NEW APPROACH IN CALIBRATION OF PASSIVE PERMEATION SAMPLERS USED FOR VOC’s SAMPLING FROM THE AIR

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7th Passive Sampling Workshop and Symposium
RESTON, VA, USA, 24-26.04.2007

Mister Chairman
Ladies and Gentlemen

First of all I would like to thank the Organizing Committee for this kind invitation to Reston.

It gives me an opportunity to present the new approach in the field of **calibration of passive permeation samplers** used for VOLATILE ORGANIC COMPOUNDS sampling from Indoor Air.

Where do I come from?

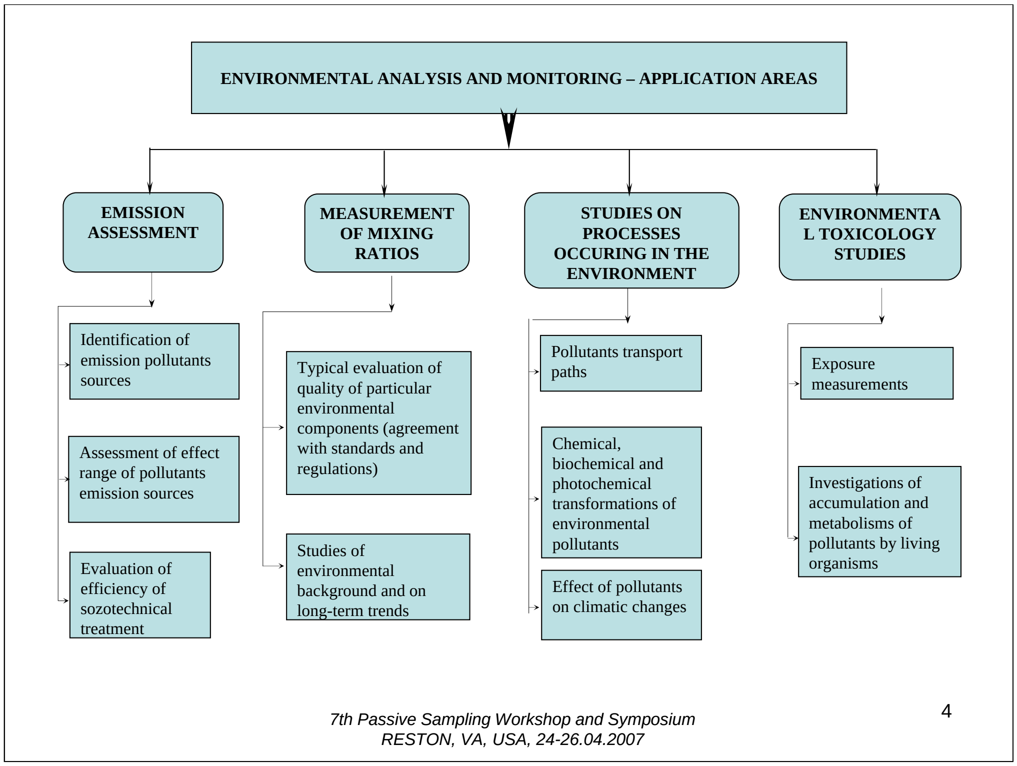
Together with Dr Bozena ZABIEGAŁA we have come from Gdańsk in Poland.

We work at the Chemical Faculty of the Gdańsk University of Technology.

Gdańsk University of Technology, Gdańsk, Poland

Gdańsk is an Hanzeatic city which in 1997 celebrated its MILLENIUM .

Gdańsk University of Technology is an **old school** founded in 1904.



ENVIRONMENTAL ANALYSIS AND MONITORING – APPLICATION AREAS

EMISSION ASSESSMENT
- Identification of emission pollutants sources
- Assessment of effect range of pollutants emission sources
- Evaluation of efficiency of sozotechnical treatment

MEASUREMENT OF MIXING RATIOS
- Typical evaluation of quality of particular environmental components (agreement with standards and regulations)
- Studies of environmental background and on long-term trends

STUDIES ON PROCESSES OCCURING IN THE ENVIRONMENT
- Pollutants transport paths
- Chemical, biochemical and photochemical transformations of environmental pollutants
- Effect of pollutants on climatic changes

ENVIRONMENTAL TOXICOLOGY STUDIES
- Exposure measurements
- Investigations of accumulation and metabolisms of pollutants by living organisms

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According to more and more common opinion, **analytics and monitoring** of environmental pollutants constitute the **two pillars** on which the entire **environmental science** is based.

There are at least **four goals** of environmental analytics and monitoring.

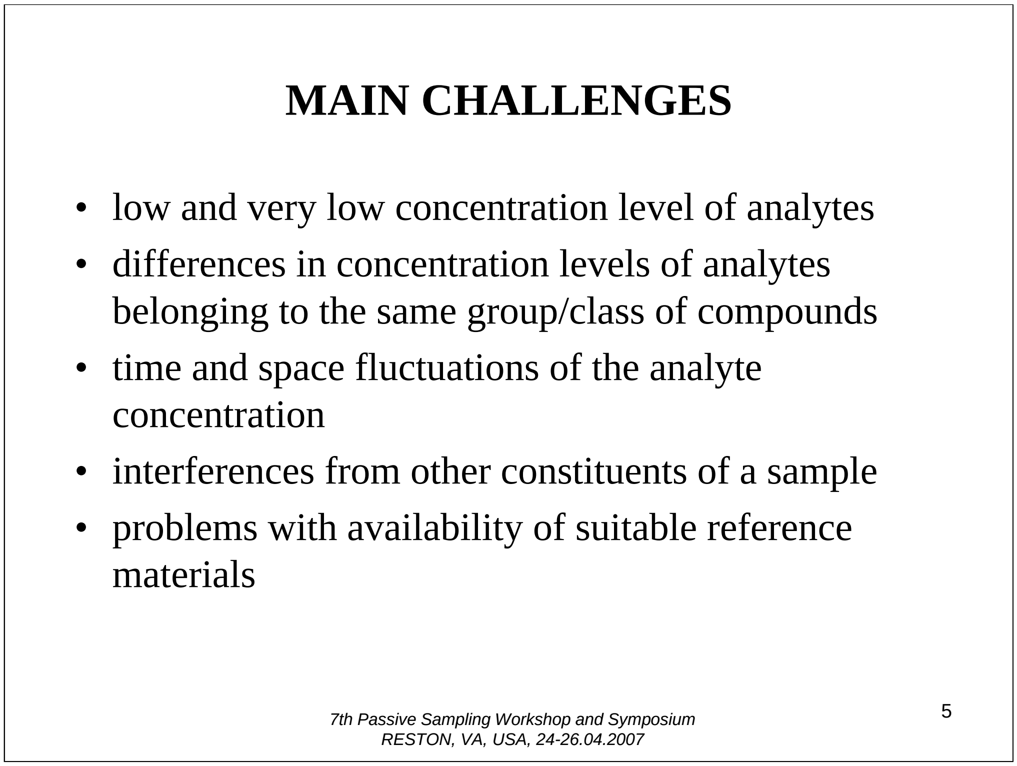
There are as follows:

-**emission assessment**

-**measurement of mixing ratios** of different types of anthropogenic and biogenic pollutants

-studies of processes and **environmental fate** of different xenobiotics

-ecotoxicological studies.



MAIN CHALLENGES

- low and very low concentration level of analytes
- differences in concentration levels of analytes belonging to the same group/class of compounds
- time and space fluctuations of the analyte concentration
- interferences from other constituents of a sample
- problems with availability of suitable reference materials

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Main challenges in environmental analytics and monitoring originate from:

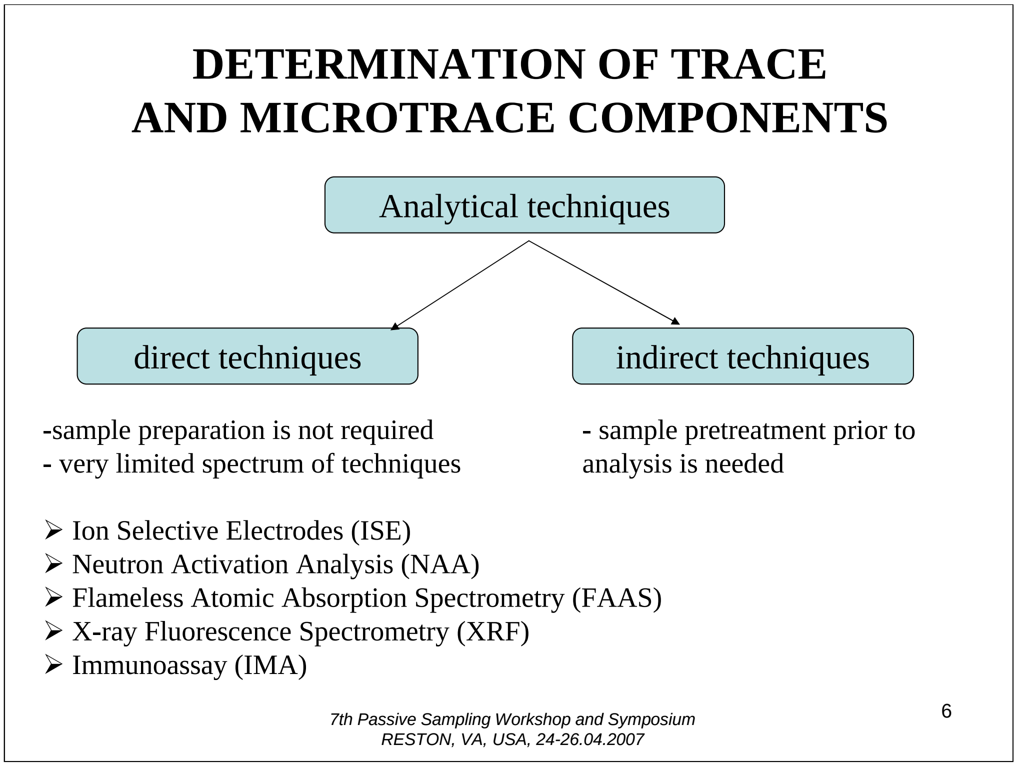
•**low and very low concentration level of analytes**

•differences in concentration levels of analytes belonging to the same group/class of compounds

•**time and space fluctuations of analyte concentrations**

•interferences from other constituents of a sample under investigation

•problems with availability of suitable reference materials – needed for validation of analytical procedures and calibration of measuring devices.



DETERMINATION OF TRACE AND MICROTRACE COMPONENTS

Analytical techniques

direct techniques

indirect techniques

-sample preparation is not required
- very limited spectrum of techniques

- sample pretreatment prior to analysis is needed

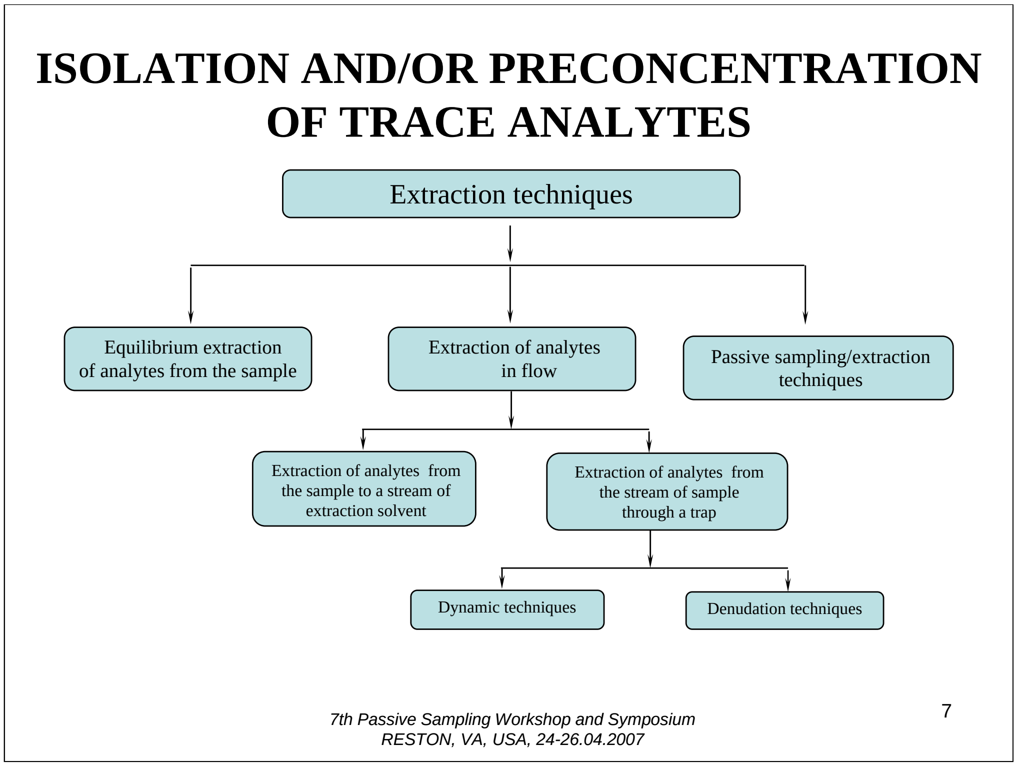
- ➢ Ion Selective Electrodes (ISE)
- ➢ Neutron Activation Analysis (NAA)
- ➢ Flameless Atomic Absorption Spectrometry (FAAS)
- ➢ X-ray Fluorescence Spectrometry (XRF)
- ➢ Immunoassay (IMA)

All analytical techniques which can be applied for determination of trace and microtrace components can be divided into two groups:

-**direct techniques-** which do not require the sample pretreatment and

-indirect techniques- when specific steps of **sample pretreatment** prior to the final determination of analytes are needed.

Unfortunately, the spectrum of direct techniques is very limited.



ISOLATION AND/OR PRECONCENTRATION OF TRACE ANALYTES

Extraction techniques

Equilibrium extraction of analytes from the sample

Extraction of analytes in flow

Passive sampling/extraction techniques

Extraction of analytes from the sample to a stream of extraction solvent

Extraction of analytes from the stream of sample through a trap

Dynamic techniques

Denudation techniques

In this situation an additional step of **isolation and preconcentration of analytes** from different matrices has to be introduced to analytical protocols.

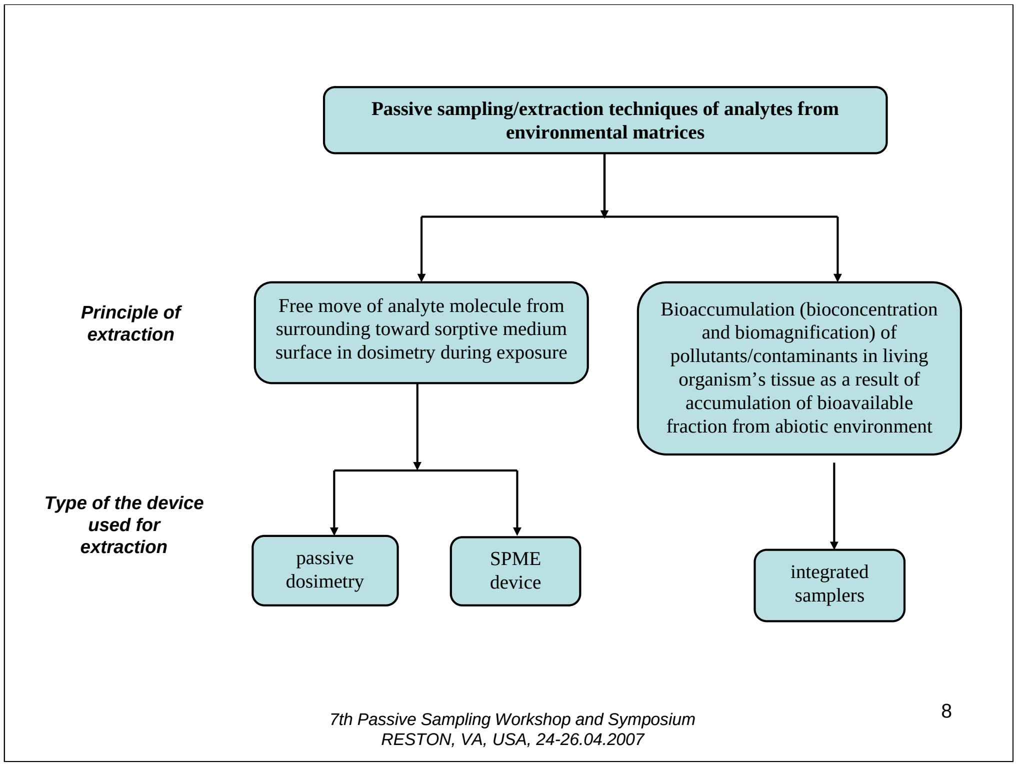
These techniques can be **divided into three main groups**.

It means:

•**Equilibrium extraction** of analytes from the sample,

-**Extraction of analytes in flow**,

-**Passive extraction techniques** known also as passive techniques of sampling the analytes



Passive sampling/extraction techniques of analytes from environmental matrices

Principle of extraction

Free move of analyte molecule from surrounding toward sorptive medium surface in dosimetry during exposure

Bioaccumulation (bioconcentration and biomagnification) of pollutants/contaminants in living organism's tissue as a result of accumulation of bioavailable fraction from abiotic environment

Type of the device used for extraction

passive dosimetry

SPME device

integrated samplers

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Taking into account variety of methodological approaches and specific designs of passive units, one can propose different classification.

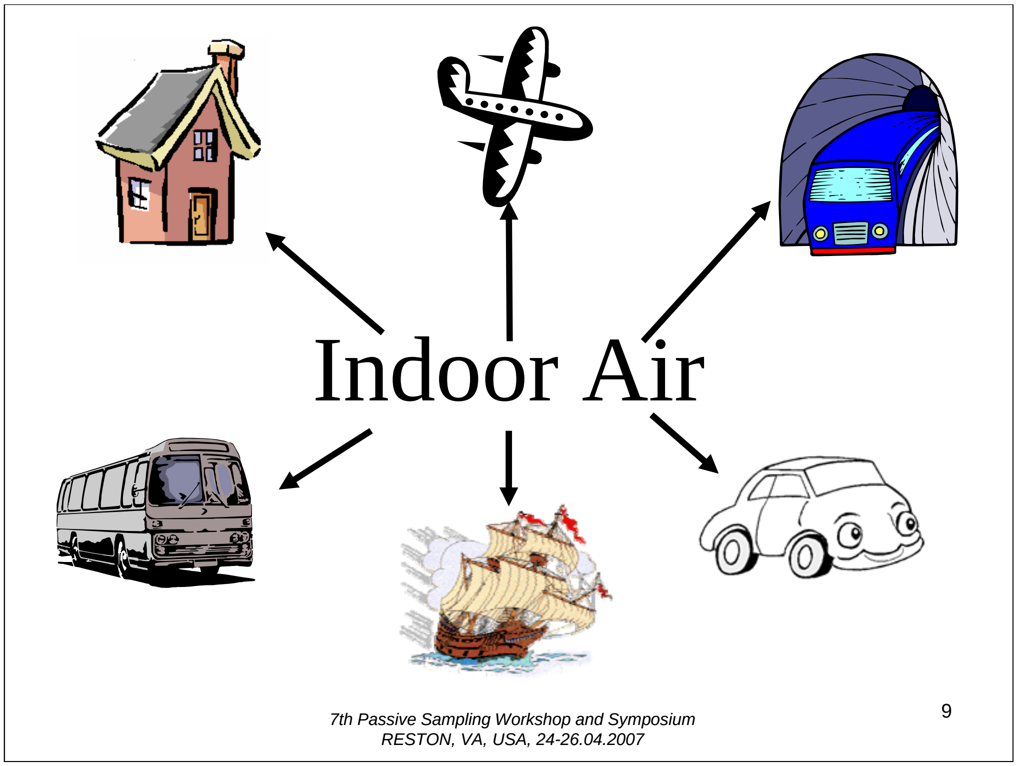
It seems, that the most important bases of classification are:

-principle of extraction

-construction of extraction devices.

There is no doubt that passive techniques of extraction of analytes become more and more useful and popular.

I would like to draw your attention to possibility of utilization of living organisms as specific passive samplers.



Indoor Air

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The term ‘indoor air” pertains to the air in enclosed environment.

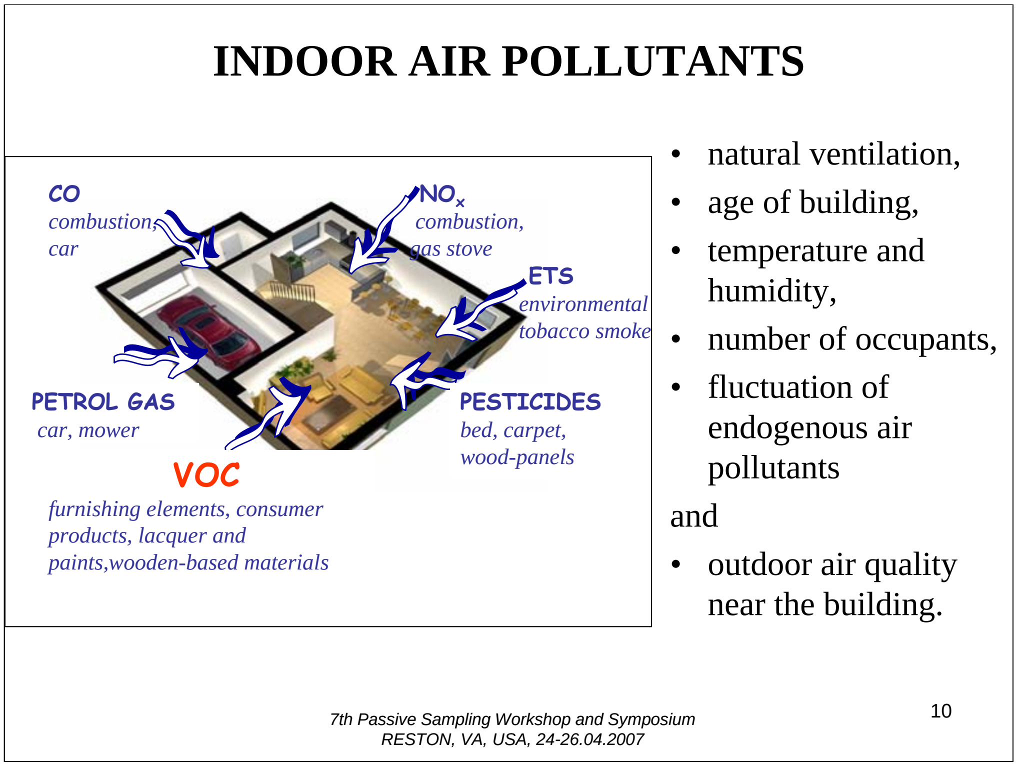
Indoor air means not only air in homes, but also in all places for which regulations concerning workplaces are not applicable.

Indoor air quality is an important parameter, which can affect

-human health

and

-good self-feeling.



INDOOR AIR POLLUTANTS

CO
combustion,
car

NO_x
combustion,
gas stove

ETS
environmental
tobacco smoke

PETROL GAS
car, mower

PESTICIDES
bed, carpet,
wood-panels

VOC
furnishing elements, consumer
products, lacquer and
paints,wooden-based materials

- natural ventilation,
- age of building,
- temperature and humidity,
- number of occupants,
- fluctuation of endogenous air pollutants

and

- outdoor air quality near the building.

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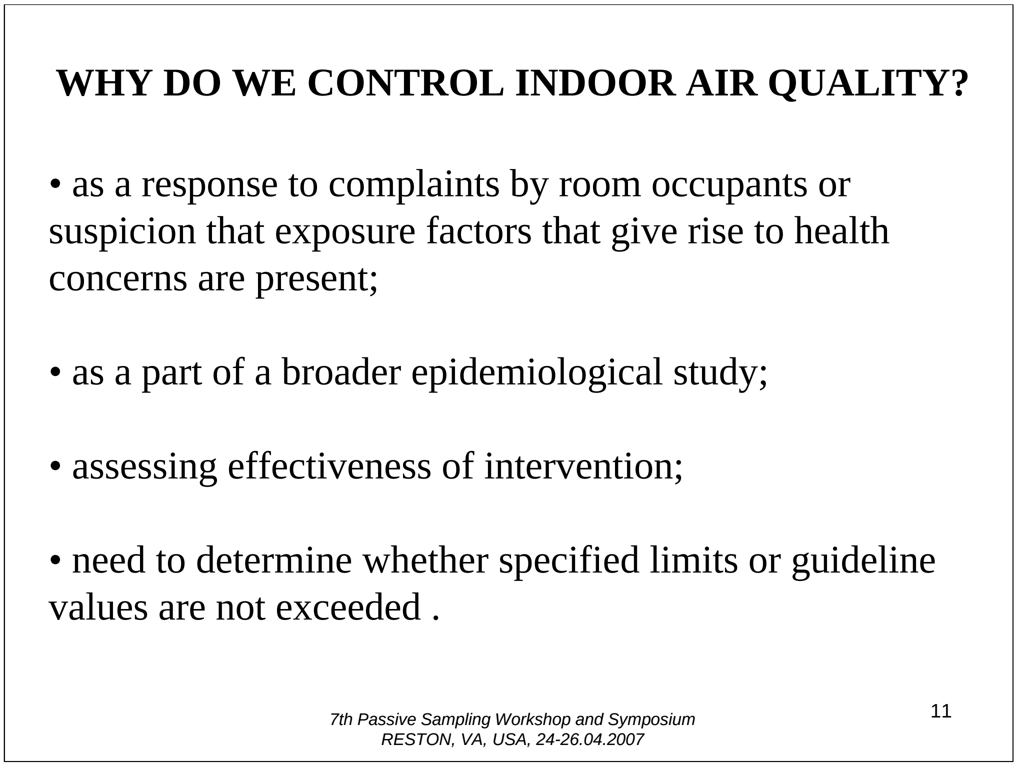
All sources of indoor air pollutants can be divided into two groups:

-**endemic** –it means internal sources and

-**external** or outdoor sources of emission of pollutants.



WHY DO WE CONTROL INDOOR AIR QUALITY?

- as a response to complaints by room occupants or suspicion that exposure factors that give rise to health concerns are present;
- as a part of a broader epidemiological study;
- assessing effectiveness of intervention;
- need to determine whether specified limits or guideline values are not exceeded .

The care for quality of indoor air in present times becomes more and more important.

Taking into account **the amount of time spent by humans indoors**, evaluation of indoor air quality should be as objective as possible.

Indoor air environment investigations may be undertaken for a variety of reasons:

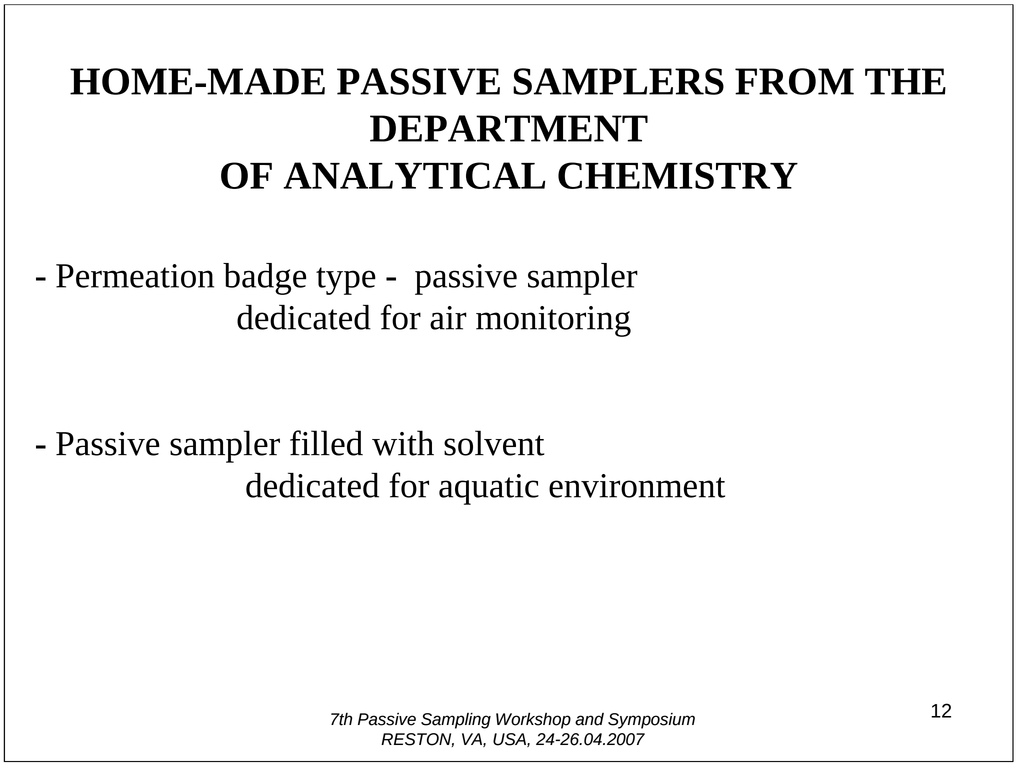
-**as a response to complaints or suspicions that exposure reached dangerous level or**

-as a part of a broader epidemiological study.

Indoor Air Quality is studied also in order to:

-assess effectiveness of undertaken countermeasures,

-**verify whether specific limits and guidelines are not exceeded.**



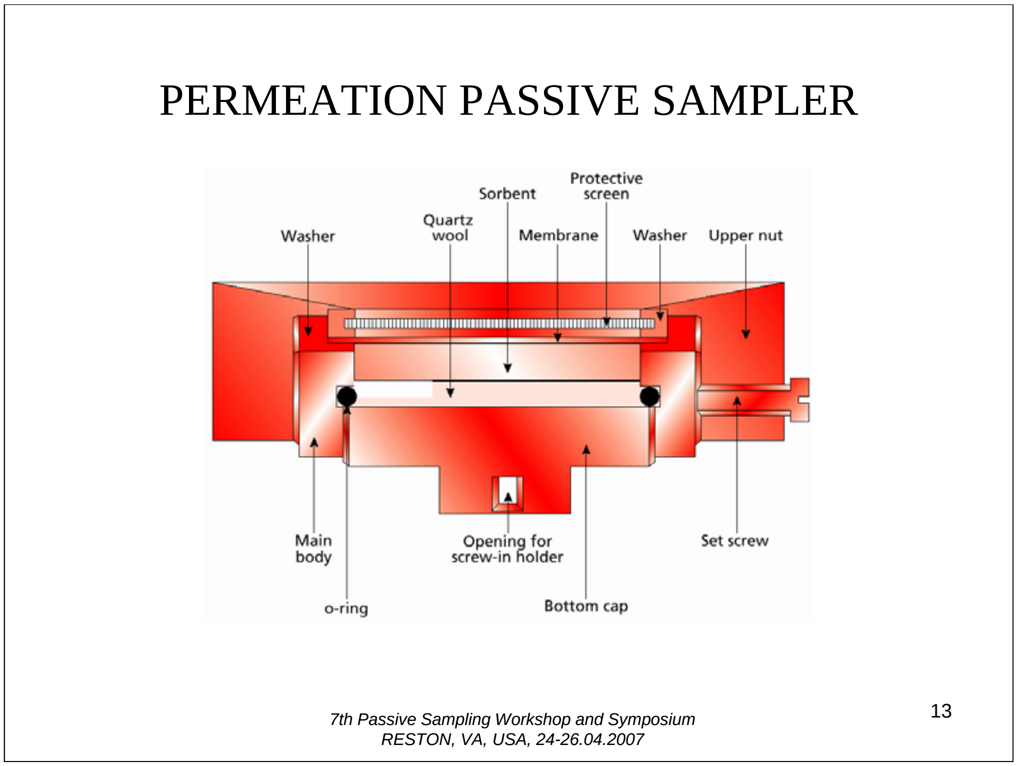
HOME-MADE PASSIVE SAMPLERS FROM THE DEPARTMENT OF ANALYTICAL CHEMISTRY

- Permeation badge type - passive sampler
  dedicated for air monitoring

- Passive sampler filled with solvent
  dedicated for aquatic environment

Since late 1980’s, our research team from the Department of Analytical Chemistry of the Chemical Faculty of Gdansk University of Technology have been involved in **application of passive extraction techniques in environmental studies**.

We have decided to use a home-made badge-type, passive permeation sampler in order to sample Volatile Organic Compounds from Indoor air.



PERMEATION PASSIVE SAMPLER

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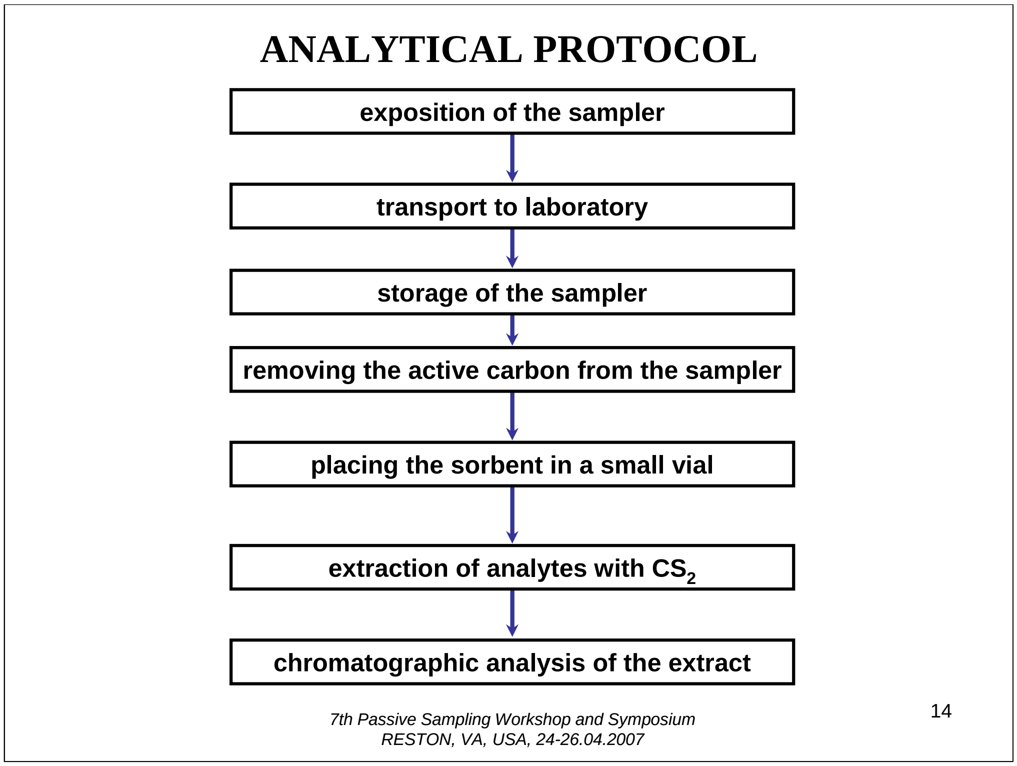
Volatile organic analytes permeate through a membrane and are retained in the active carbon bed.

Membrane made of PDMS foil of 75 micrometer thickness **is the heart** of the sampler.



ANALYTICAL PROTOCOL

exposition of the sampler

transport to laboratory

storage of the sampler

removing the active carbon from the sampler

placing the sorbent in a small vial

extraction of analytes with CS_2

chromatographic analysis of the extract

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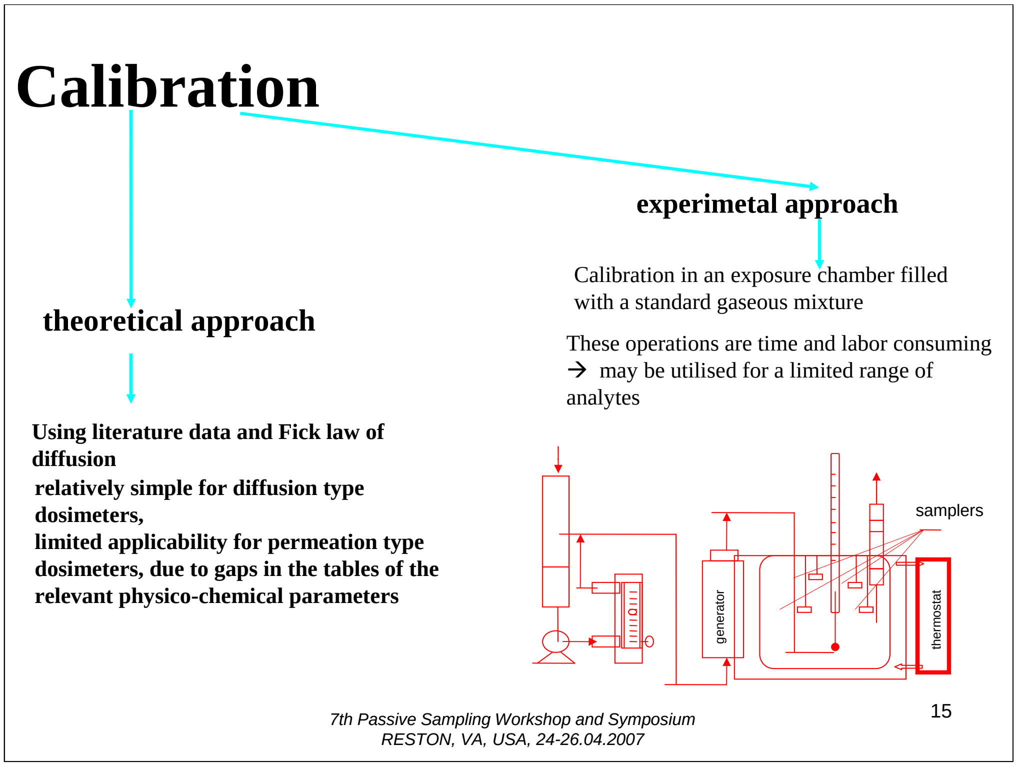
Analytes retained in the sampler are desorbed with CS_2 after the exposure period. Aliquots of extract obtained are subsequently analysed chromatographically.



Calibration

theoretical approach

Using literature data and Fick law of diffusion

relatively simple for diffusion type dosimeters,

limited applicability for permeation type dosimeters, due to gaps in the tables of the relevant physico-chemical parameters

experimetal approach

Calibration in an exposure chamber filled with a standard gaseous mixture

These operations are time and labor consuming
→ may be utilised for a limited range of analytes

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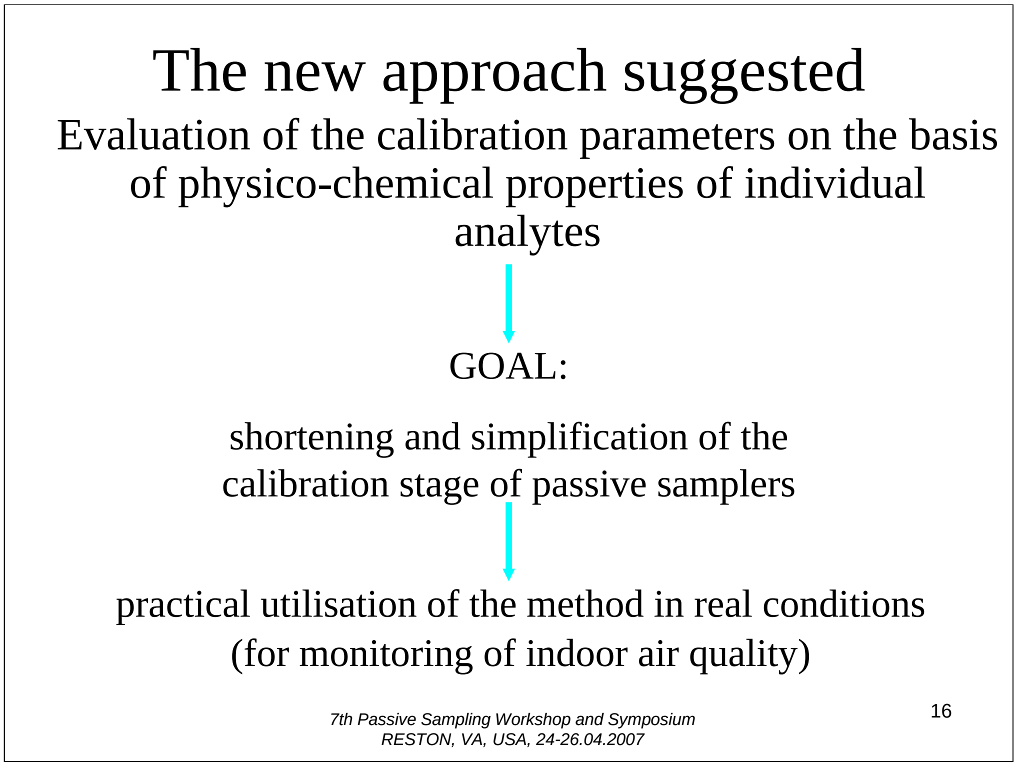
The **main drawback** of the analytical protocols used for determination of VOC's **in indoor air** and based on **application of passive samplers** at the step of sampling the analytes is the NECESSITY of CALIBRATION of new samplers in order to evaluate calibration parameters.

Experimental calibration of set of samplers is a labour - and time consuming task.



The new approach suggested

Evaluation of the calibration parameters on the basis of physico-chemical properties of individual analytes

↓

GOAL:

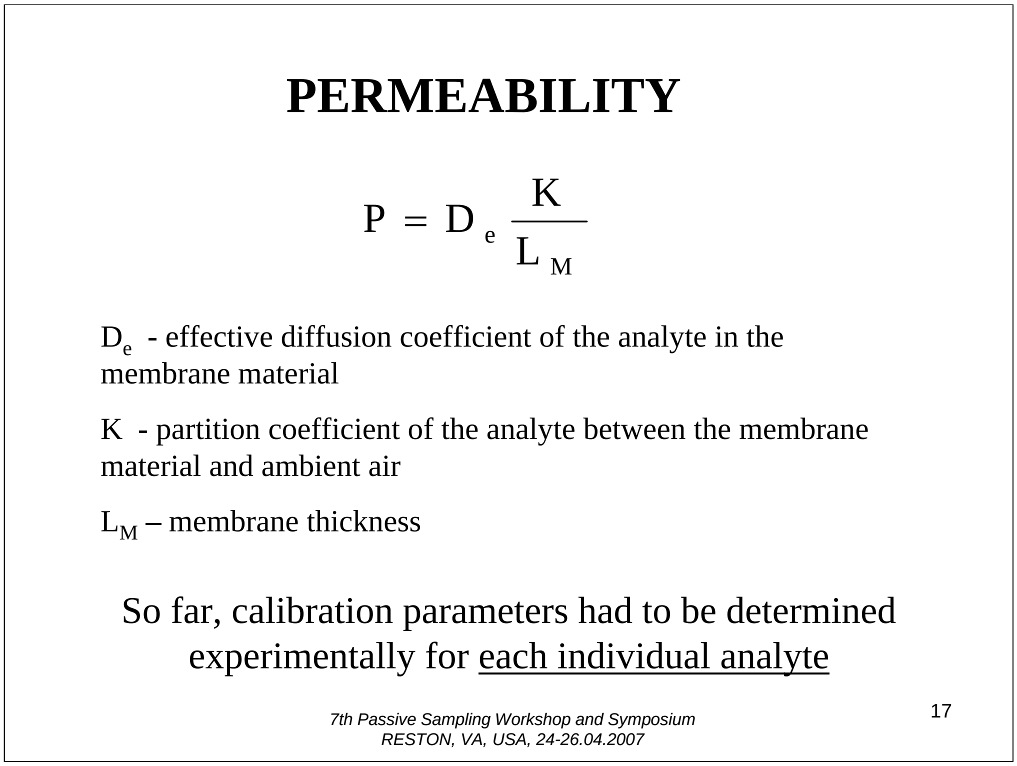
shortening and simplification of the calibration stage of passive samplers

↓

practical utilisation of the method in real conditions (for monitoring of indoor air quality)

Our idea was:

to find **relationships** between **physico-chemical properties** of analytes and their calibration parameters.



PERMEABILITY

$$P = D_e \frac{K}{L_M}$$

D_e - effective diffusion coefficient of the analyte in the membrane material

K - partition coefficient of the analyte between the membrane material and ambient air

L_M – membrane thickness

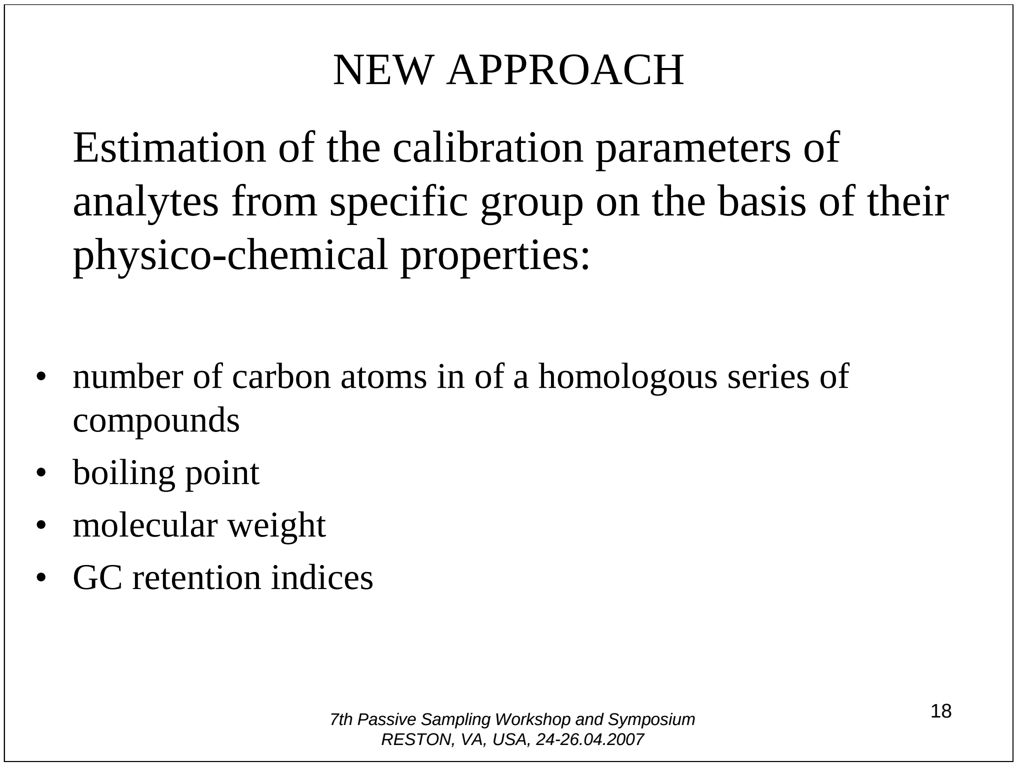
So far, calibration parameters had to be determined experimentally for <u>each individual analyte</u>

Calibration parameters are **compound dependent**, because **permeability** through a membrane depends on:

-**Diffusion of the analyte through the membrane and**

-Its **partition between the membrane material and surrounding air**.

Due to this, calibration parameters must be determined for each compound individually.



NEW APPROACH

Estimation of the calibration parameters of analytes from specific group on the basis of their physico-chemical properties:

- number of carbon atoms in of a homologous series of compounds
- boiling point
- molecular weight
- GC retention indices

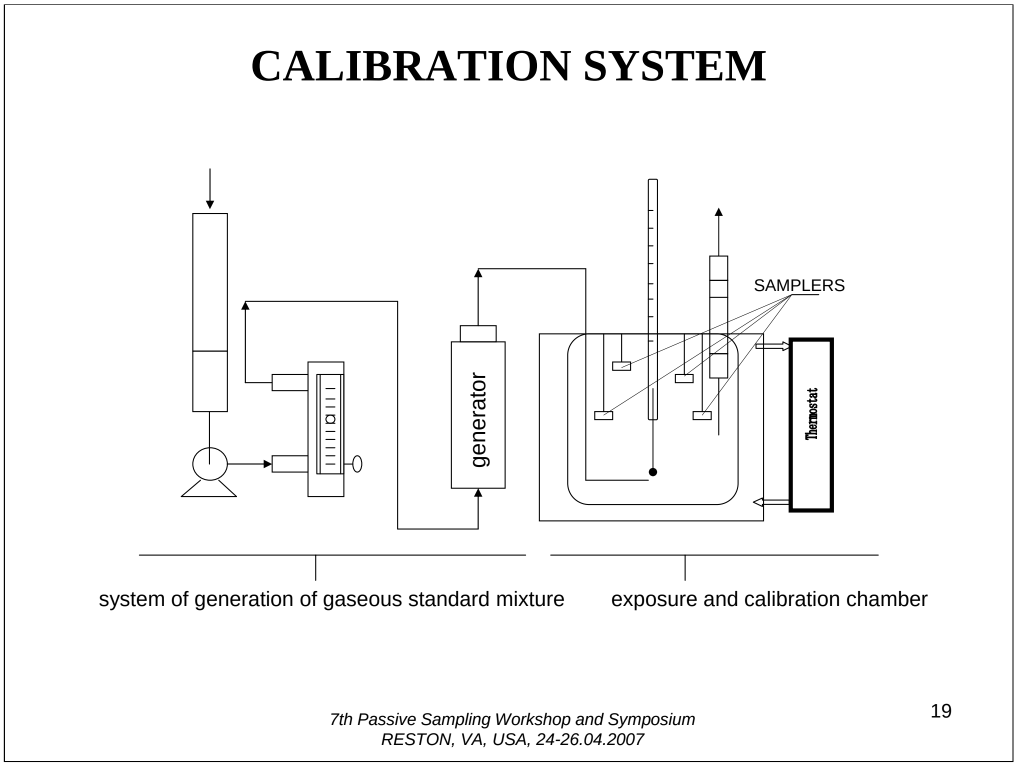
It seems, that it is possible to use, for evaluation of calibration parameters, such **physico-chemical properties** of analytes as:

- the number of carbon atoms in a molecule
- boiling point of a compound
- its molecular weight.

There is also a possibility to assess the **values of calibration constants** on the basis of **GC retention indices**.

One condition must be fulfilled:

- Analytes should belong to the same family, it means to the same homologous series of chemical compounds.



CALIBRATION SYSTEM

system of generation of gaseous standard mixture

exposure and calibration chamber

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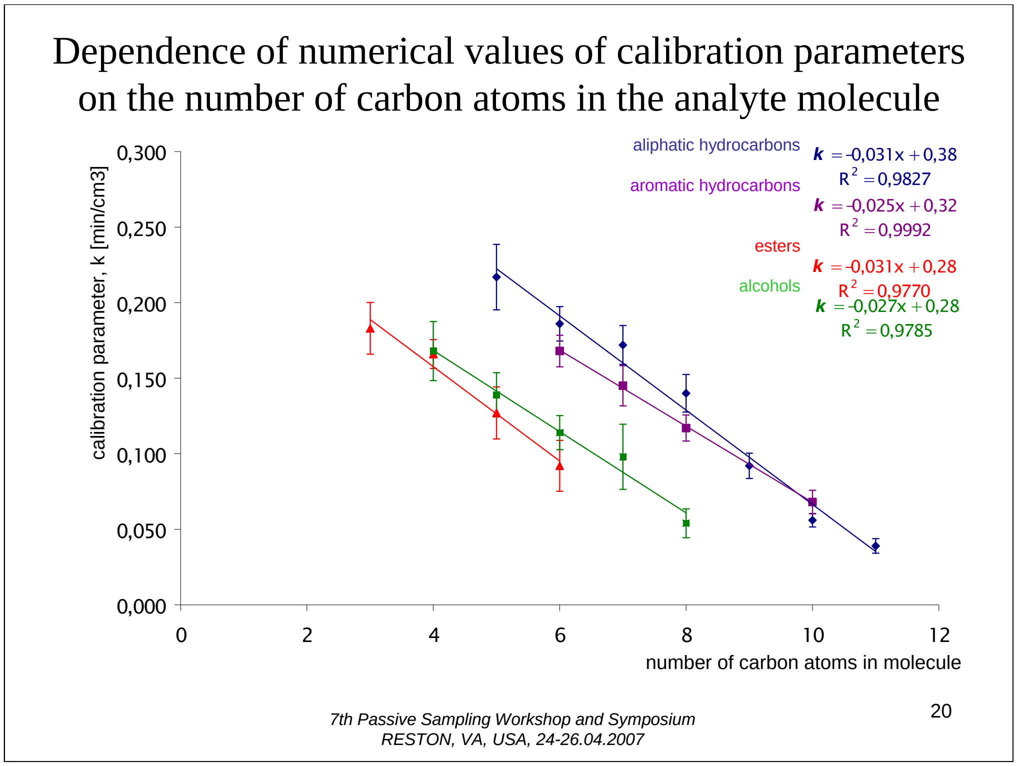
Our system used for experimental calibration of permeation passive samplers consists of:

-system of generation of gaseous standard mixtures

-thermostated exposure chamber in which permeation passive samplers are placed.

It seems, that the most suitable **source of stream of analytes** are **permeation tubes** placed in the **generator**.



Dependence of numerical values of calibration parameters on the number of carbon atoms in the analyte molecule

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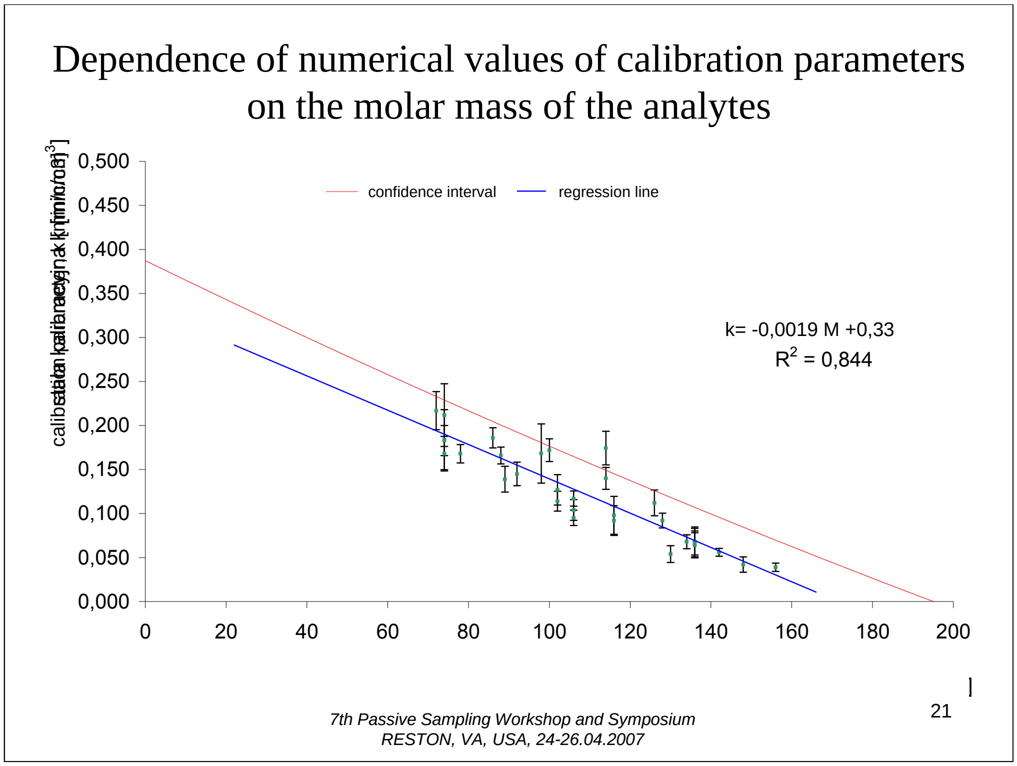
We have found quite a good correlation between **calibration parameters** and the **number of carbon atoms in the analyte molecule**.



Dependence of numerical values of calibration parameters on the molar mass of the analytes

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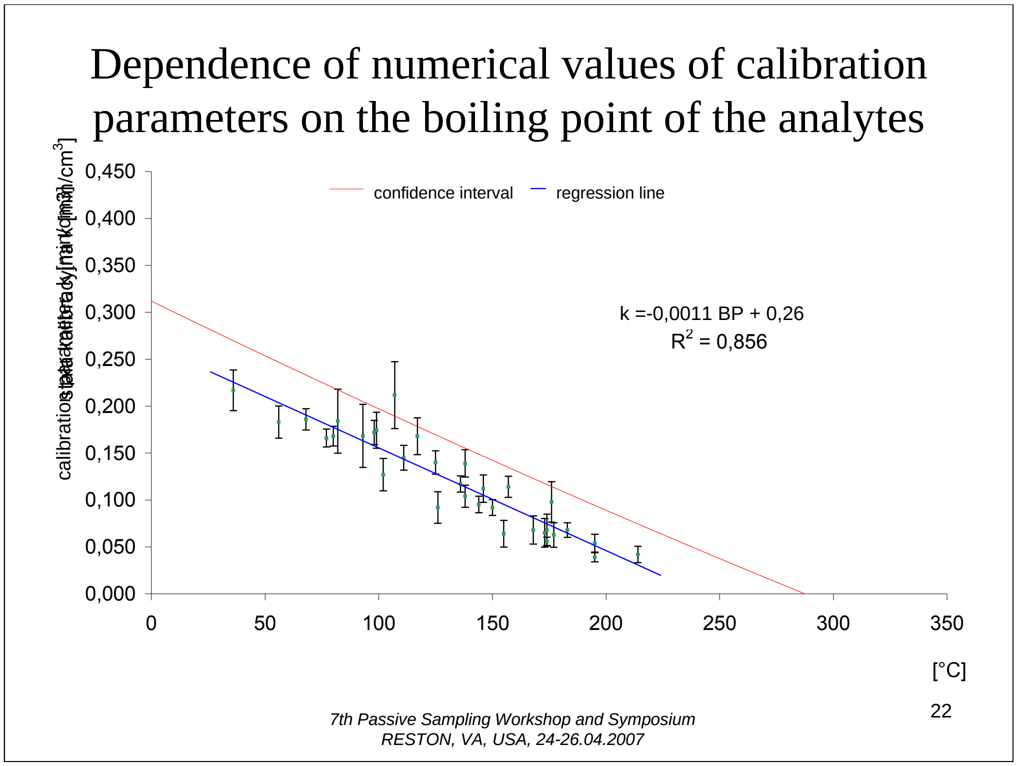
There is also a **very good relationship** between **calibration parameters** and the **molar mass** of the analytes.



Dependence of numerical values of calibration parameters on the boiling point of the analytes

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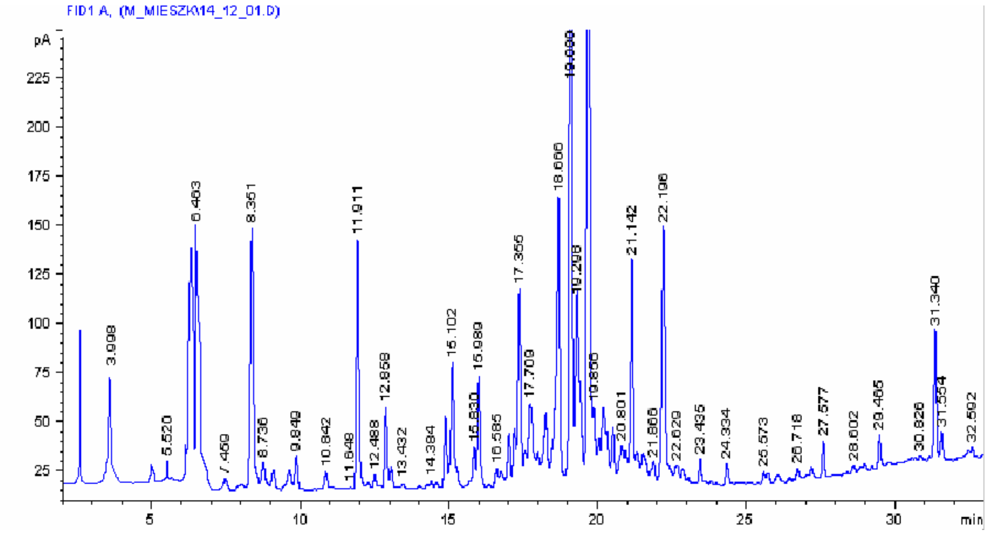
The **same type of relationship** we have found between **calibration parameters** and the **boiling point of the analytes**.

Volatile Organic Compounds in indoor air



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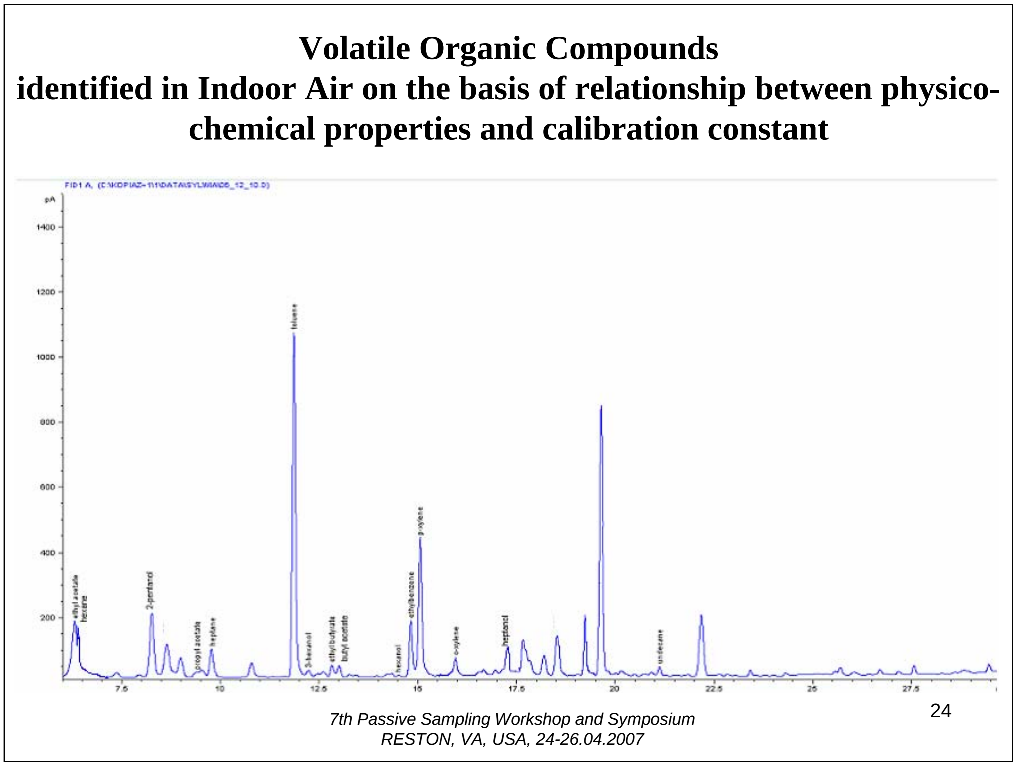
Chromatogram presented in this figure has been obtained during the analysis of sample of analytes retained on sorbent bed in permeation passive sampler.

This chromatogram, will have some analytical value, if all or at least the major peaks will be identified and quantified.



Volatile Organic Compounds identified in Indoor Air on the basis of relationship between physico-chemical properties and calibration constant

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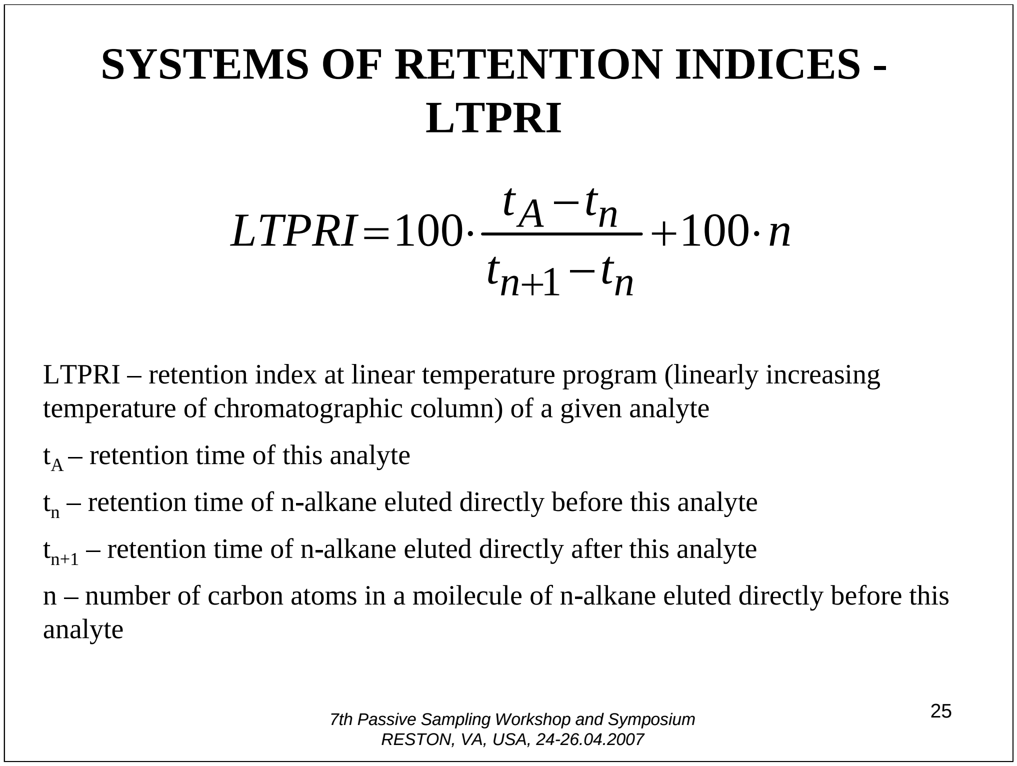
On this chromatogram, I would like to show **volatile organic compounds** present in **indoor air** for which **calibration parameters** have been assessed on the basis of the proposed approach.

There are **14 compounds identified** for which calibration parameters are known.



SYSTEMS OF RETENTION INDICES - LTPRI

$$LTPRI = 100 \cdot \frac{t_A - t_n}{t_{n+1} - t_n} + 100 \cdot n$$

LTPRI – retention index at linear temperature program (linearly increasing temperature of chromatographic column) of a given analyte

t_A – retention time of this analyte

t_n – retention time of n-alkane eluted directly before this analyte

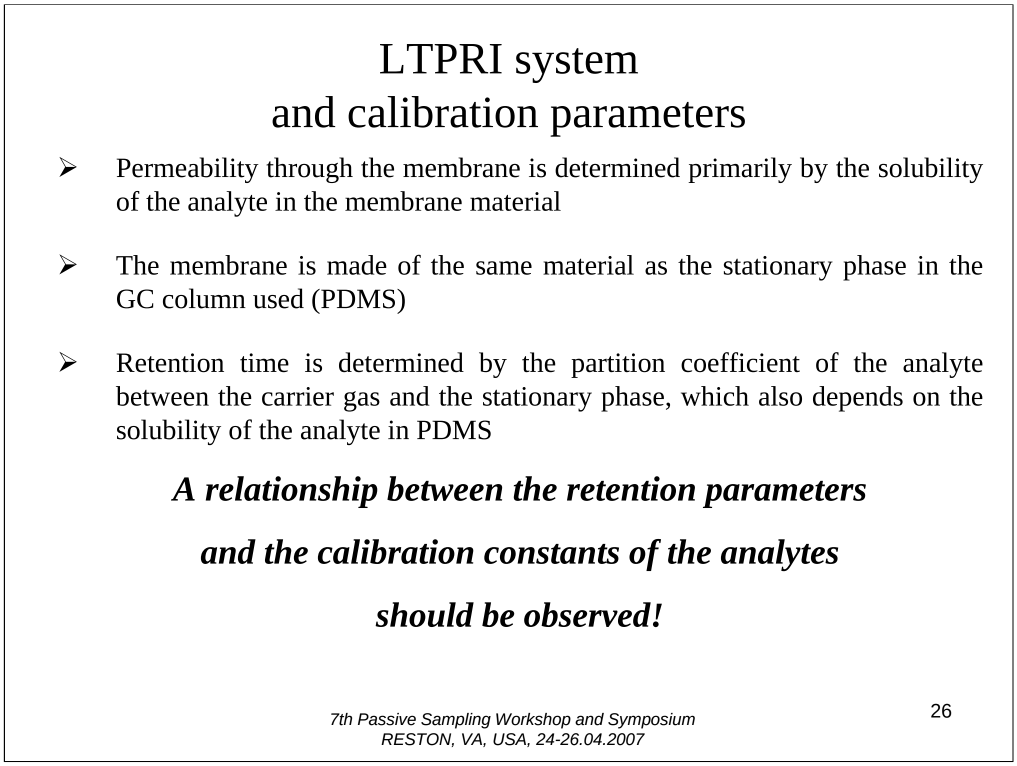
t_{n+1} – retention time of n-alkane eluted directly after this analyte

n – number of carbon atoms in a moilecule of n-alkane eluted directly before this analyte

We have also decided to verify the possibility of use of system **of retention indices** to facilitate the step of calibration of passive permeation samplers.

LTPRI system is based on KOVATS RETENTION INDICES.

This system was proposed in 1963.



LTPRI system
and calibration parameters

- Permeability through the membrane is determined primarily by the solubility of the analyte in the membrane material
- The membrane is made of the same material as the stationary phase in the GC column used (PDMS)
- Retention time is determined by the partition coefficient of the analyte between the carrier gas and the stationary phase, which also depends on the solubility of the analyte in PDMS

A relationship between the retention parameters

and the calibration constants of the analytes

should be observed!

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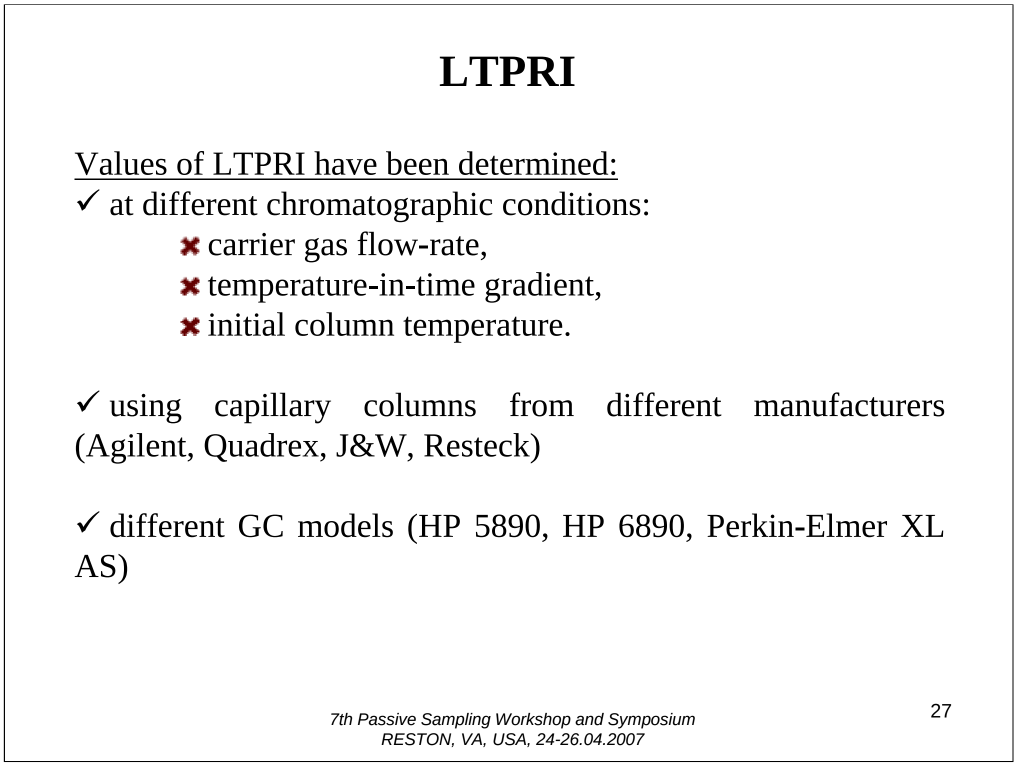
There should be a **relationship** between the **retention parameters** and the **calibration constants** of analytes.

This **statemen**t is connected with the fact, that **retention time** is **controlled** by the **partition coefficient** of the analyte between the carrier gas and the stationary phase in chromatographic column.

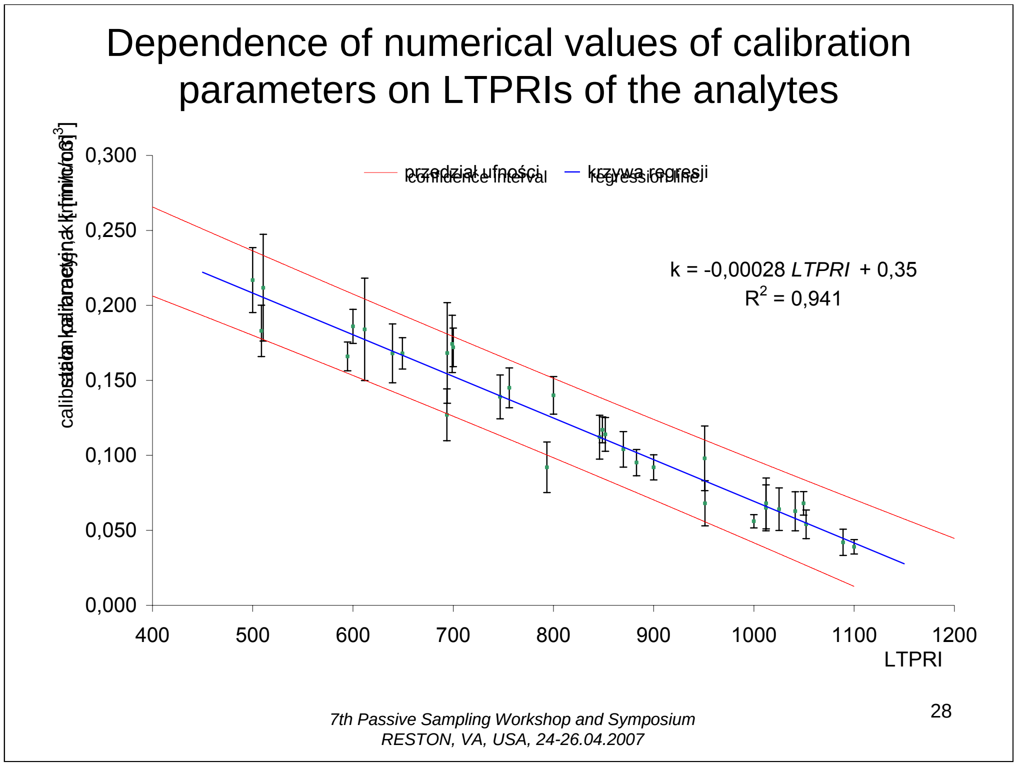


LTPRI

Values of LTPRI have been determined:

- ✓ at different chromatographic conditions:
  - ✖ carrier gas flow-rate,
  - ✖ temperature-in-time gradient,
  - ✖ initial column temperature.
- ✓ using capillary columns from different manufacturers (Agilent, Quadrex, J&W, Resteck)
- ✓ different GC models (HP 5890, HP 6890, Perkin-Elmer XL AS)

Numerical values of LTPRI for a **wide group of analytes** have been determined at different **chromatographic conditions**.



Dependence of numerical values of calibration parameters on LTPRIs of the analytes

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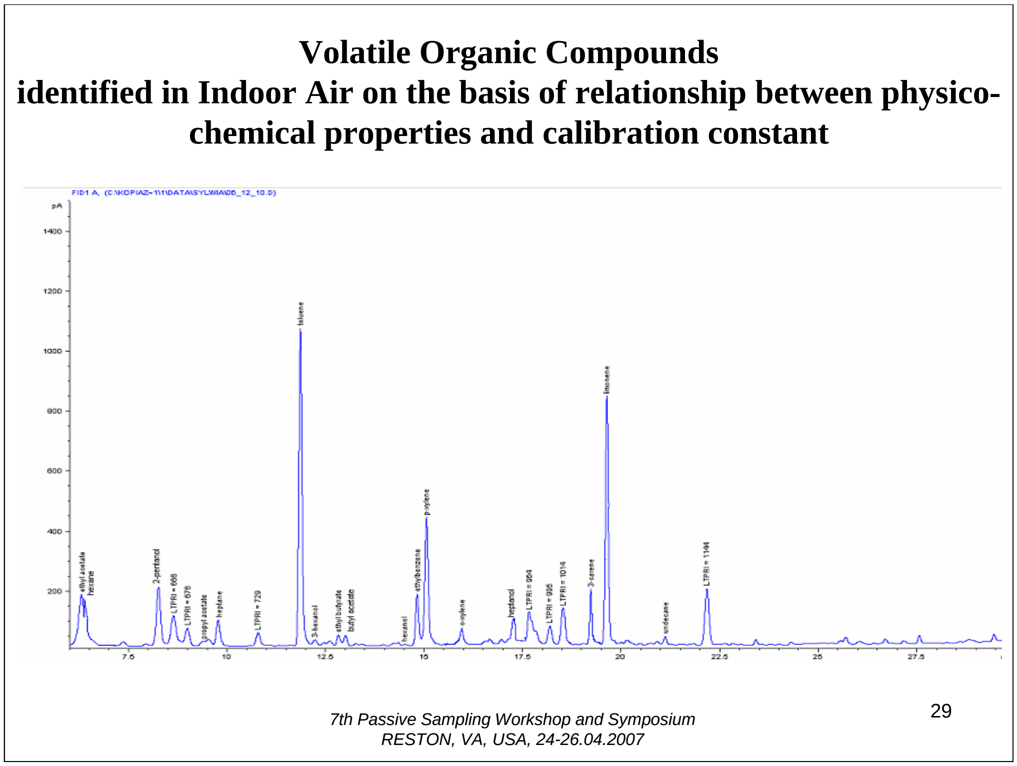
Finally we have **found quite a good correlation** between **calibration constant** of our passive sampler and **LTPRI values**.



Volatile Organic Compounds identified in Indoor Air on the basis of relationship between physico-chemical properties and calibration constant

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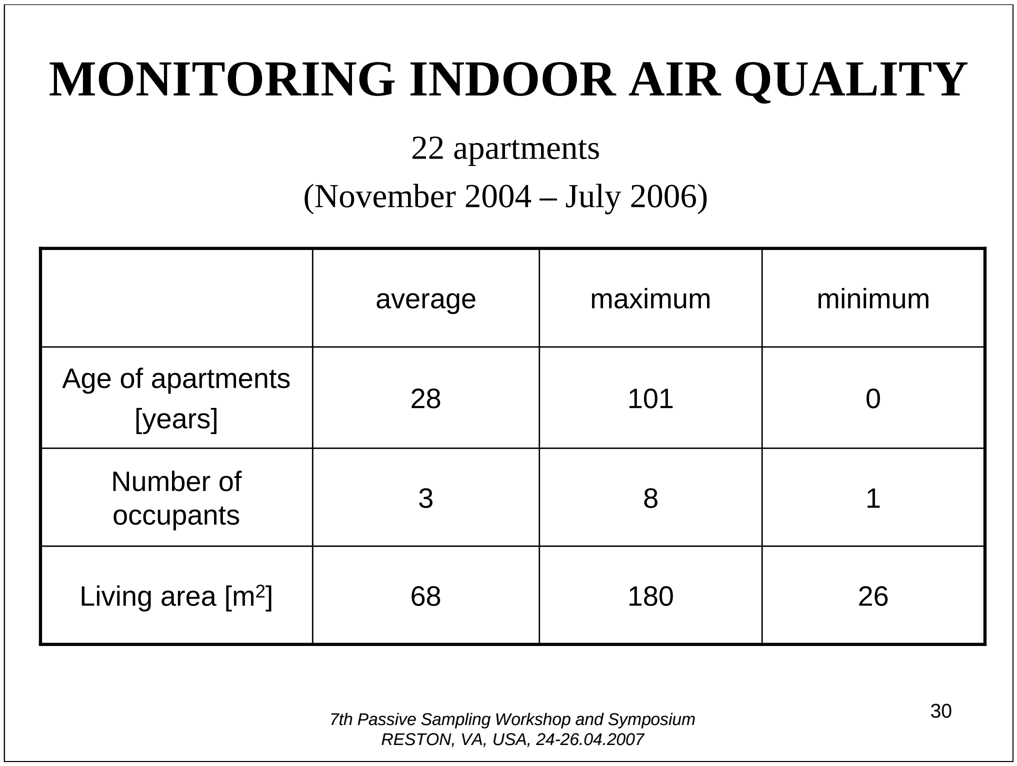
With the use of **linear temperature programmed retention indices approach** we can estimate calibration constants values for all compounds, which are presented on the chromatogram.

There are 24 volatile organic compounds identified with calibration constants evaluated on the basis of LTPRI approach.

There were only 14 compounds identified on the basis of the first approach, it means when physicochemical properties of analytes belonging to the same homologous series are taken into consideration.



MONITORING INDOOR AIR QUALITY

22 apartments
(November 2004 – July 2006)

	average	maximum	minimum
Age of apartments [years]	28	101	0
Number of occupants	3	8	1
Living area [m^2]	68	180	26

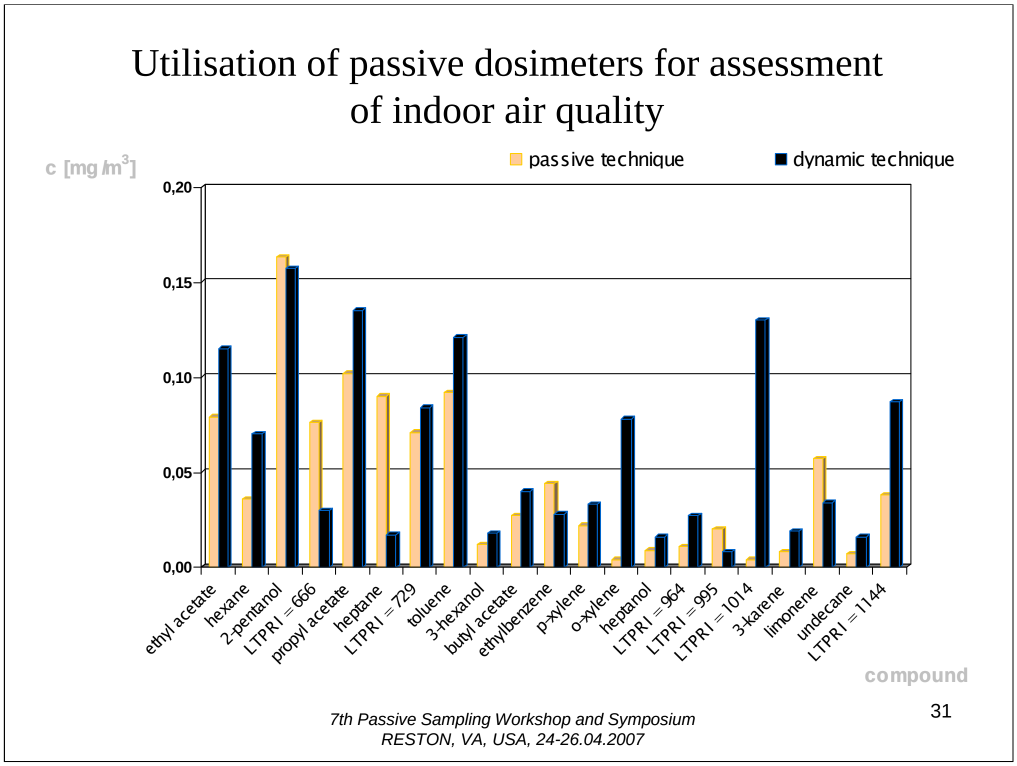
It is high time to tell some words about the application of our samplers in analytical practice.

We have studied the level of concentration of VOLATILE ORGANIC COMPOUNDS in 22 selected dwellings within the TRICITY area.

Tricity is a **urban agglomeration composed of Gdansk, Gdynia and Sopot** and situated on the **southern Baltic Sea coast**.

Studies were carried out in period since November 2004 till July 2006.

After the exposure samplers have been transported to laboratory.



Utilisation of passive dosimeters for assessment of indoor air quality

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Dynamic technique based on application of:

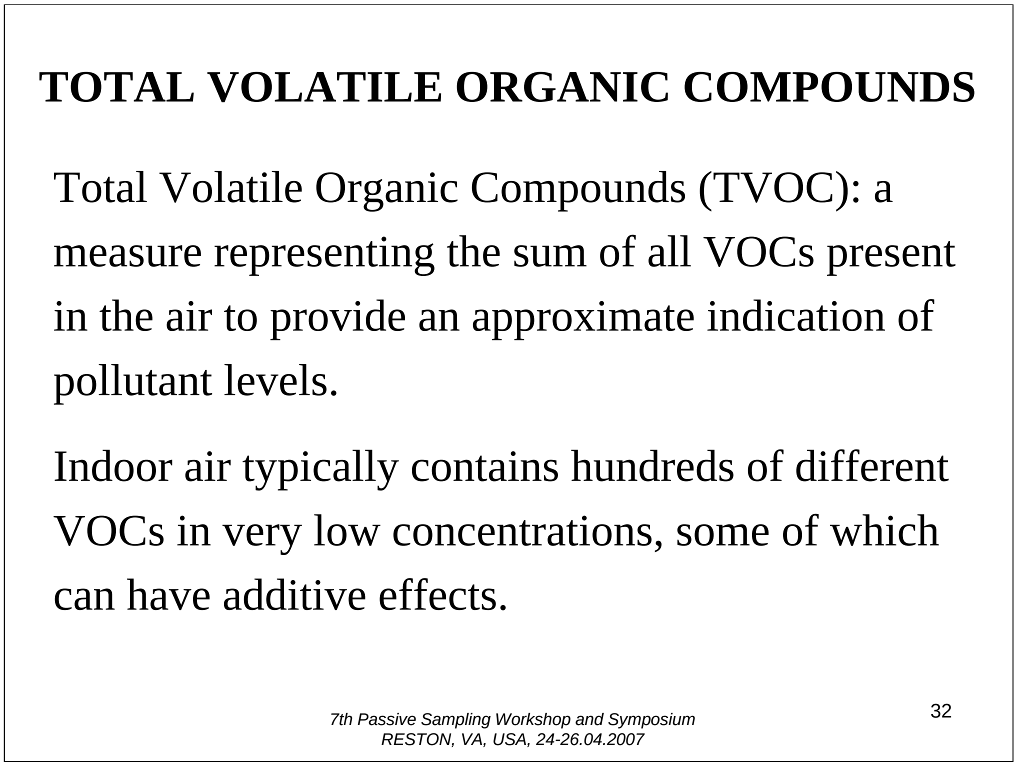
-Suitable pump,

-Flowmeter

-Sorbent tube

has been used as a REFERENCE technique of **sampling the analytes** from indoor air.

It is worthy to remember that **analytical protocol** carried out in **laboratory** is the **same for both techniques** of sampling the analytes.



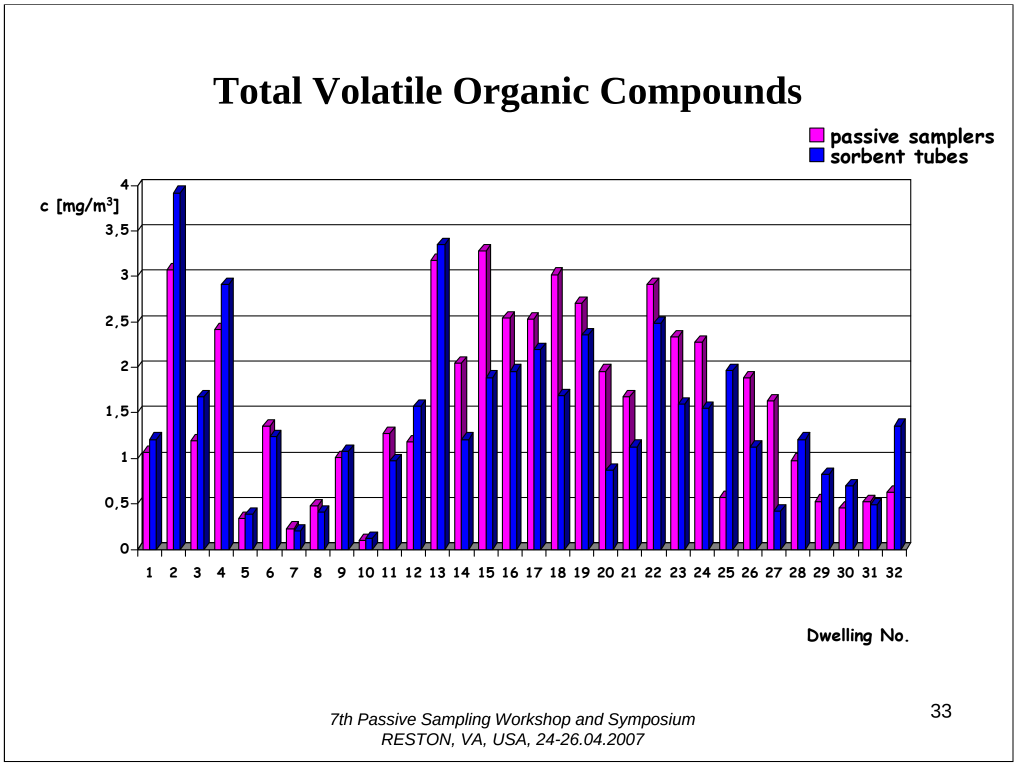
TOTAL VOLATILE ORGANIC COMPOUNDS

Total Volatile Organic Compounds (TVOC): a measure representing the sum of all VOCs present in the air to provide an approximate indication of pollutant levels.

Indoor air typically contains hundreds of different VOCs in very low concentrations, some of which can have additive effects.

Very often on the basis of analytical results, the value of **Total Volatile Organic Compounds** (TVOC’s) is calculated.

This parameter is useful in practice and can be used for the **preliminary classification** of **quality of indoor air** in different enclosed environment.



Total Volatile Organic Compounds

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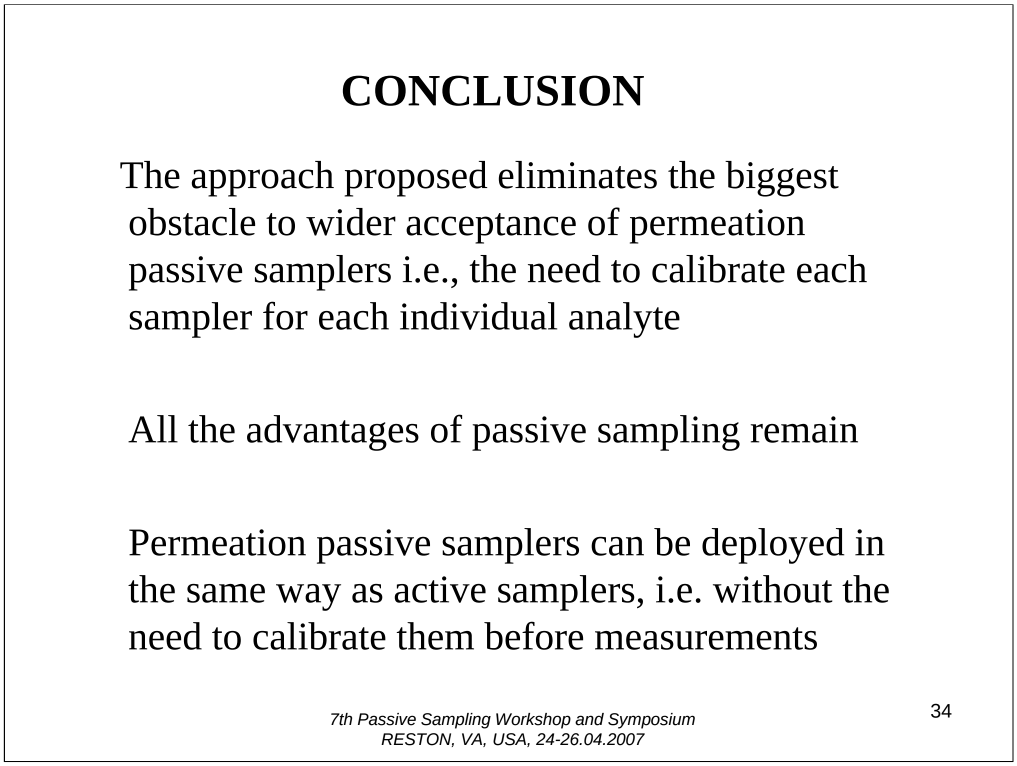
I would like to show you the comparison of the results of determination of **Total Volatile Organic Compounds** in 32 selected **Tricity dwellings**.

Generally no significant differences between **passive and dynamic sampling techniques** were observed.



CONCLUSION

The approach proposed eliminates the biggest obstacle to wider acceptance of permeation passive samplers i.e., the need to calibrate each sampler for each individual analyte

All the advantages of passive sampling remain

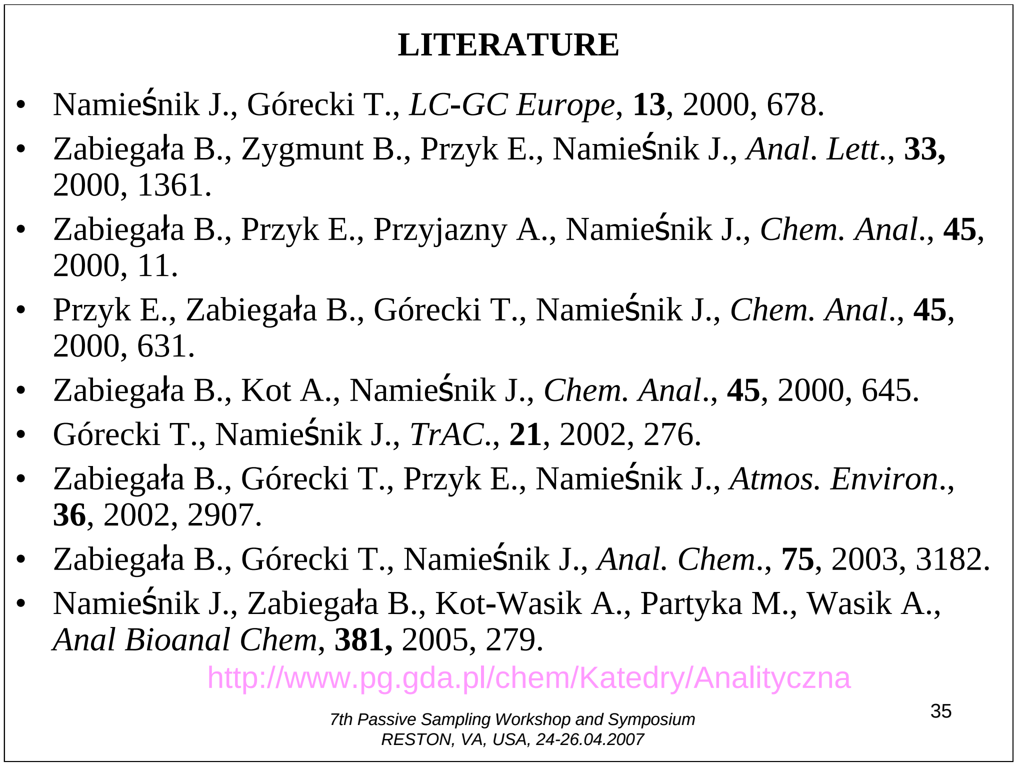
Permeation passive samplers can be deployed in the same way as active samplers, i.e. without the need to calibrate them before measurements

The approach proposed in this presentation **allows to eliminate** fundamental **limitation** of **permeation passive sampling**.

It is possible to estimate the values of the calibration constants on the basis of:

-**physico-chemical properties** of the analytes and/or

-**their GC retention parameters.**



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We think that this **new approach** in the field of **calibration of passive dosimeters will simplify analytical work** and make it possible to **apply passive dosimeters** on a larger scale.

More information on our research you can find in our publications.

The whole list is easily **accessible on homepage** of the Department of Analytical Chemistry.

Please, do not hesitate to contact me during this conference or later by e-mail.

35TH INTERNATIONAL SYMPOSIUM
OF ENVIRONMENTAL ANALYTICAL CHEMISTRY

35 ISEAC'08
22-26 June 2008, Gdańsk, Poland

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I would like to inform you that the 35th International symposium on Environmental Analytical Chemistry will take place in Gdansk in 2008.

As the Chairman of the Organizing Committee I have a pleasure to invite you. YOU ARE WELCOME!

AUTHORS

7th Passive Sampling Workshop and Symposium
RESTON, VA, USA, 24-26.04.2007

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Finally, I would like to introduce to you

the whole team from my Department of Analytical Chemistry and coauthors of this presentation:

-dr Bożena ZABIEGAŁA, who is present here

- dr Monika PARTYKA **who carried out the major part of these studies** as her PhD thesis.

THANK YOU FOR YOUR ATTENTION

7th Passive Sampling Workshop and Symposium
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