GENERATION OF GASEOUS STANDARD MIXTURES
PROBLEMS AND CHALLANGES

Marta Słomińska, Piotr Konieczka, Jacek Namieśnik

Department of Analytical Chemistry
Chemical Faculty
Gdansk University of Technology
G. Narutowicza 11/12 Str.
80-233 Gdańsk, Poland
tel: (58) 347 10 10
fax: (58) 347 26 94
e-mail: *chemanal@pg.gda.pl*

BREATH ANALYSIS 2014
8th International Conference on Breath Research and Cancer Diagnosis

INTRODUCTION

GDAŃSK UNIVERSITY OF TECHNOLOGY

QUALITY ASSURANCE / QUALITY CONTROL SYSTEM (QA/QC)

ISO/IEC

CHEMICAL METROLOGY

TRACEABILITY OF ANALYTICAL MEASUREMENTS

VALIDATION OF ANALYTICAL PROCEDURES

UNCERTAINTY VALUE

INTERLABORATORY COMPARISONS

REFERENCE MATERIALS

INTRODUCTION

GDAŃSK UNIVERSITY OF TECHNOLOGY

Material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

CERTIFIED REFERENCE MATERIALS

PRIMARY REFERENCE MATERIALS

MATRIX-FREEE
Pure substances
Calibration standards
Standard gas mixtures

MATRIX
Quality control materials, (QCM)
Laboratory reference materials, (LRM)
Secondary reference materials, (SecRM)

NON-CERTIFIED REFERENCE MATERIALS

COMPOSITION OF STANDARD GAS MIXTURES

MEASURAND(S) / ANALYT(-ES)

+

CARRIER GAS

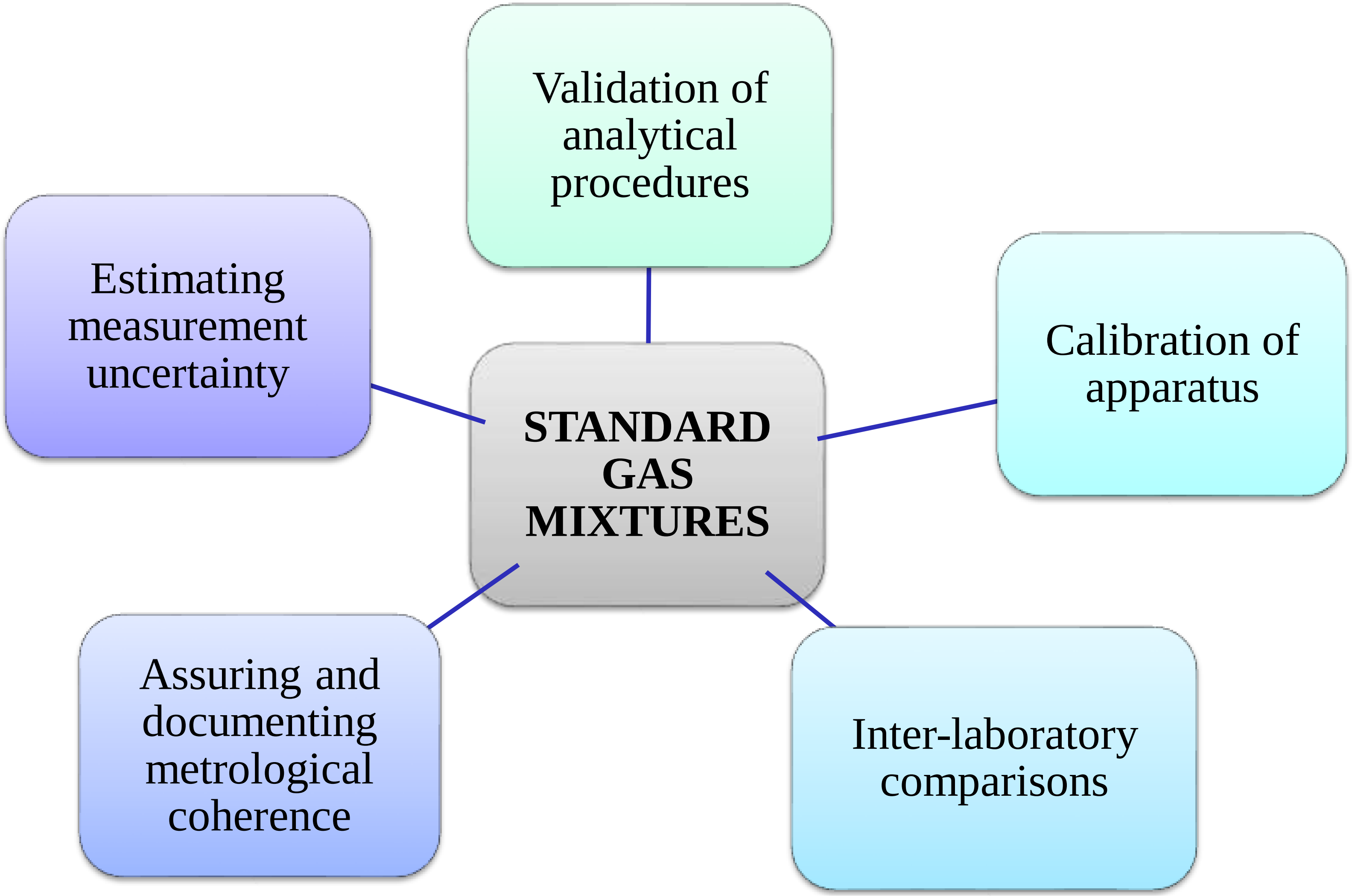
Zero gas - *specific type of gaseous mixture*

TYPES OF GASEOUS MEDIA STUDIED BY ANALYTICAL CHEMISTS

- atmospheric air
- indoor air
- workplace atmosphere
- gases in technological installations
- the waste gases from technological installations and materials
- **gases exhaled by humans**
- gaseous components of biogenic emissions

FIELD OF APPLICATION OF STANDARD GAS MIXTURES

GDAŃSK UNIVERSITY OF TECHNOLOGY



TECHNIQUES OF PREPARATION OF STANDARD GAS MIXTURES

STATIC TECHNIQUES

Introduction of known volume of the component into a known volume of diluting gas

1. pressurized
2. atmospheric pressure

DYNAMIC TECHNIQUES

Introduction of the stream of analytes into the stream of diluting gas

MIXED TECHNIQUES

Exponential dilution

STATIC TECHNIQUES

PRESSURIZED

- MANOMETRIC
- VOLUMETRIC
- GRAVIMETRIC

AT ATMOSPHERIC PRESSURE

- SINGLE FIXED-VOLUME CHAMBER,
- DOUBLE FIXED-VOLUME CHAMBER,
- CHAMBER OF VARIABLE VOLUME

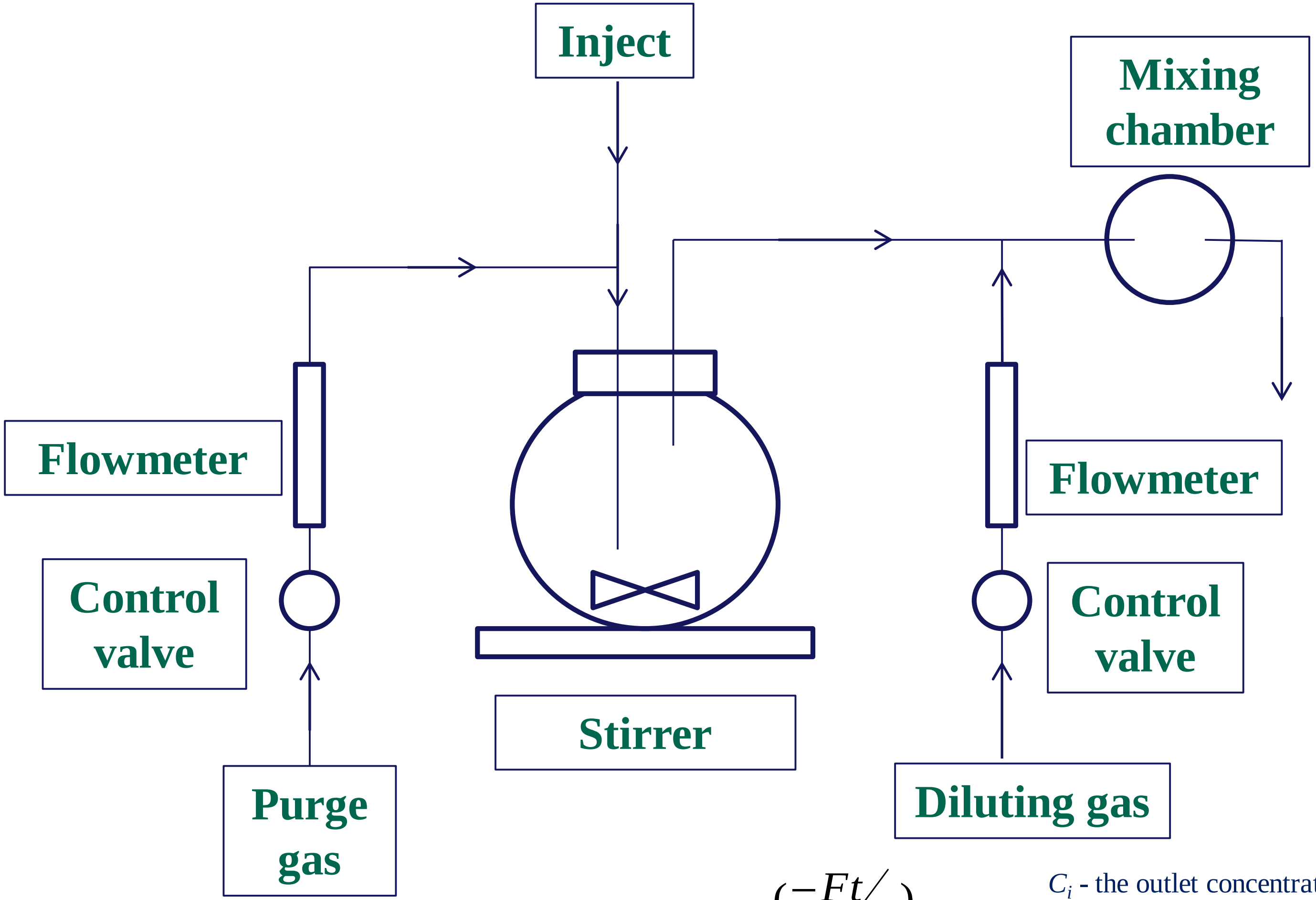
DYNAMIC TECHNIQUES

THE STREAM OF DILLUTING GAS

- Permeation
- Diffusion
- Thermal decomposition of surface compounds
- Electrolysis;
- Periodic injection of gaseous analytes into the stream of diluting gas;
- Mixing of gas streams
- Evaporation
- Autodilution
- Chemical reaction

SGM

MIXED TECHNIQUE- EXPONENTIAL DILUTION FLASK (EDF)

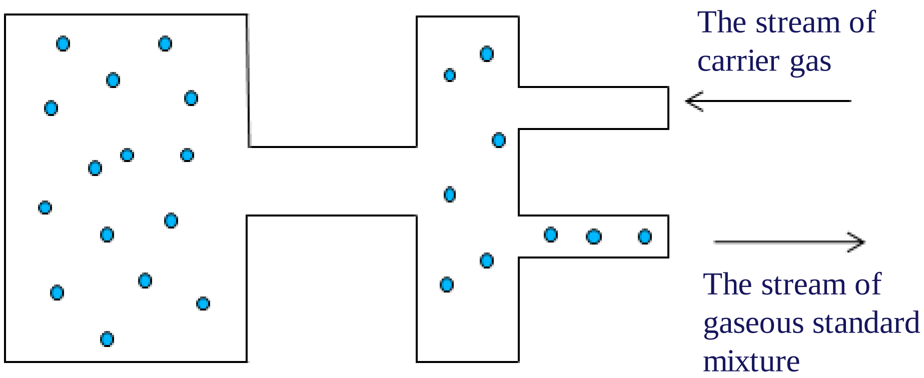


$$C_i = C_0 e^{(-Ft/V)}$$

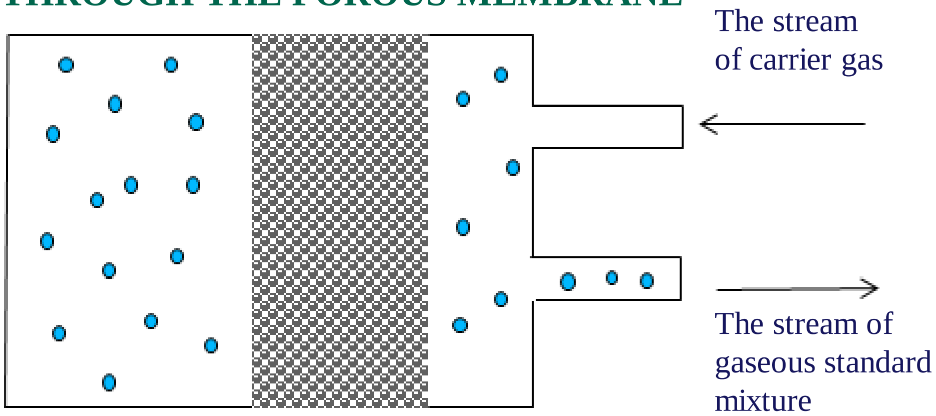
C_i - the outlet concentration of analyte *i*,
C_0- the initial concentration of analyte *i* in the exponential dilution flask,
F -the volumetric flow rate of dilution gas,
t - the time after sample introduction,
V - the volume of the flask or container

APPLICATION OF DIFFUSION TECHNIQUE FOR GENERATION OF STANDARD GAS MIXTURES

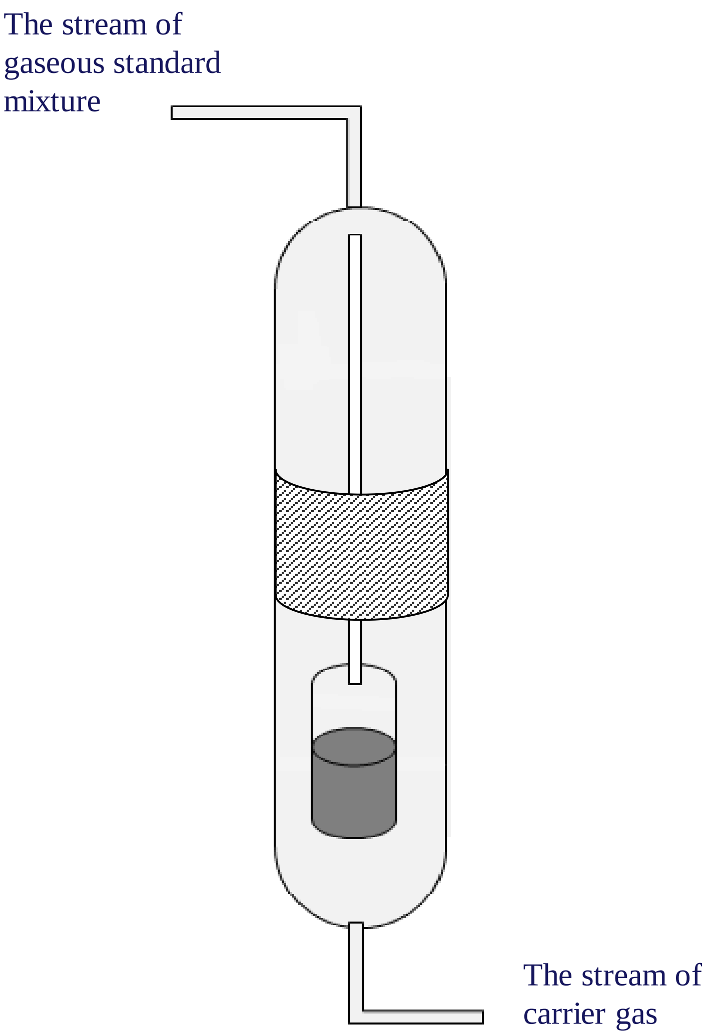
DIFFUSION MECHANISM
a) THROUGH THE CAPILLARY



DIFFUSION MECHANISM
b) THROUGH THE POROUS MEMBRANE



DIFFUSION TUBE



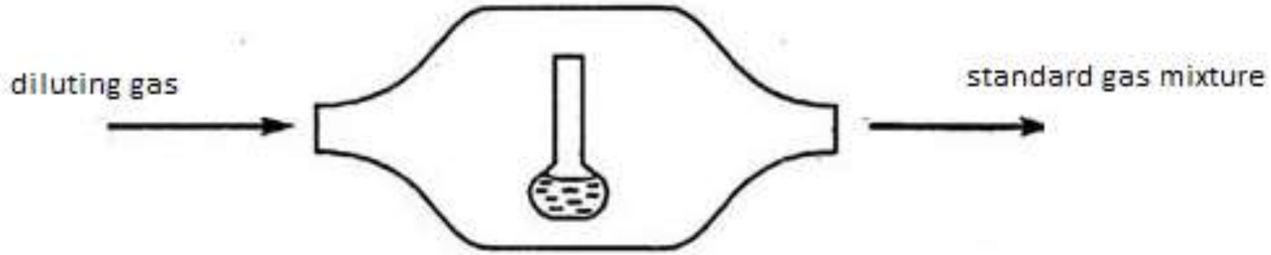
FIELD OF APPLICATION OF DIFFUSION PROCESS FOR GENERATION OF STANDARD GAS MIXTURES

ANALYTES	CAPILLARY LENGTH [cm]	CAPILLARY INNER DIAMETER [mm]	T [° C]	FLOW RATE [l/min]
aromatics *terpenes* *halocarbons* *hexane*	1-20	0.025-4	25 - 75	*n.d.*
ICl *IBr* Br_2 I_2	2.5-20	0.1-2.15	25	0.5
formaldehyde	7.9	4.9	35[a] 230[b]	0.75
2,3- DCDD	3	n.d.	75 - 100	0.5 - 2

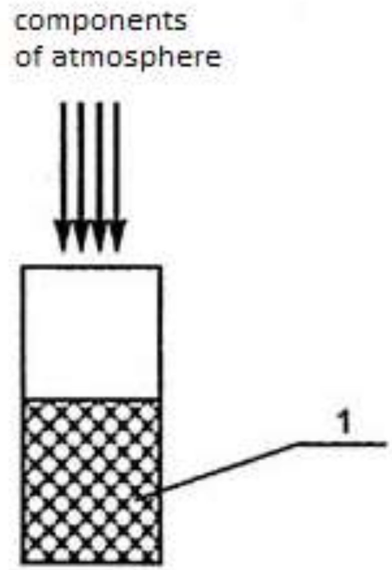
ANALYTICAL ASPECTS OF APPLICATION OF DIFFUSION PROCESS

GDAŃSK UNIVERSITY OF TECHNOLOGY

PREPARATION OF STANDARD GAS MIXTURES



THE ENRICHEMENT OF VOLATILE COMPONENTS OF ATMOSPHERE



PERMEATION AS A SUITABLE PROCESS FOR GENERATION OF STREAM OF MEASURAND

GDAŃSK UNIVERSITY OF TECHNOLOGY

PERMEATION - involves the diffusion of molecules, called the permeant, through a membrane or interface. Permeation works through diffusion; the permeant will move from high concentration to low concentration across the interface.

Fick's Law of Diffusion

$$J = -D\left(\frac{dC}{dx}\right)$$

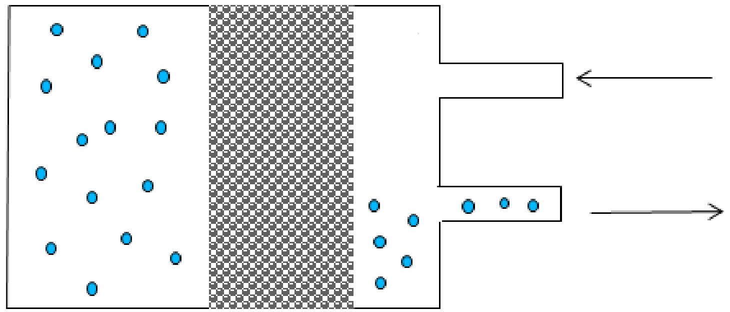
J - the flux per unit area of permeant through the polymer
D - the diffusion coefficient
$\frac{dC}{dx}$ *– concentration gradient*

$$C = \frac{22{,}45R}{MQ}$$

C- concentration of the analyte in standard gas mixture
R- permeation rate
Q- flow rate of the stream of carrier gas
M- molecular weight

PERMEATION TUBES AS A SOURCE OF ANALYTES IN THE STREAM OF GASEOUS MIXTURE

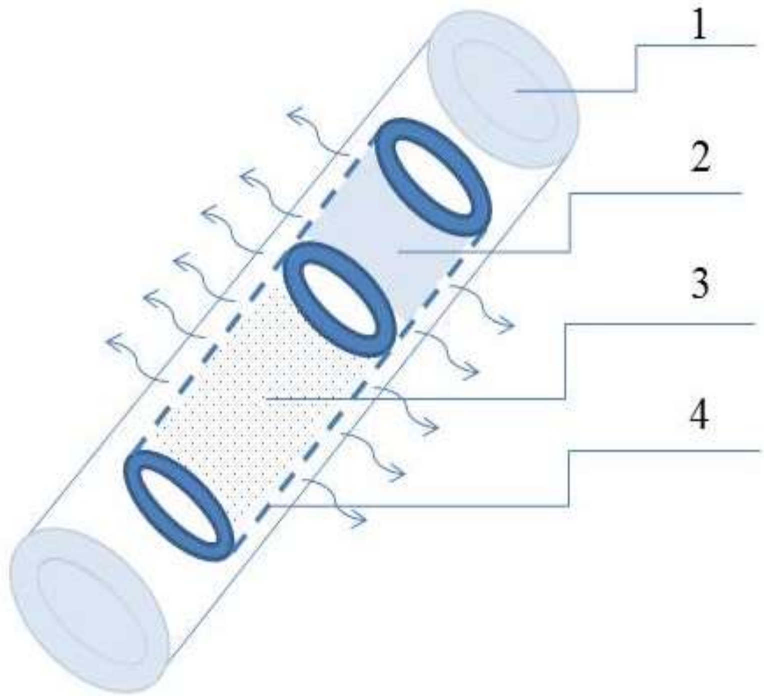
PERMEATION MECHANISM



$$q_d = \frac{CQ}{22{,}4/M}$$

q_d – permeation rate [ng/min]
C – concentration [ppm]
Q - flow rate [mL/min]
M- molecular weight [g/mol]

PERMEATION TUBE

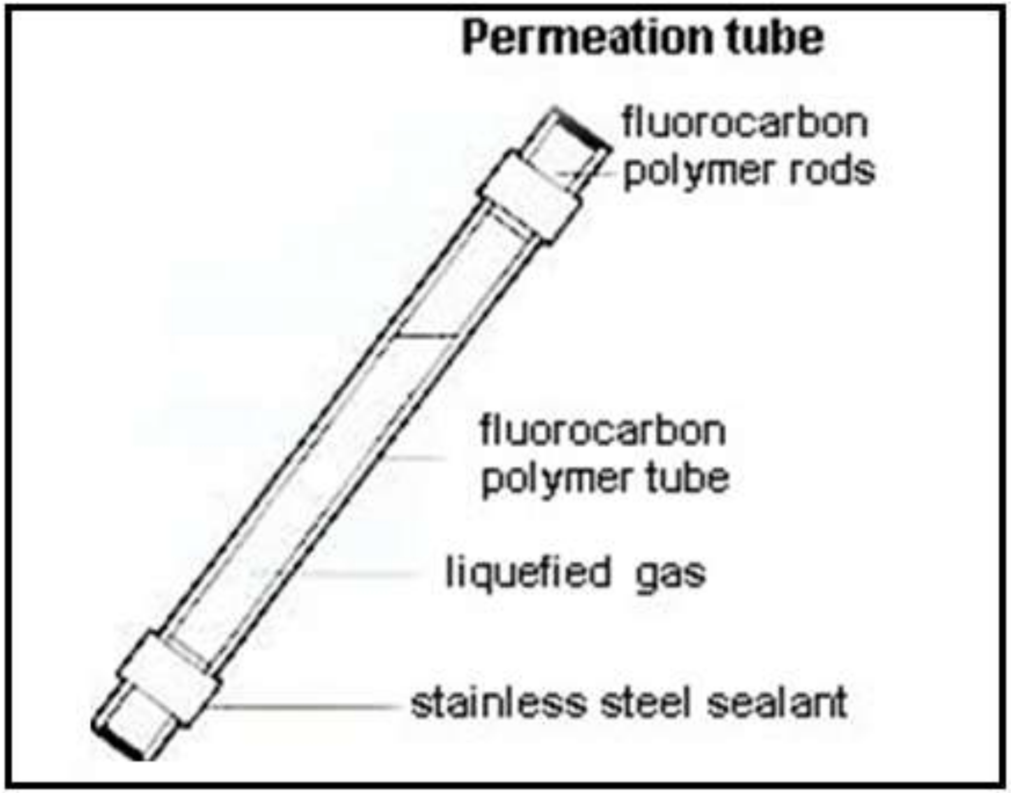


1- seal
2- liquid phase
3- gas phase
4- permeable membrane

APPLICATION OF PERMEATION DEVICES

TYPES OF MEMBRANES APPLIED IN PERMEATION DEVICES		
N°	Material of memebrane	Analyte
1.	PDMS-FS	$n\text{-}C_4H_{10}$ CH_4
	PDMS	$n\text{-}C_4H_{10}$ CH_4
2.	PTFE (Teflon®)	BTX
3.	cork "Amadia"	He N_2 O_2 CO_2
4.	Matrimid® (poliimid 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diamino-phenylidane)	H_2 (purity 99,5%)
5.	PTFE	styrene phenole aldehydes
6.	PTFE	SF_6
7.	-	NO_2 in nitrogene

PERMEATION TUBES USED FOR GENERATION OF STANDARD GASEOUS MIXTURES

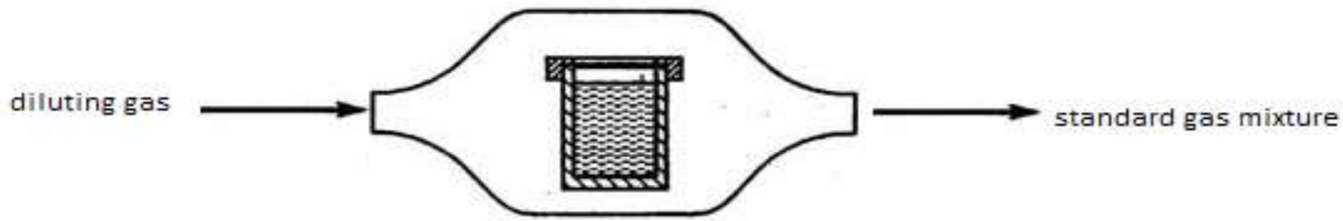


www.gastec.co.jp
GASTEC CORPORATION

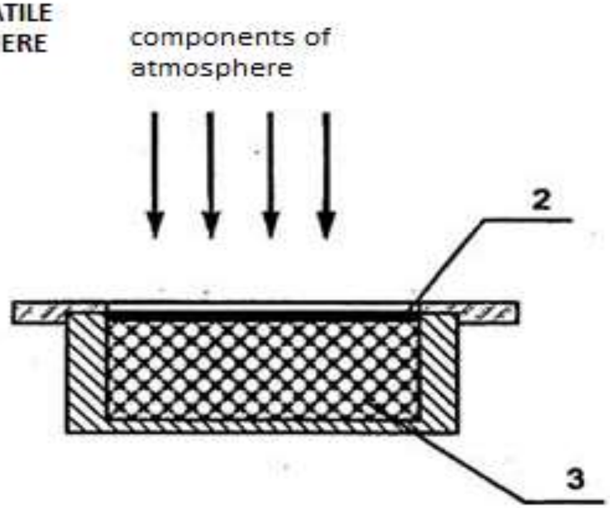
ANALYTICAL ASPECTS OF APPLICATION OF PERMEATION PROCESS

GDAŃSK UNIVERSITY OF TECHNOLOGY

PREPARATION OF STANDARD GAS MIXTURES



THE ENRICHMENT OF VOLATILE COMPONENTS OF ATMOSPHERE



DIFFUSION AS A SUITABLE PROCESS OF GENERATION OF STREAM OF MEASURAND

GDAŃSK UNIVERSITY OF TECHNOLOGY

Fick's Law of Diffusion

$$J = -D\left(\frac{dC}{dx}\right)$$

J - the flux per unit area of permeant through the polymer
D - the diffusion coefficient
$\frac{dC}{dx}$ *– concentration gradient*

$$C = \frac{R}{dQ}$$

R- diffusion rate
d- density of analyte vapour
Q - flow rate of the stream of carrier gas

TRENDS IN DEVELOPMENT OF TECHNIQUES OF GENERATION OF GASEOUS STANDARD MIXTURES

BUBBLER SYSTEM (VSGM)

- ease of use
- applicable for wide spectrum of organic compounds in wide range of concentration
- low cost of production and operation

TGA, TTG

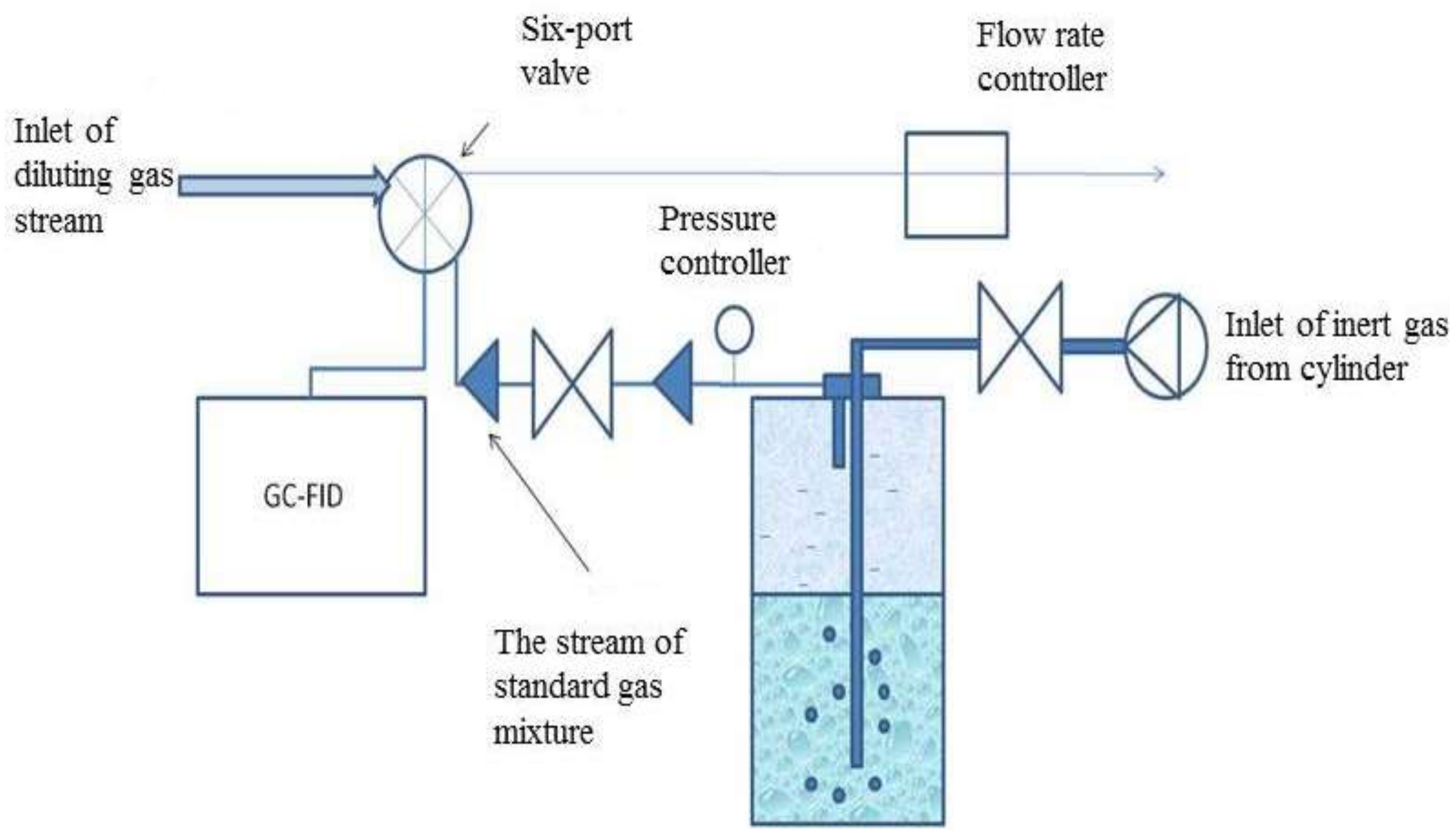
- short time of preparation of standard gas mixture
- applicable for wide spectrum of organic compounds in wide range of concentration (ppm-ppb)
- possibility of obtaining standard gas mixture with low concentration of analytes in wide range of pressure with the possibility of real controlling of the concentration
- high precision of the technique

THERMAL DECOMPOSITION OF SURFACE COMPOUNDS

- possibility of application in case of toxic, reactive, volatile and of unpleasant smell
- elimination of errors connected with weighing of the carrier sample
- possibility to produce single- and multi-constituent standard mixtures
- lack of effect of the water content on the amount of liberated analyte (glass fibres)

4. *BUBBLER SYSTEMS FOR GENERATION OF STANDARD GAS MIXTURES*

Vapour Standard Gas Mixture System (VSGM)

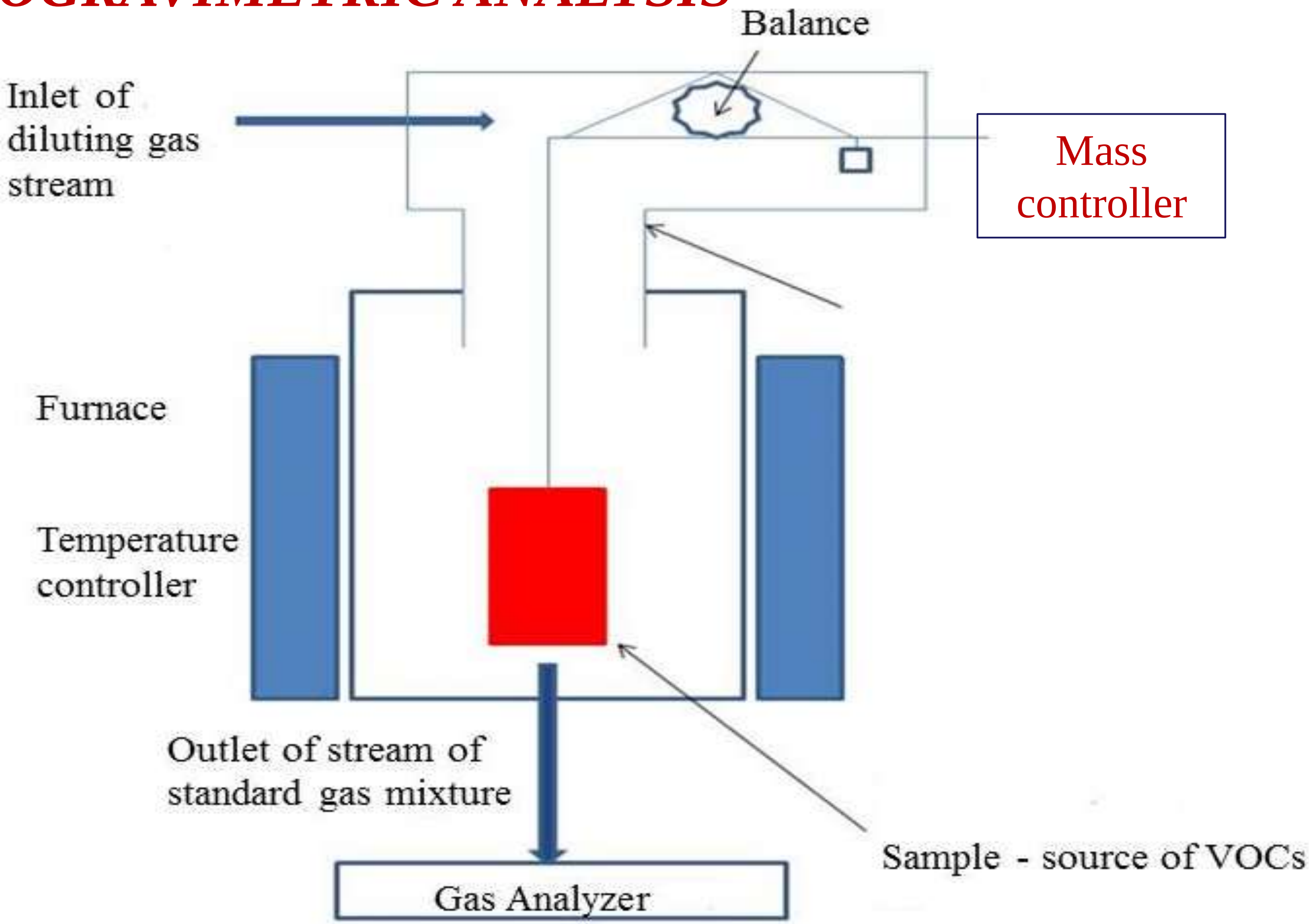


TYPES OF VAPOUR STANDARD GAS MIXTURES SYSTEMS (VSGM) APPLICABLE IN LABORATORY PRACTICE

TYPE OF SYSTEM	MATRIX	ANALYTE	CONCENTRATION IN GASEOUS MIXTURE [mg/m^3]
E-01	liguid	phenol	1-120
U-06	solid sorbent	benzene	1-1700
U-11	solid sorbent	acetone	1-1600
U-13	solid sorbent	methanol	1-900
U-15	solid sorbent	n-propanole	1-540
M-07	liquid	toluene	1-1200
M-08	liquid	ethylbenzene	1-1100
M-03	liquid	o-xylene	1-600
M-04	liquid	m-xylene	1-800
M-05	liquid	p-xylene	1-850
G-01	liquid	acetaldehyde	1-2600

VSGM-U- solid matrix, low dynamic of system, maximum flow rate of carrier gas stream -200ml/min for gas inlet pressure -15 kPa;
VSGM-M/E- liquid matrix, high dynamic of system, maximum flow rate of carrier gas stream – 400 ml/min for gas inlet pressure 15-20 kPa

5. *THE SYSTEMS BASED ON THE WEIGHNING TECHNIQUES - THERMOGRAVIMETRIC ANALYSIS*



ADVANTAGES OF STATIC AND DYNAMIC TECHNIQUES OF GENERATION OF STANDARD GAS MIXTURES

GDAŃSK UNIVERSITY OF TECHNOLOGY

	DYNAMIC TECHNIQUES	STATIC TECHNIQUES
ADVANTAGES	▪ possibility of preparing greater volume of gas mixture in a wide range of analytes' concentrations with required accuracy, ▪ elimination of adsorption process which results in losing of analytes, ▪ homogeneity and stability of prepared standard gas mixture ▪ possibility of preparing and introducing the mixture to the measurement system under different conditions of temperature, pressure and flow rate	▪ simple to carry out, ▪ low-cost of apparatus

DISATVANTAGES OF STATIC AND DYNAMIC TECHNIQUES OF GENERATION OF STANDARD GAS MIXTURES

GDAŃSK UNIVERSITY OF TECHNOLOGY

	DYNAMIC TECHNIQUES	STATIC TECHNIQUES
DISADVANTAGES	▪ necessity of having the gaseous analytes sources, ▪ necessity of controlling the flow rate of stream of diluting gas ▪ difficulties arising from stopping of generation of standard gas mixture	▪ time-consuming and inaccurate procedure ▪ losses of analytes due to adsorption and condensation on the walls of the chambers, ▪ impossible to storage in amounts sufficient to reuse, ▪ stratification during the stage of storage, ▪ unsuitable for unstable and reactive compounds

GDAŃSK UNIVERSITY OF TECHNOLOGY

3. *THERMAL DECOMPOSITION OF SO-CALLED SURFACE COMPOUNDS AS A SOURCE OF STREAM OF ANALYTE*

STEPS OF THE PROCEDURE

1. Chemical modification of surface compound

- Homogeneity structure;
- Homogeneity distribution of active centre
- Strictly definited porosity
- Mechanical strenght

2. Thermal decomposition of surface compound

- Purity of material;
- Range of temperature;
- Homogeneity of surface after chemical modification

3. Generation of standard gas mixture

- Flow rate of diluting gas stream;
- Temperature of decomposition process of surface compound;
- size of sample;
- Time of generation of standard gas mixture

Milestones in the application of thermal decomosition process for generation of standard gas mixtures

2012

- preparation of matrix free reference material of ethene in the form of glass fibers covered with thin layer of aluminum– CERTIFICATION OF MATERIAL

2008

- Trials with GLASS FIBERS COVERED WITH ALUMINUM for preparation of standard gas mixtures of methyl chloride and ethene

2007

- PATENT modified silica gel for preparation of standard gas mixtures

2006

- Carrier: SILICA GEL; standard gas mixture – ACETONE,

2004

- Use of TRIMETHYLAMINE for chemical modification, Carrier: SILICA GEL; standard gas mixture – ETHENE, METHYL CHLORIDE;

2001

- Carrier-POROUS GLASS

2000

- Carrier: SILICA GEL; standard gas mixture – ETHENE;

1997

- Carrier: SILICA GEL; standard gas mixture – AMMONIA, METHYLAMINE, DIETHYLAMINE, TRIETHYLAMINE;

1996

- Development of calibration technique for TD-GC-MS system
- Carrier: SILICA GEL; standard gas mixture – n- **PROPANETHIOL;**

1992

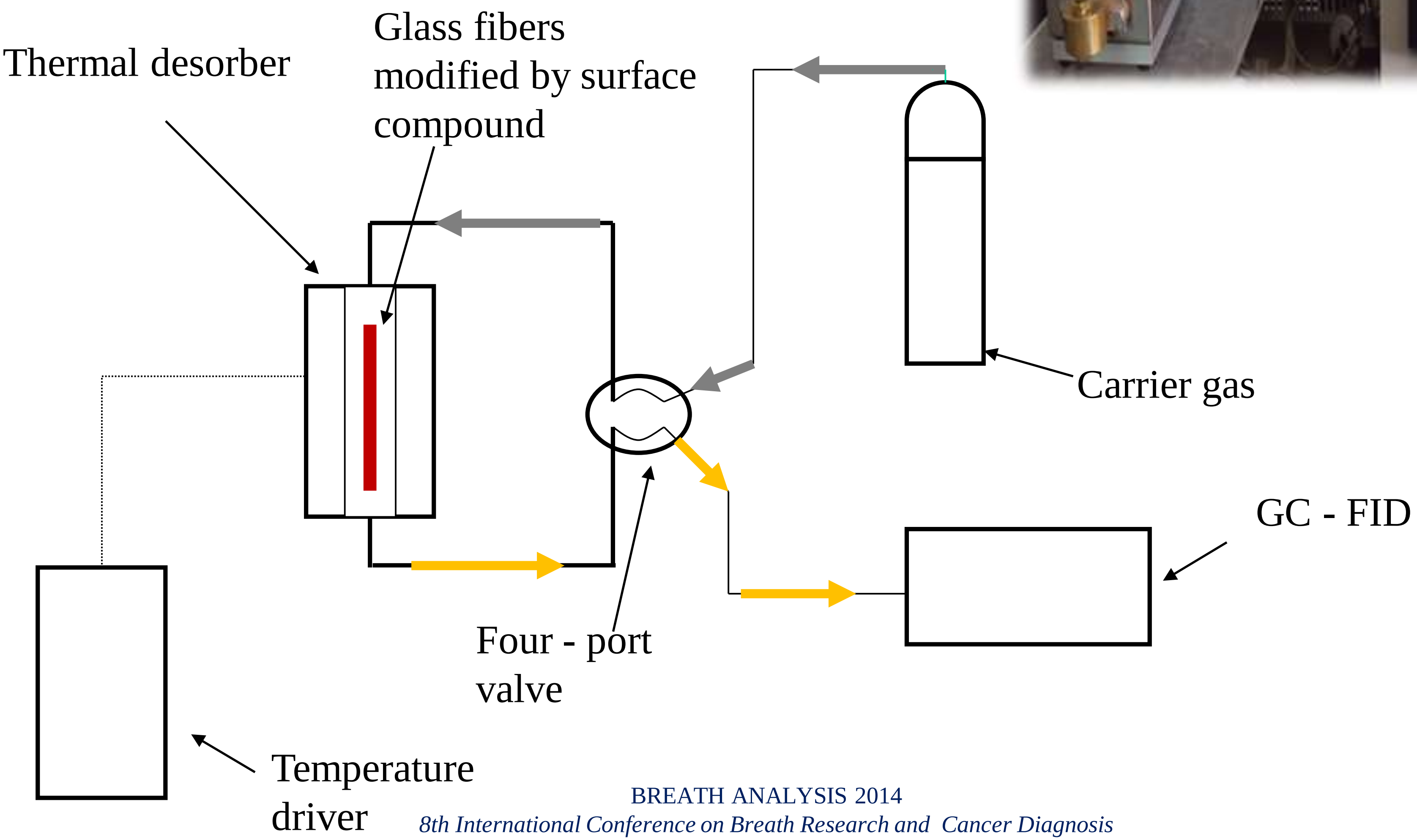
- Carrier: SILICA GEL; standard gas mixture – ISOTHIOCYANATE;

1991

- Concept of application of apropriate surface compounds for obtained reference materials; Carrier: SILICA GEL; standard gas mixture– THIOLES;

APPARATUS SET UP FOR THE THERMAL DECOMPOSITION OF SURFACE COMPOUNDS

TD-GC-FID



The aim of the project is to produce 6 new certified reference materials, which can be regarded as a response to the needs of Polish analytical laboratories in the field of environmental analysis

I. MATRIX - FREE REFERENCE MATERIALS OF BTX COMPOUNDS

- preparation of a matrix-free BTX reference materials in the form of glass fibres coated with a thin layer of aluminium,
- the surface of glass fibres is chemically modified with a specific compound,
- as a result of thermal decomposition a specific analyte (benzene, toluene or xylenes) is formed.

II. ENVIRONMENTAL REFRENCE MATERIALS

<u>Different matrix</u>

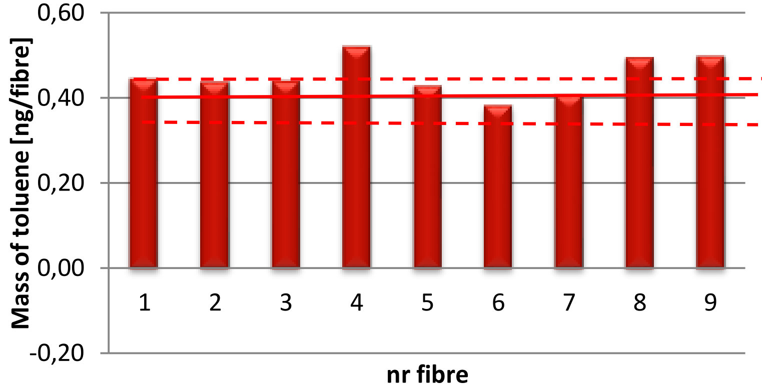
1. soil
2. sediment
3. biological tissues (FISHES, BIRDS)

<u>Wide range of analytes</u>

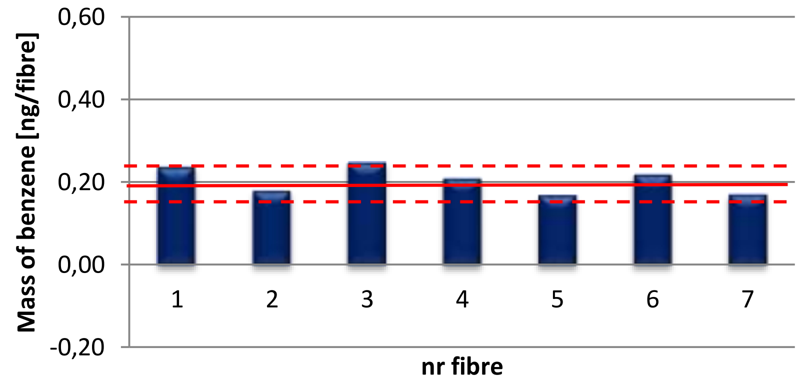
1. WWA
2. PCB
3. Heavy metals

THE RESULTS OBTAINED DURING THE PRODUCTION OF MATRIX FREE REFERENCE MATERIALS OF BTX COMPOUNDS

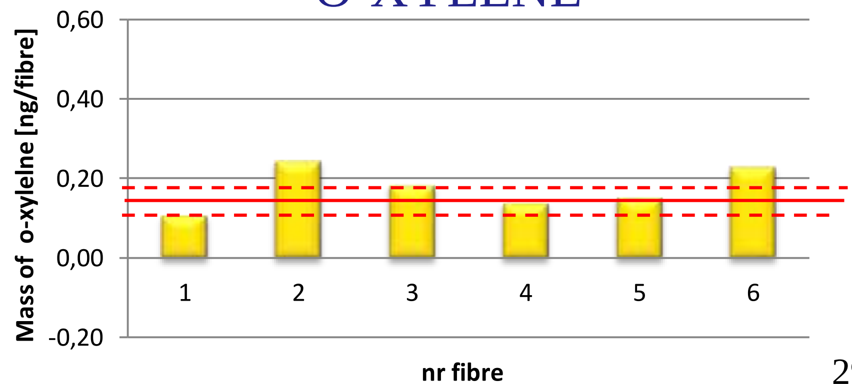
TOLUENE



BENZENE



O-XYLENE



LIST OF PAPERS DEALING WITH PROBLEMS OF PREPARATION OF SGM's

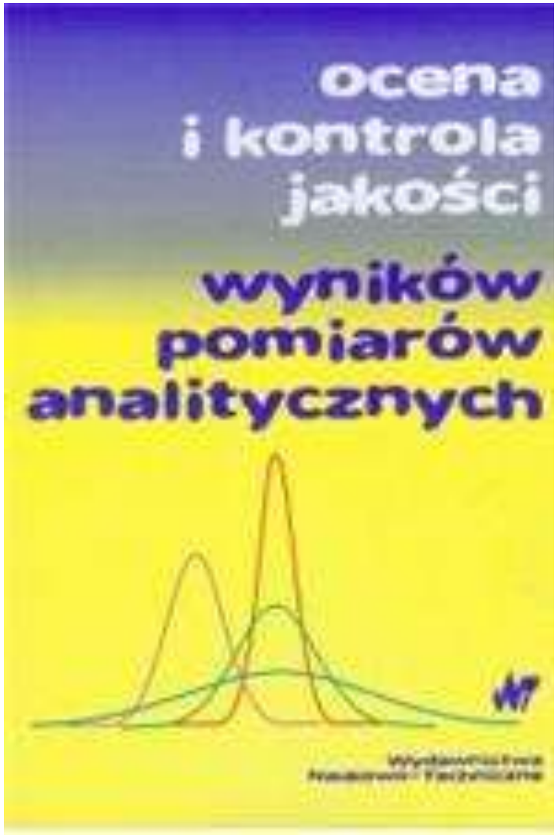
GDAŃSK UNIVERSITY OF TECHNOLOGY

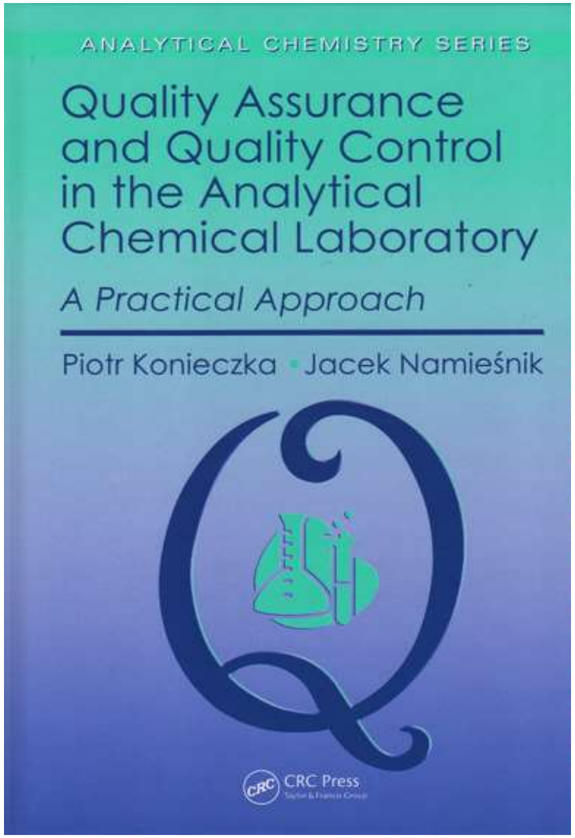
Review papers

1. M. Słomińska, P. Konieczka, J. Namieśnik, *Trends Anal. Chem.* **29** (2010) 419.
2. M. Słomińska, S. Król, J. Namieśnik, *Crit. Rev. Environ. Sci. Technol.* **43** (2013) 1417-1445.
3. M. Słomińska, P. Konieczka, J. Namieśnik, *Analityka* **2** (2010) 31.
4. K. Kupiec, P. Konieczka, J. Namieśnik, Crit. Rev. Anal. Chem. **39** (2009) 60-69.
5. M. Słomińska, P. Konieczka, J. Namieśnik,, *Crit. Rev. Environ. Sci. Technol.*,
6. P. Konieczka, A. Świtaj - Zawadka, J. Namieśnik, *Trends Anal. Chem.* **23** (2004) 450-458.
7. E. Przyk, A. Świtaj-Zawadka, J. Szczygelska-Tao, A. Przyjazny, J.F. Biernat., J. Namieśnik, *Crit. Rev. Anal. Chem.* **33** (2003) 249-267.

Original papers

1. M. Słomińska, P. Konieczka, J. Namieśnik, *Anal. Bioanal. Chem.* **405** (2013) 1773-1778
2. J. Namieśnik, B. Zygmunt, A. Jastrzębska, J. Chromatogr. A **885** (2000) 405-418.
3. A. Naganowska- Nowak, P. Konieczka, J. F. Biernat, J. Szczygelska- Tao, A. Przyjazny, J. Namieśnik, *Anal. Bioanal. Chem.* **388** (2007) 1725-1731
4. A. Świtaj-Zawadka, E. Przyk, J. Szczygelska-Tao, J. Wójcik, J.F. Biernat, J. Namieśnik, B. Zygmunt, *J. Sep. Sci.* **26** (2003) 1057-1062
5. E. Przyk, A. Świtaj-Zawadka, P. Konieczka, J. Szczygelska-Tao, J. F. Biernat, J. Namieśnik, *Anal. Chim. Acta* **488** (2003) 89-96.
6. P. Konieczka, M. Prokopowicz, B. Zygmunt, J.F. Biernat, J. Namieśnik, *Chromatogr. Suppl.* **51** (2000) 249-260.
7. E. Przyk, P. Konieczka, J. Szczygelska- Tao, R. Teschner, J. F. Biernat, J. Namieśnik, *J. Chromatogr. A* **928** (2001) 99.


ocena
i kontrola
jakości
wyników
pomiarów
analitycznych


ANALYTICAL CHEMISTRY SERIES
Quality Assurance and Quality Control in the Analytical Chemical Laboratory
A Practical Approach
Piotr Konieczka • Jacek Namieśnik
CRC Press

Department of Analytical Chemistry

Chemical Faculty

Gdańsk University of Technology

http://chem.pg.edu.pl/katedra-chemii-analitycznej/strona-glowna

Department of Analytical Chemistry
Chemical Faculty
Gdańsk University of Technology

GDAŃSK UNIVERSITY OF TECHNOLOGY

Scientific activity

- Development of new methods of determining trace components in samples of complex matrix
- Development of new methodologies for environmental monitoring and biomonitoring
- Designing, constructing and testing analytical characteristics of prototype control-measurement devices,
- Assessing pollution of particular abiotic environmental compartments and determining processes occurring in these compartments (transport, degradation…)
- Assessing environmental fate of xenobiotics and bioaccumulation processes in tissues and organs of living organisms,
- Applying modern analytical techniques to check quality of food products
- Development of new techniques of producing materials of special properties and/or high purity grade tested with use of chromatographic techniques,
- Organizing interlaboratory studies and proficiency testing.

MODAS - NEW REFERENCE MATERIALS FOR ENVIRONMENTAL ANALYSIS

GDAŃSK UNIVERSITY OF TECHNOLOGY

SILESIAN UNIVERSITY OF TECHNOLOGY

WARSAW UNIVERSITY OF TECHNOLOGY

WROCŁAW UNIVERSITY OF TECHNOLOGY

NICOLAUS COPERNICUS UNIVERSITY

UNIVERSITY OF WARSAW

LGC STANDARDS SP. Z O.O.

INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY

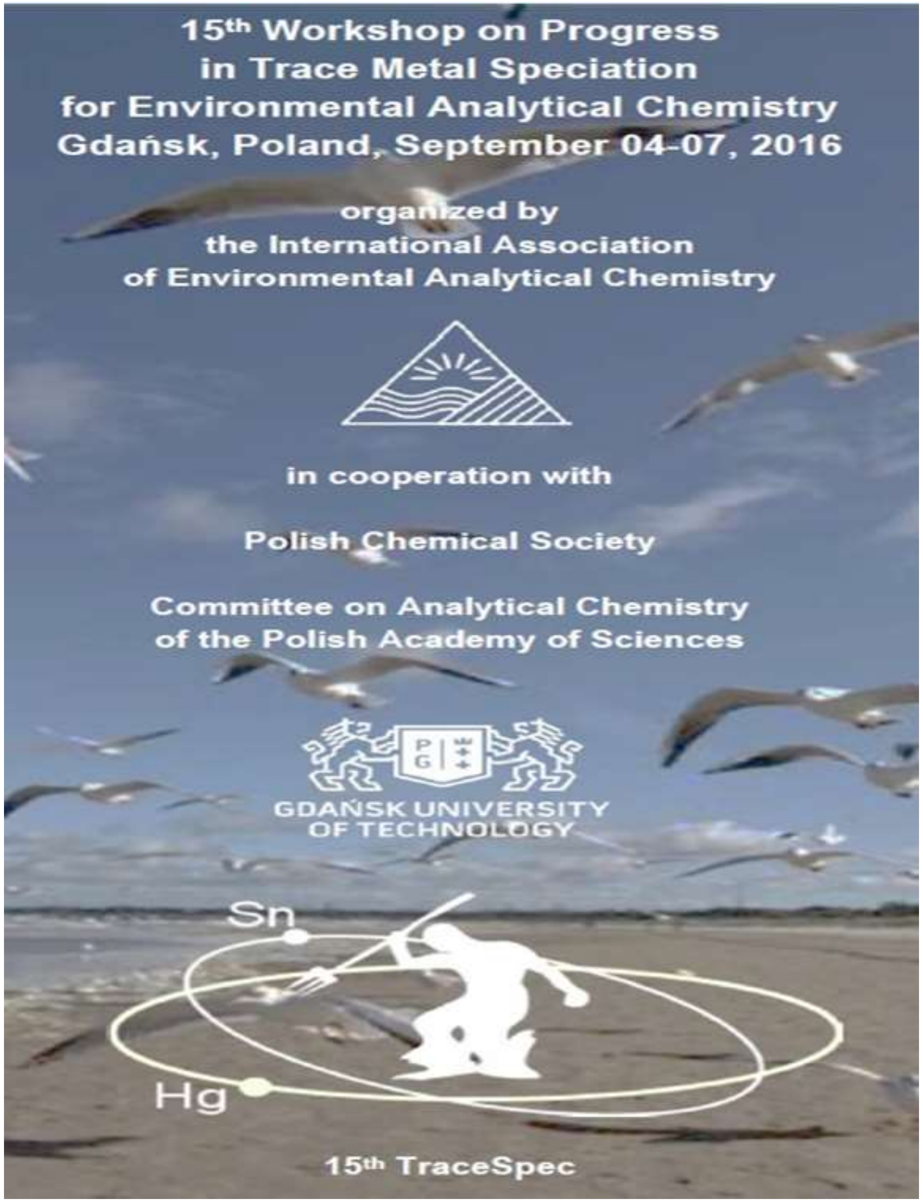
INVITATION

TraceSpec 2016

15th Workshop on Progress in Trace Metal Speciation for Environmental Analytical Chemistry

Gdańsk, Poland, September 04-07, 2016

Info: http://chem.pg.edu.pl/tracespec/
CONTACT: chemanal@pg.gda.pl



GDAŃSK UNIVERSITY OF TECHNOLOGY

GDAŃSK UNIVERSITY OF TECHNOLOGY

Thank you for your attention!