. Sci. Technol. A 19(1), Jan/Feb 2001, 1-8.

3 Operating Instructions

3.1 General

The PAS 2000CE / DC2000CE is a sensitive electronic instrument which also contains fragile glass components and should therefore always be handled very carefully. All mechanical and electrical shocks should be avoided!

The following general guidance should be followed during operation of the PAS2000CE / DC2000CE instruments:

Warning

1. Never operate the instrument if the cover is removed.
2. Maintenance and repair work should only be done by trained personnel.
3. Power supply: the external power supply/battery charger can be operated at both 230V or 110V.
4. Care should be taken under extremely humid conditions! The monitor should be prevented from becoming wet. (If the sensor got wet and is not working properly, it should be placed into a dry place and left there for 1-2 days. This may restore the proper functioning.)
5. **Do not expose the instrument directly to rain or snow!**

The PAS2000CE / DC2000CE is a battery-powered particle measuring sensor. In the battery-mode it can be used continuously for 4-6 hours. When connected to the recharger/power supply unit it can be run continuously without interruption while the battery is being charged at the same time.

The measurement values are stored in the internal memory, as well as the time interval chosen between two measurements. The internal memory of the sensor consists of 16kByte "circular memory" which means it starts at address 0 and ends at address 16383. If more data values are recorded they will overwrite the stored data starting again at address 0. The size of the memory allows the storage of approximately 8000 data points. Note that the PAS2000CE / DC2000CE does not perform a continuous measurement but records individual values each time the chosen time interval has passed. **This value which appears on the display and is stored in the internal memory is the average value of the last six measurements.** The measurement and storage time intervals, however, differ and with this also the obtained resolution of the measurements for the different interval settings. This is summarized in following table:

mode	storage time interval	Measurement and display time interval	resolution of measurement
0	10 sec.	5 sec.	30 sec.
1	20 sec.	5 sec.	30 sec.
2	30 sec.	5 sec.	30 sec.
3	60 sec.	10 sec.	60 sec.
4	120 sec.	20 sec.	120 sec.

3.2 External Features

Fig. 6 (a and b) displays the elements of the front and back panel of the PAS2000CE - DC2000CE. In the Fig. 6c the LCD is diplayed in more detail.

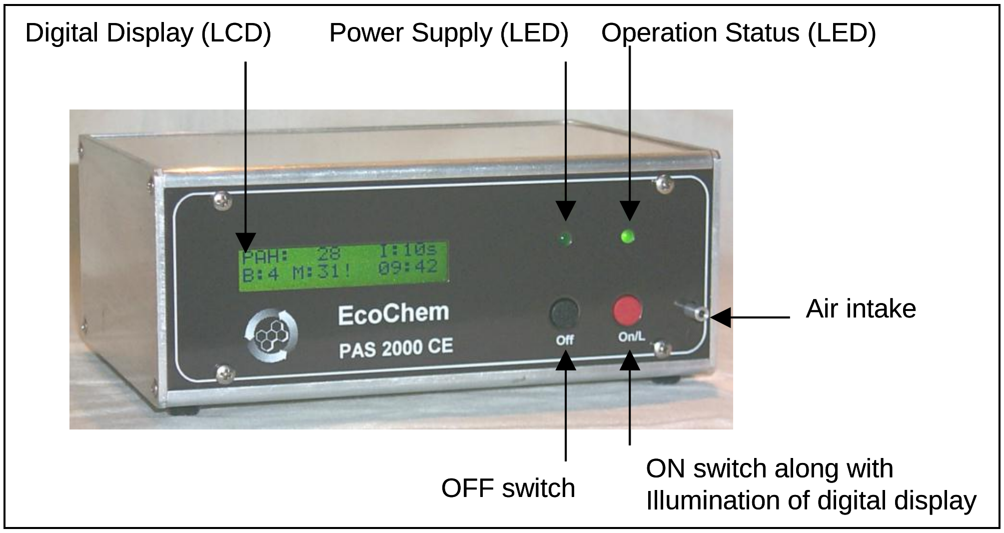


Fig 6a: Front Panel of the PAS 2000CE / DC2000CE

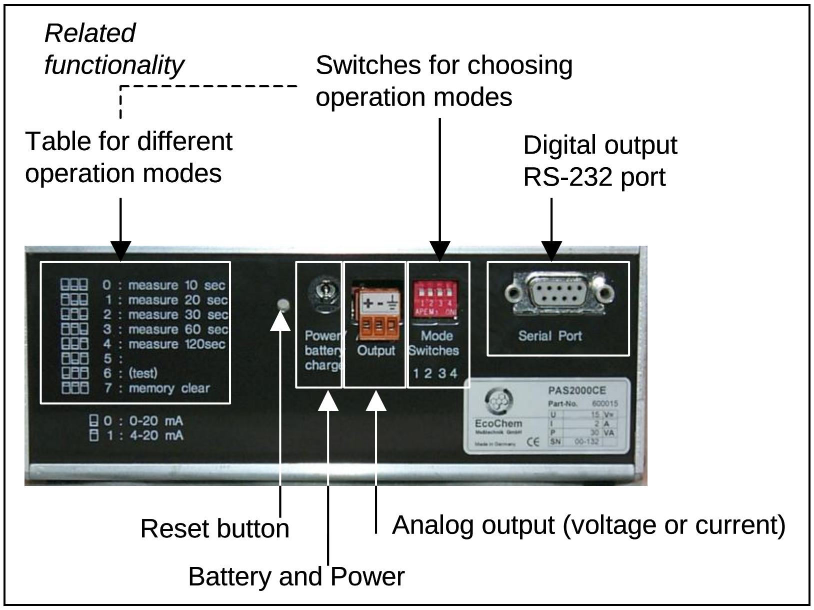


Fig 6b: Back Panel of the PAS 2000CE / DC2000CE

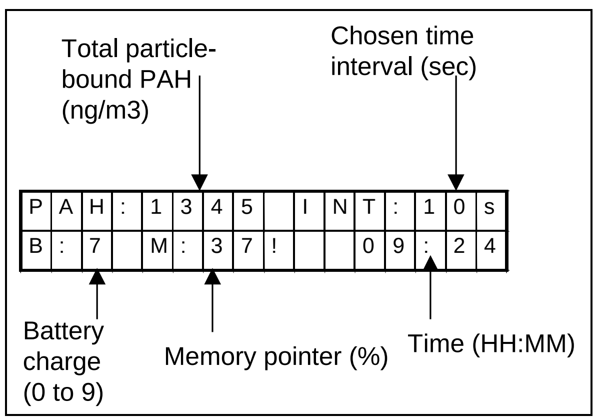


Fig 6c: LCD display of the PAS 2000CE / DC2000CE

3.3 Starting a Measurement

The ON/L switch activates the instrument and also illuminates the digital display but only for as long as the button is pressed -this helps to minimize energy use.

If the monitor is in use, the right LED lits to indicate this operation status. The OFF button deactivates the instrument. It needs to be pressed only briefly (like the ON/L switch) but may not react immediately as the internal program allows termination only during a certain "window".

Therefore in many cases the instrument will switch off only with some delay after the button was pressed.

The air inlet is the only part protruding the front panel so that tubing (e.g. silicone) can be used to extent the inlet. The maximum length of the tubing should not exceed 1m). If the instrument is switched on, the pump can be heard. For running any measurements the operation mode switch has to be in either position 0, 1, 2, 3 or 4 (to select measuring intervals of 10, 20, 30, 60 or 120 sec).

Attention

A change of the interval time becomes effective only after switching the instrument off and then on again!

After briefly pressing the ON switch the LCD displays the present date and time until the next full minute. A one minute initialisation phase follows. Then the measurement starts and the display shows the information as depicted in Fig. 4 c.

The upper line displays the last measured value and the chosen interval time. The value represents approximately the concentration of the total particle bound PAH in ng/m^3 or particle surface area in mm^2/m^3 (see chapter 2 for an explanation of this).

Attention

This value should only be understood as an approximation of the particle-bound PAH concentration or particle surface area, as this is influenced by many factors and conditions which are not yet fully understood.

The lower line displays the current time, the memory "fill level" (in percent) and the charge level of the battery. **An exclamation mark (!) behind the memory level indicates that the memory is filled and the data values are already being overwritten!** The charge level values are from 9 (fully charged) to 0 (empty battery). These values are NOT to be interpreted as hours! When the battery is empty the instrument is switched off automatically. All data until this time are secured in the internal memory. In this situation the battery needs to be recharged.

Attention

The charging of the battery is only to be done with the accompanying power supply/recharger as other models may damage the instrument!

It takes approximately 8 hours to fully recharge the batteries. It is not possible to overcharge the batteries, i.e. when they are left on the power supply while the monitor is switched off. For longer, continuous measuring periods the sensor can be operated while being connected to the power supply. The left LED indicates that the instrument is connected to the power supply.

3.4 Recording a Measurement

When you take a measurment, the values can can recorded in several ways:

By default, the value can recorded in the internal memory of the PAS 2000CE - DC2000CE with an appropriate time stamp. You can then download this data onto your PC.

You can also obtain a real-time analog output in the form of a voltage or current. Connect an appropriate data acquisition device to the port on the back panel of the PAS 2000CE - DC2000CE and you will be able to collect a real-time analog signal.

Attention

The analog output signal has a slight offset as compared to the digital values displayed on the front panel. For large values of the measurment signal this offset is insignificant – however for small values the offset is noticeable.

Attention

While collecting real-time data using the analog output, the PAS 2000CE / DC2000CE instrument must be connected to external power. You will not obtain an analog output signal if you are operating the instrument using the internal battery

By default, the PAS 2000CE / DC2000CE is shipped with an analog output signal of 0 to 10 volts. The scaling for this signal is:

Attention

0 to 4000 ng/m^3 corresponds to 0 to 10 volts for the PAS 2000CE

0 to 1000 mm^2/m^3 correspond to 0 to 10 volts for the DC 2000CE

For some data acquisition applications, it may be desirable to obtain an analog current output from the instrument. Under such circumstances you will obtain an analog output signal of 0 to 20 mA. The scaling for this signal is:

Attention

0 to 4000 ng/m^3 corresponds to 0 to 20 mA

0 to 1000 mm^2/m^3 correspond to 0 to 20 mA for the DC 2000CE

In order to obtain an analog current output, you will have to open the instrument and make a jumper change on the main board of the instrument. The jumper marked as 2 should be removed for obtaining 0 to 20 mA current output.

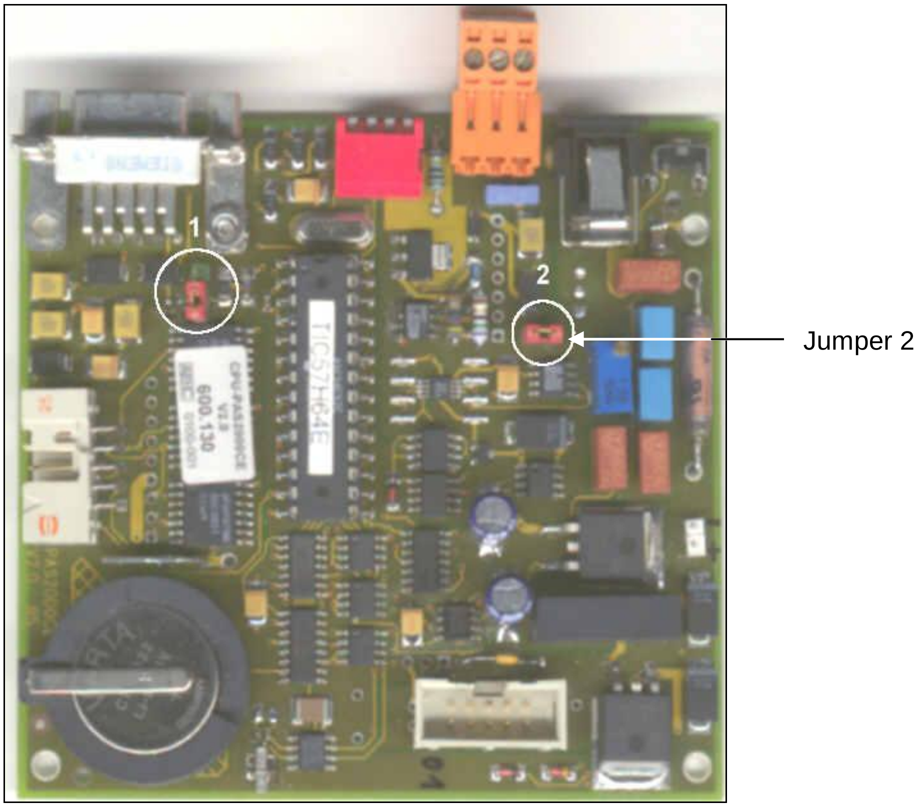


Fig. 7: Main board of the instrument showing Jumper 2 location

Finally some users like to collect analog data with a live zero. Under such circimstances the analog signal is changed from 0 -10 volts to 2-10 volts and 0-20 mA to 4-20 mA. In order to make this change use the dip switch on the back panel of the instrument.

Attention	For the live zero setting, scaling of the actual variables will be modified : 0 to 4000 ng/m^3 will correspond to 2 to 10 volts or 4 to 20 mA. 0 to 1000 mm^2/m^3 will correspond to 2 to 10 volts or 4 to 20 mA

3.5 Terminating a Measurement

To switch off the instrument, the OFF button is briefly pressed. This does not cause an immediate interruption, but is a command to the internal computer to switch off at the next suitable time. This may take some time and cannot be accelerated by repeatedly pressing the OFF button.

△ **Attention**	In case of a failure of the internal program or some other difficulties the sensor will fail to switch off as described above (by software mode). In such instances a termination has to be forced by pressing the OFF button for approximately 10 sec.!

3.6 Accessories

Accompanying the sensor are the following utilities:

- power supply/battery charger unit (including a power cable)
- serial port cable RS232 to connect monitor to a MS-DOS computer
- 3.5" disk with software

3.7 Communicating with the Sensor

For data exchange with the sensor a MS-DOS computer is needed on which the PAS2000CE / DC2000CE software is installed. Software is available for MS-DOS, Windows 3.1 and Windows 95/98 and NT. The devices communicate via the RS232 serial port (connect the data port on backside of monitor with the supplied serial port cable to a serial port of your computer).

The software package includes the following files:

airqual.exe,	**aqm.exe**,	aqm.tkn,	debug.exe,	fbasic.exe,	(aqm.pas),
(aqmset.pas),	(tickit.exe),	(fbasic.lib),	(token3.lib),	(macros.lib),	(uhr.lib),
(adc.lib),	(rs232.lib)	(aqmset.exe)	and the subdirectory „daten“		

These files are needed for the communication between monitor and computer as well as the operation of the built-in processor of the monitor. When operating under Windows 3.1, 95/98 or NT the program AIRQUAL.EXE is needed. It is used to read the measured data from the memory of the instrument. It can also be used to set the internal clock of the sensor.

The entire software should be installed onto the hard disk of a MS-DOS computer. Conveniently it is loaded in a directory called for example C:\AQM. Upon installation of the program two routines are available. The first one (Read Data) downloads the data from the internal memory of the monitor into files on the connected computer. The second routine (Set Clock) is used to change the time of the internal monitor clock.

3.7.1 Communications Using MS-DOS

In the MS-DOS mode the program AQM.EXE is used. **In this case the subdirectoy "daten" will contain the readout files. This should not be renamed as this file location subdirectory is used throughout the program and an alteration would thus cause a program failure**.

Read Data

Go to the directory C:\AQM. Start the program AQM.EXE by typing AQM and pressing ENTER. Follow the instructions given by the program.

A new file is created for each date when a measurement was performed. The file name is generated using the date when the values were recorded and has the format "AQyymmdd.000". In the file name the first two figures identify the device; the last figure is incremented if a file with identical name already exists (e.g. AQ970424.230, AQ970424.231, AQ970425.230....). The created files are stored in the subdirectoy "daten". The datafiles created are ASCII (text) files with two columns separated by a tabulator. The first column contains the time and the second column the measured PAH values. For further analysis of the data the files can easily be imported into spreadsheet programs like e.g. "MICROSOFT EXCEL".

Set Clock

Go to the directory C:\AQM. Start the program AQM.EXE by typing AQM and pressing ENTER. Follow the instructions given by the program. While the time is only entered for hours and minutes, the LCD display will indicate seconds as well. After pressing ENTER the clock will start a new minute. Therefore, if the time is to be set very precisely, one should wait with pressing the ENTER key until the begin of a new minute. The hours are to be set according to the European style which is on a 24 h basis. Midnight is 00. 2am is 02. Noon is 12, and 3pm is 15. The new time is shown on the LCD panel. Switch off the sensor after setting its internal clock.

3.7.2 Communications with Personal Computer

Use the program AIRQUAL.EXE to communicate with the sensor under Windows. Start the program by double-clicking its icon in the file manager (If you want to create a new icon for this program in the program manager refer to a Windows manual for further instructions). After starting the program a dialog window with further instructions for the user appears on the computer screen.

Read Data

The monitor must be switched off and the right serial port must be selected. Then choose the option Data Read and turn on the monitor. This initiates the program to start reading the stored data. The monitor LCD displays:

Data being send! Wait…

When the transfer is finished the monitor has to be switched off before it is used again for further actions.

To secure the data on your disk the displayed files in the window have to be selected (use mouse or tab key to select them) and then saved by clicking on the **Save Files** button. Another window opens which lets you choose the directory and a new file name (if desired) for the data to be stored. Verification of the file name is required for each file name being displayed!

Set Clock

Monitor must be again switched off and after choosing the right port the field **Set Watch** is selected. Turning on the monitor opens a new window in which both date and time can be changed. Both values are then displayed on the monitors LCD. Switch monitor off and on for further actions.

3.8 Clear Memory

Independently of the computer communication the monitor offers the possibility to clear the internal memory from all previously stored data. This will be useful at the beginning of a new series of measurements, or when all other data have been secured. Set the mode switch to position 7 and switch on the sensor. The internal memory will now be completely cleared. This does not require any action with the computer. Also, the RS232 cable (which connects the monitor with a computer) is not necessary.

This command will be executed without any warning!

Attention

On the LCD display the following line appears:

```
CLEAR MEMORY !   WAIT...
```

and after the second line displays

```
FINISHED....
```

the monitor can be switched off. Don't forget to reset the mode switch to one of the normal measurement modes.

Attention	Modes 5 and 6 (test) are basically unoccupied mode switch settings and should therefore not be used for any measurements

3.9 System Program for the Monitor

The instrument is controlled by a PIC-processor with an integrated BASIC-interpreter. The BASIC program (aqm.tkn) is stored in an EEPROM. Data being stored in an EEPROM will be secured even in case of interrupted power supply. Severe external impacts (like strong electric fields) or internal routing errors may lead to program failures. In such a case the operating program has to be reinstalled.

In order to reinstall the operating program onto the monitor proceed in the following way:

1. Open the PAS 2000CE / DC2000CE and switch the jumper marked as 1 in the other position (only two positions are possible).

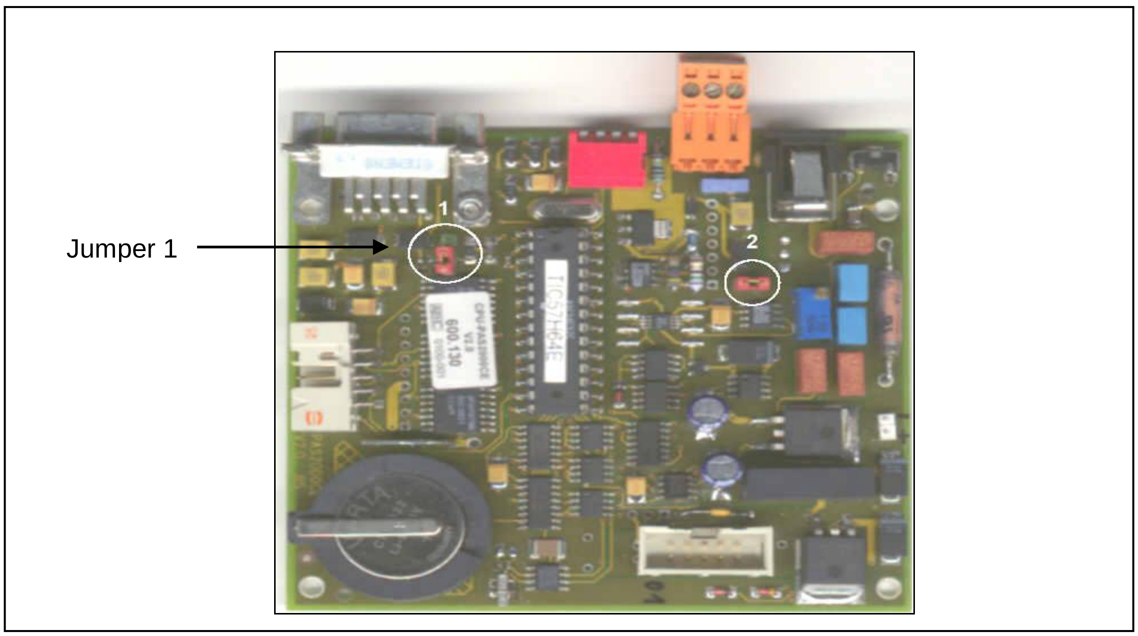


Fig. 8: Main board of the instrument showing Jumper 1 location

2. Connect the serial port of the computer (port 1 or 2) to the serial port on the back side of the monitor.

3. Switch on the computer. In case your computer automatically starts WINDOWS, exit WINDOWS to go to MS-DOS. Change to the directory containing all the monitor-related files (e.g. C:\AQM)

4. Switch on the monitor. Then wait for about 10 sec.

At the DOS prompt of your computer enter the following line:

debug X aqm (for X enter the serial port number, i.e 1 or 2)

press **<ENTER>**

the following line will be displayed on the screen:

```
i.  Reset TICKit for debugging now...
```

6. Press the reset button on the back side of the monitor (see Fig. 4 b) using a small screw driver or something similar.

7. On the computer you will see a window appearing with lines similar to the ones displayed :

```
TICKit DEBUG Version 3.0 VersaTech Electronics-
(c)1995
connect to TICKit
Token: E0          PC: 0DCA    Command:
console active, attached via COMx to TICKit...
```

at the command prompt type the two letters:

D (to download)

and then

Y (Yes to o.k. the question)

No <ENTER> is required after these two letters.

This will cause the program to be downloaded, with many digits appearing in the window.

After the downloading is finished it will be verified, which can take some time (several minutes). Do not interrupt the process at this level as the installation of the system program will be incomplete!

The following lines will subsequently appear without any further action needed:

```
5160 bytes loaded from file.....
....
Program Downloaded.....    and VERIFIED!
....
Token: E0          PC: 0DCA    Command:
```

8. At this final line - where a command is awaited - you will type

Q (Quit)

The program is now installed and the sensor will start to measure. The serial cable can be removed and the sensor is ready for new measurements.

Attention

Stored data from previous measurements will not get lost if the program is installed again!

9 Open the PAS 2000CE / DC2000CE and switch the jumper marked as 1 in the other position (this will set the switch back to the same position as it was before we did the software download).

4 SERVICE AND MAINTENACE

This User's Guide does not contain instructions for doing Service and Maintenance of the PAS 2000CE and DC 2000CE instruments. Both instruments are sensitive electronic devices and should be serviced only by appropriately trained personnel. Depending upon usage of the instruments, it is typically recommended that the instrument be sent back to the factory for service and maintenance every 12 to 24 months.

5 TECHNICAL SPECIFICATIONS

Display	16 characters with 2 lines LED
Power	115 volts AC / 60 Hz & 220 volts AC / 50 HzMax.
	Battery 15 volts Lithium Metal Hydride
Range	0 to 4000 ng / m^3 for PAS 2000CE
	0 to 1000 mm^2 / m^3 for DC 2000CE
Lower Threshold	~ 1 ng / m^3 total particle-bound PAH
	~ 1 mm^2 / m^3 (actual calibration is site-specific)
Response time	< 10 seconds (adjustable)
Digital Output	RS - 232 (for data download and program upload)
Analog Output	0 – 10 volts or 0 – 20 mA
Sample gas	Built-in pump with flowrate controlled at 1 L/min
Operating temp	40 to 104 ºF (5 to 40ºC)
Dimensions	Height x Width x Depth = 3in x 7in x 5in (68mm x 175mm x 124mm)
Weight	3 lb. (1.5 kg)
Data Storage	8000 Data Points (each data point consisting of : Time, Value)
Data Download	User-friendly PC-compatible graphical software used for downloading the collected data. Flat ASCII file output can also be generated for further analysis (e.g. Microsoft Excel format).

Appendix A – Discussion on Polycyclic Aromatic Hydrocarbons

A.1 Introduction

Polycyclic aromatic hydrocarbons (PAH) are associated with the incomplete burning of fossil fuels, wood, garbage, tobacco, charbroiled meat or other organic materials. They are usually found in complex mixtures, such as soot or tar. There are over 100 different PAH molecules.

PAH are organic molecules made up of carbon and hydrogen atoms having at least two fused aromatic rings; that is, two benzene rings which share a common border. These compounds are solids with generally high melting and boiling points (see Fig. A.1). They are planar and nonpolar and are extremely insoluble in water. Vapor pressures for pure PAH vary and this factor can greatly affect the amount that can be adsorbed onto particulate matter.

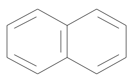
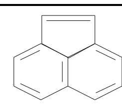
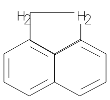
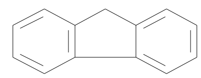
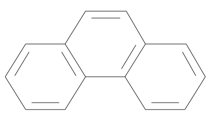
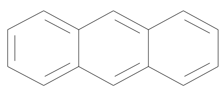
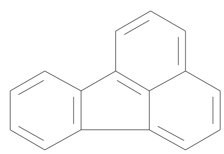
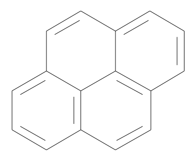
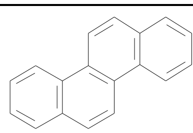
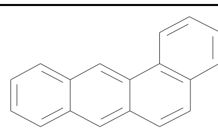
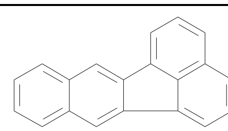
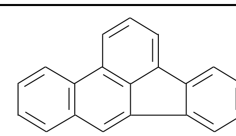
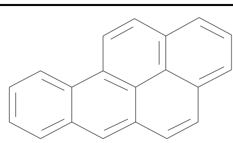
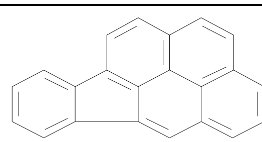
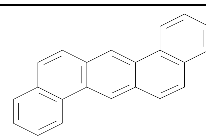
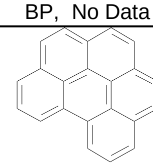
 Naphthalene MW = 128.2 MP = 80.2 °C BP = 217.9 °C	 Acenaphthylene MW = 152.2 MP = 92 - 93 °C BP = 265 - 275 °C	 Acenaphthene MW = 154.2 MP = 95 °C BP = 279 °C	 Fluorene MW = 166.2 MP = 116.5 °C BP = 295 °C
 Phenanthrene MW = 178.2 MP = 100 °C BP = 340 °C	 Anthracene MW = 178.2 MP = 218 °C BP = 342 °C	 Fluoranthene MW = 202.3 MP = 110.8 °C BP = 393 °C	 Pyrene MW = 202.3 MP = 156 °C BP = 393 °C
 Chrysene MW = 228.3 MP = 255 °C BP = 448 °C	 Benzo(a)anthracene MW = 228.3 MP = 160 °C BP = 435 °C	 Benzo(k)fluoranthene MW = 252.3 MP = 215.7 °C BP = 480 °C	 Benzo(b)fluoranthene MW = 252.3 MP = 168.3 °C BP, No Data
 Benzo(a)pyrene MW = 252.3 MP = 178.5 °C BP = 311 °C (at 10 torr)	 Indeno(1,2,3-c,d)pyrene MW = 276.3 MP = 163.6 °C BP = 530 °C	 Dibenzo(a,h)anthracene MW = 278.4 MP = 262 °C BP, No Data	 Benzo(g,h,i)perylene MW = 276.3 MP = 273 °C BP = 550 °C

Fig. A.1: Typical PAH compounds and physical properties (MW - Molecular Weight, MP - Melting Point, BP - Boiling Point)

A.2 PAH Formation

PAH present in the environment are a result of incomplete combustion rather than commercial production. In fact, only three PAH: acenaphthene, acenaphthylene and anthracene, are produced in significant quantities for use in chemical manufacturing processes. Waste products containing PAH are considered hazardous wastes and their generation, treatment, storage and disposal are all regulated. They are commonly destroyed by incineration or bioremediation. Degradation by landfarming processes and bioreactors are innovative techniques which have been successful.

The amount of PAH formed due to incomplete burning will depend upon the raw material and the combustion efficiency of the source. The formation mechanism occurs in the gas phase with subsequent transition to the particulate form generally found in the atmosphere. It is theorized that PAH are created both by the degradation of large fuel molecules and by polymerization of small organic molecules within the hydrocarbon flames.

While PAH compounds are found in the gas phase, those in the atmosphere are primarily associated with particulate matter. Vapor phase material adsorbs on particles as the gas stream cools through hydrogen bonding. Condensation may also be a mechanism for particle formation, but apparently PAH vapor pressures are not high enough in most combustion sources for this to occur.

A large mass fraction of the PAH can be associated with ultrafine particles. Ninety to ninety-five percent of particulate PAH are associated with particle diamters less than 3.3 μm and the peak distributions are localized between 0.4 and 1.1 μm (Baek, 1991). In the presence of high particulate concentrations nearly complete adsorption of PAH onto particles may be expected. Temperature is another factor affecting particle-bound versus vapor states. Experiments involving fly ash samples taken from the same release stream show that considerably more particulate PAH is associated with fly ash at a lower temperature (5 °C) than at a high temperature (290 °C).

The particle to gas phase concentrations for PAHs have been modeled as (EPA 1996) :

$$K_p = \frac{F / TSP}{A}$$

where

K_p Partitioning constant ($m^3\ \mu g^{-1}$)

TSP Concentration of total suspended particulate matter ($\mu g\ m^{-3}$)

F Particle - bound concentration ($\mu g\ m^{-3}$)

A Gas phase concentration ($\mu g\ m^{-3}$)

Using the above formulation, we now define

$$\varphi = \frac{F}{A + F} = \frac{K_p\ TSP}{K_p\ TSP + 1}$$

where

φ Fraction of the total compound that is on the particle phase

Several references (EPA 1996, Pankow 1991, Yamasaki 1982 and Baek 1991) provide further information regarding the evaluation of K_p for different compounds and enumerate values obtained at different locations.

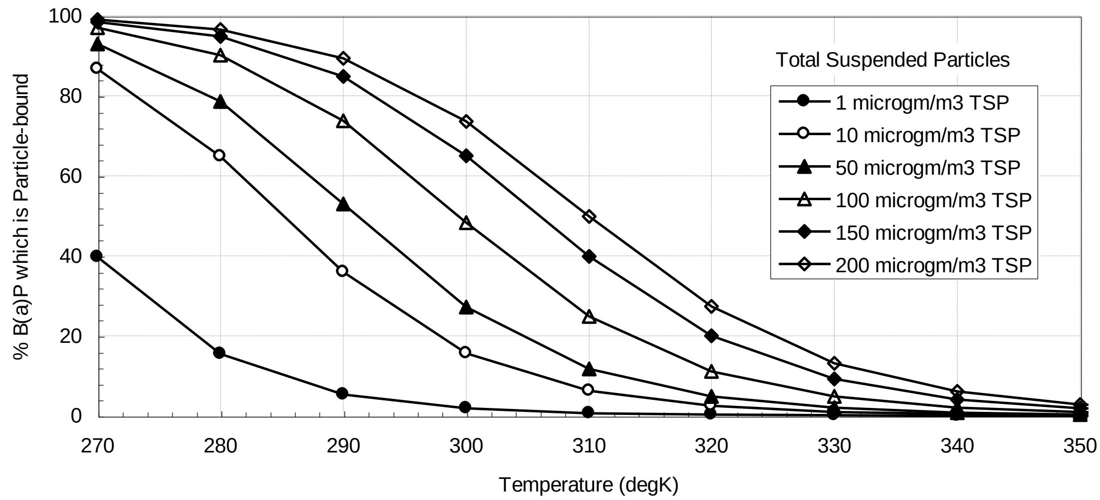


Fig. A.2: Particle-bound PAH as a function of Temperature and Total Suspended Particulate Matter (graph created using data from Baek, 1991)

A.3 Sources of PAH

PAH are released into the atmosphere through natural and anthropogenic processes. Natural sources include emissions from volcanoes and forest fires. Anthropogenic sources produce greater amounts of PAH by far. They can be released into surface water through discharges from industrial plants and waste water treatment plants and soils at hazardous waste sites if they escape storage containers.

The single largest source of PAH emissions to the air is the burning of wood in homes due to inefficient combustion and lack of emission controls (Baek, 1991; Ramdahl, 1982). Cars and trucks are also major contributors. Stationary sources account for 80% of annual PAH emissions with the rest attributed to mobile sources. For indoor air, tobacco smoke, gas cooking and heating appliances and kerosene space heaters can increase PAH levels.

Many of the current combustion processes and certain industrial processes such as coke production or petroleum refining have led to the widespread presence of PAH in industrial and ambient atmospheres. Combustion is a major source of PAH pollutants, encompassing industrial operations and power plants using fossil fuels, waste incinerators, domestic heaters and vehicles powered by gasoline or diesel fuels. Emissions of PAH from fossil fuel combustion can vary over several orders of magnitude depending upon the particular fuel and combustion conditions. Emissions of PAH from burning coal or wood for residential space heating are several orders of magnitude greater than those from gas or oil burning. Urban and highly industrialized environments contain higher levels of PAH than do rural locations. Industrial and commercial sources of PAH can be categorized according to processes associated with a certain fuel type or combustion unit.

Annual emissions of polycyclic organic matter, a category encompassing PAH, have been broken down as follows (NRC, 1983):

- 39% Open burning
- 38% Residential heating
- 22% Automobiles and trucks
- 1% Industrial boilers

The fate of PAH in the environment depends on how easily they dissolve in water and how easily they evaporate into the air. In general, PAH do not dissolve easily in water. PAH released into the atmosphere can be transported long distances. For particle-bound PAH atmospheric residence time and transport distance will depend upon the size of the particles to which they are adsorbed. They are removed by wet and dry deposition onto soil, water and vegetation. In water they can volatilize, photolyze, oxidize, biodegrade, bind into suspended particles or sediments or accumulate in aquatic organisms. In sediments, they can biodegrade or accumlate in aquatic organisms. PAH in soil can volatilize, degrade or accumulate in plants. They can also migrate into the groundwater and be transported within an aquifer.

Stationary External Combustion	Residential Heating, Industrial and Commercial Heat and Steam Generation
Stationary Internal Combustion	Reciprocating Engines, Gas Turbines
Waste Incineration	Municipal, Industrial, Commercial, Medical, Landfill Gas, Hazardous, Scrap Tire, Sewage Sludge
Metals Industry	Aluminum, Iron and Steel, Secondary Lead Smelting
Petroleum Refining	Catalytic Cracking, Other
Asphalt Products	Asphalt Roofing Manufacturing, Hot Mix Asphalt Production
Coke Production	Coke Ovens, Byproduct Recovery Plants
Cement Manufacturing	Portland Cement Manufacture
Pulp and Paper Industry	Furnaces and Kilns
Open Burning	Wildfires, Scrap Tire Burns, Agricultural Plastic Film Burning, Coal Refuse Burning, Other
Mobile Sources	On-road Vehicles, Aircraft, Locomotives, Marine Vessels
Miscellaneous	Carbon Black Manufacture, Wood Treatment, Carbon Regeneration, Cigarette Smoke, Wood Charcoal Production, Crematories, Gasoline Distribution, Rayon Fiber Manufacture, Commercial Charbroilers

Table A.1: Common sources of PAH

A.4 Human Exposure to PAH

A.4.1 Exposure of the General Population

People are exposed to mixtures of PAH at home, outdoors and at work. The greatest sources of exposure to the general population include inhalation of tobacco smoke, wood smoke, contaminated air and ingestion of food. Exposure pathways can be characterized as follows:

- ***Respiration:*** The most likely exposure pathway is breathing in PAH attached to dust or other particles in the air. Non-occupational respiratory exposure is mainly to tobacco smoke and urban air. It has been estimated that smoking one pack of cigarettes a day results in exposure of up to 5 μg/day of carginogenic PAH (Menzie, 1992). Urban air pollution is from various sources, including vehicle exhausts and combustion products from residential and industrial heating. Background levels of PAH in ambient air are reported to be 0.02 to 1.2 nanograms/m^3 in rural areas and 0.15 to 19.3 nanograms/m^3 in urban areas (DHHS, 1995).

- ***Ingestion:*** PAH have been found in some drinking water supplies due to contamination with pollution, runoff from asphalt and used motor oil. PAH levels in drinking water range from 4 to 24 nanograms/liter.

  Major sources of PAH in foods include curing smokes, contaminated soil, polluted air and water and cooking at high temperatures. PAH in a typical U.S. diet is estimated at less than 2 micrograms/kilogram of food or 1 to 5 μg/day.

- ***Skin Contact:*** Exposure can also occur via contact with contaminated soil, soot or tar. Mineral oils and refined petroleum products used in cosmetics and medicinal products have also been shown to contain PAH.

It has been estimated that the general population is exposed to total PAH levels of 0.207 μg/day from air, 0.027 μg/day from water and 1.6 to 16 μg/day from food (Santodonato, 1981). It should be noted that the uncertainty in measurement of PAH in food is greater than that from air or water. However, the estimates are thought to be accurate within one order of magnitude, so that food was predominant among exposure sources. Another factor to consider is the fact that PAH which are swallowed are generally absorbed more slowly by the body than those inhaled.

PAH can enter all the body tissues containing fat. This is because PAH are nonpolar so they tend to dissolve readily in and cross the lipoprotein membranes of mammalian cells. Once PAH are injected into the bloodstream they are rapidly and widely distributed. The demonstrated toxicity of many PAH in organs remote from the site of their administration confirms this. They tend to be stored mostly in the kidneys, liver and fat. Smaller amounts are stored in the spleen, adrenal glands and ovaries. Animal studies show that PAH do not tend to be stored in the body for long periods of time. Most of them leave the body within a few days, primarily in the feces and urine.

A.4.2 PAH Levels in the Environment

While PAH air levels have been monitored at many locations, it is important to understand sampling complexities before making any comparisons between studies. As mentioned before, three-ring PAH compounds generally exist in the vapor phase in the atmosphere, where as five- and six- ringed PAH are predominantly found in the particle phase and four-ringed compounds exist in both phases. Thus, to measure total PAH levels both particulate and gaseous samples must be taken. However, early studies used filter sampling methods, which only measured particle-phase PAH, underestimating total PAH concentrations.

Trends suggested by studies indicate that urban PAH levels are higher than rural ones and concentrations in the winter exceed those in the summer:

- Pucknat (1981) summarized 1970 data from the U.S. National Air Surveilance Network reporting benzo[a]pyrene concentrations at 120 U.S. cities ranged from 0.2 - 19.3 ng/ m^3 whereas nonurban levels were 0.1 - 1.2 ng/ m^3.

- Greenberg (1985) evaluated particle-phase PAH levels in New Jersey. The geometric mean concentrations of tn PAH compounds were 0.03 to 0.62 ng/ m^3 in urban areas and 0.01 to 0.12 ng/ m^3 in rural areas during the summer. In the winter, these values ranged from 0.40 to 11.15 ng/ m^3 in urban areas and 0.08 to 1.32 ng/ m^3 in rural areas.

A.4.3 Occupational Exposures

Occupational exposures to PAH are prevalent in petroleum refining, metalworking, coke production, anode manufacture and aluminum production. They also associated with manufacturing processes involving the use of coal tar, pitch, asphalt, creosote, soot and anthracene oil. Engine exhausts containing PAH emissions are found in a wide variety of occupational settings. Some levels measured in various workplaces appear below (DHHS, 1995):

Petroleum Refinery, Fluid Catalytic Cracking and Delayed Coker Units	10 μg /m^3 total PAH
Petroleum Refinery, Bitumen Processing Units	1 - 40 μg /m^3 total PAH
Petroleum Refinery, De-asphalting Unit	2.5 - 49.8 μg /m^3 total PAH
Metalworks, Cutting Area	66 ng/ m^3 total PAH
Metalworks, Hardening Area	90 ng/ m^3 total PAH
Metalworks, Extruding Oilshave Area	106 ng/ m^3 total PAH
Aluminium Reduction Plant	0.03 - 53 μg /m^3 benzo[a]pyrene
Coke Plant, Oven Operations	0.15 - 6.72 μg /m^3 benzo[a]pyrene
Roofing, Removing Coal Tar Pitch Roof and Applying Asphalt Roof	10.2 μg /m^3 total PAH

Table A.2: Workplace exposure to PAH for various occupation (DHHS, 1995)

A.5 PAH Toxicity

The linkage between PAH and cancer can be traced back to observation in London in the 1700's that scrotal cancer in chimney sweeps was due to their occupational exposure to soot. A century later, occupational skin cancers in the coal tar industry of Germany were noted. By the early 1900's it was widely recognized that soot, coal tar and pitch are all carcinogenic for man. Soon after it was discovered that the carcinogenic activity in coal tar resided in the benzo[a] pyrene it contains. In addition to the skin cancers which were noted initially, there have also been several reports indicating that higher incidences of respiratory tract and upper gastrointestinal tract tumors are associated with occupational exposures to PAH.

Many PAH are recognized as potent carcinogens. Epidemiological studies have reported an increase in lung cancer in humans exposed to coke oven emissions, roofing tar emissions and cigarette smoke. Each of these mixtures contains a number of PAH. Cancer associated with exposure to PAH-containing mixtures in humans occurs predominantly in the lungs due to inhalation and skin due to dermal contact. Animal studies have reported respiratory tract tumors from inhalation exposure to benzo[a] pyrene; forestomach tumors, leukemia and lung tumors from oral exposures; and skin tumors from dermal exposures (DHHS, 1995).

Chronic non-cancer effects to long-term exposure to benzo[a]pyrene in humans has resulted in dermatitis, photosensitization in sunlight, irritation of the eyes and cataracts. People exposed to PAH and respirable particles in a rubber plant reported bloody vomit, breathing problems, chest pains, throat irritation and abnormalities in chest X-rays. Studies have shown that human lung cells can metabolize PAH into reactive intermediates, meaning inhalation exposure can result in toxicity to the respiratory tract. Animal studies have reported effects on the blood and liver from oral exposure to benzo[a] pyrene and effects on the immune system from dermal exposure to benzo[a] pyrene (DHHS, 1995).

No information is available on the reproductive or developmental effects of PAH in humans. Animal studies have indicated that benzo[a] pyrene, via oral exposure, induces reproductive toxicity, including a reduced incidence of pregnancy and decreased fertility. Developmental effects, such as a reduced viability of litters and reduced mean pup weight, have also been noted from oral exposure to benzo[a] pyrene in animals (DHHS, 1995).

A recent technical publication (Denissenko et al, 1996) provides a direct link between a defined cigarette smoke carcinogen (Benzo[a]pyrene) and human cancer mutations. Using techniques of molecular biology, the authors explcitly show how Benzo[a]pyrene brings about mutations resulting in human lung cancer.

A.6 Regulations and Advisories in USA

The U.S. EPA has categorized PAH as Hazardous Air Pollutants and has proposed regulations governing major sources. It has also developed reference doses for anthracene (0.3 mg/kg/day), acenaphthene(0.06 mg/kg/day), fluoranthene (0.04 mg/kg/day), fluorene(0.04 mg/kg/day) and pyrene (0.03 mg/kg/day). However, no reference concentrations exist for any PAH (DHHS, 1995).

OSHA regulates the benzene-soluable fraction of coal tar pitch volatiles and mineral oil mists, which contain several PAH compounds. Engineering controls and work practices must be used to reduce occupational exposures below and 8-hour time weighted average of 0.2 mg/m^3 for coal tar pitch volatiles and 5 mg/m^3 for mineral oil mist. The ACGIH classifies PAH as confirmed human carcinogens and specifies the same limits as OSHA (DHHS, 1995).

U.S. EPA has set an ambient water quality criteria for protection of human health at 0.0028 ug/L for PAH exposure due to ingestion of water and organisms. PAHs are regulated by the Clean Water Effluent Guidelines in the Code of Federal Regulations. They are classified as Total Toxic Organics for electorplating and metal molding and casting sources. They have specific regulatory limitations for point source categories including organic chemicals, plastics, synthetic fibers, cokemaking and nonferrous metals manufacturing (DHHS, 1995).

The Emergency Planning and Community Right-to Know standards (EPCRA) regulate PAH by requiring owners and operators of certain facilities to report the release of those chemicals into the environment each year (DHHS, 1995).

Under the Resource Conservation and Recovery Act (RCRA), several PAH are considered hazardous wastes when they are discarded commercial chemical products, off-specification species, container residues and spill residues (DHHS,1995).

A.7 References

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Appendix B – Discussion on Particle Surface Area and Related Concepts