GENERATION OF GASEOUS STANDARD MIXTURES
PROBLEMS AND CHALLENGES

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INTRODUCTION

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

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INTRODUCTION

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

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

PRIMARY 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

- Estimating measurement uncertainty
- Validation of analytical procedures
- Calibration of apparatus
- Inter-laboratory comparisons
- Assuring and documenting metrological coherence

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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

Known volume of gaseous analyte/(-s)

SGM

Known volume of diluting gas
**DYNAMIC TECHNIQUES**

- 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

**THE STREAM OF DILUTING GAS**

**SGM**
MIXED TECHNIQUE - EXPONENTIAL DILUTION FLASK (EDF)

\[ C_i = C_0 e^{\left(-\frac{Ft}{V}\right)} \]

- \( C_i \) - 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

The stream of carrier gas

The stream of gaseous standard mixture

The stream of gaseous standard mixture

The stream of carrier gas

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

<table>
<thead>
<tr>
<th>ANALYTES</th>
<th>CAPILLARY LENGTH [cm]</th>
<th>CAPILLARY INNER DIAMETER [mm]</th>
<th>T [°C]</th>
<th>FLOW RATE [l/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>aromatics</td>
<td>1-20</td>
<td>0.025-4</td>
<td>25 - 75</td>
<td>n.d.</td>
</tr>
<tr>
<td>terpenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>halocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>ICl</em></td>
<td>2.5-20</td>
<td>0.1-2.15</td>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td><em>IBr</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Br₂</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>I₂</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>formaldehyde</td>
<td>7.9</td>
<td>4.9</td>
<td>35&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>230&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2,3- DCDD</td>
<td>3</td>
<td>n.d.</td>
<td>75 - 100</td>
<td>0.5 - 2</td>
</tr>
</tbody>
</table>
ANALYTICAL ASPECTS OF APPLICATION OF DIFFUSION PROCESS

PREPARATION OF STANDARD GAS MIXTURES

diluting gas

standard gas mixture

THE ENRICHMENT OF VOLATILE COMPONENTS OF ATMOSPHERE

components of atmosphere

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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
- **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

The stream of carrier gas
The stream of gaseous standard mixture

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

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# TYPES OF MEMBRANES APPLIED IN PERMEATION DEVICES

<table>
<thead>
<tr>
<th>Nº</th>
<th>Material of membrane</th>
<th>Analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PDMS-FS</td>
<td>n-C₄H₁₀ CH₄</td>
</tr>
<tr>
<td>1.</td>
<td>PDMS</td>
<td>n-C₄H₁₀ CH₄</td>
</tr>
<tr>
<td>2.</td>
<td>PTFE (Teflon®)</td>
<td>BTX</td>
</tr>
<tr>
<td>3.</td>
<td>cork “Amadia”</td>
<td>He</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>4.</td>
<td>Matrimid® (poliimid 3,3’,4,4’-benzophenone tetracarboxylic dianhydride and diamino-phenylidane)</td>
<td>H₂ (purity 99,5%)</td>
</tr>
<tr>
<td>5.</td>
<td>PTFE</td>
<td>styrene phenole aldehydes</td>
</tr>
<tr>
<td>6.</td>
<td>PTFE</td>
<td>SF₆</td>
</tr>
<tr>
<td>7.</td>
<td>-</td>
<td>NO₂ in nitrogen</td>
</tr>
</tbody>
</table>
PERMEATION TUBES USED FOR GENERATION OF STANDARD GASEOUS MIXTURES
ANALYTICAL ASPECTS OF APPLICATION OF PERMEATION PROCESS

PREPARATION OF STANDARD GAS MIXTURES

diluting gas → standard gas mixture

THE ENRICHMENT OF VOLATILE COMPONENTS OF ATMOSPHERE

components of atmosphere

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DIFFUSION AS A SUITABLE PROCESS OF GENERATION OF STREAM OF MEASURAND

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)

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19
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

<table>
<thead>
<tr>
<th>TYPE OF SYSTEM</th>
<th>MATRIX</th>
<th>ANALYTE</th>
<th>CONCENTRATION IN GASEOUS MIXTURE [mg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-01</td>
<td>liquid</td>
<td>phenol</td>
<td>1-120</td>
</tr>
<tr>
<td>U-06</td>
<td>solid sorbent</td>
<td>benzene</td>
<td>1-1700</td>
</tr>
<tr>
<td>U-11</td>
<td>solid sorbent</td>
<td>acetone</td>
<td>1-1600</td>
</tr>
<tr>
<td>U-13</td>
<td>solid sorbent</td>
<td>methanol</td>
<td>1-900</td>
</tr>
<tr>
<td>U-15</td>
<td>solid sorbent</td>
<td>n-propanole</td>
<td>1-540</td>
</tr>
<tr>
<td>M-07</td>
<td>liquid</td>
<td>toluene</td>
<td>1-1200</td>
</tr>
<tr>
<td>M-08</td>
<td>liquid</td>
<td>ethylbenzene</td>
<td>1-1100</td>
</tr>
<tr>
<td>M-03</td>
<td>liquid</td>
<td>o-xylene</td>
<td>1-600</td>
</tr>
<tr>
<td>M-04</td>
<td>liquid</td>
<td>m-xylene</td>
<td>1-800</td>
</tr>
<tr>
<td>M-05</td>
<td>liquid</td>
<td>p-xylene</td>
<td>1-850</td>
</tr>
<tr>
<td>G-01</td>
<td>liquid</td>
<td>acetaldehyde</td>
<td>1-2600</td>
</tr>
</tbody>
</table>

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 WEIGHING TECHNIQUES - THERMOGRAVIMETRIC ANALYSIS

![Diagram of a system based on the weighing techniques - thermogravimetric analysis]

- **Inlet of diluting gas stream**
- **Furnace**
- **Temperature controller**
- **Outlet of stream of standard gas mixture**
- **Gas Analyzer**
- **Mass controller**
- **Sample - source of VOCs**
ADVANTAGES OF STATIC AND DYNAMIC TECHNIQUES OF GENERATION OF STANDARD GAS MIXTURES

<table>
<thead>
<tr>
<th>ADVANTAGES</th>
<th>DYNAMIC TECHNIQUES</th>
<th>STATIC TECHNIQUES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>possibility of preparing greater volume of gas mixture in a wide range of analytes’ concentrations with required accuracy,</td>
<td>simple to carry out,</td>
</tr>
<tr>
<td></td>
<td>elimination of adsorption process which results in losing of analytes,</td>
<td>low-cost of apparatus</td>
</tr>
<tr>
<td></td>
<td>homogeneity and stability of prepared standard gas mixture</td>
<td></td>
</tr>
<tr>
<td></td>
<td>possibility of preparing and introducing the mixture to the measurement system under different conditions of temperature, pressure and flow rate</td>
<td></td>
</tr>
</tbody>
</table>
**DISADVANTAGES OF STATIC AND DYNAMIC TECHNIQUES OF GENERATION OF STANDARD GAS MIXTURES**

<table>
<thead>
<tr>
<th>DYNAMIC TECHNIQUES</th>
<th>STATIC TECHNIQUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>▪ necessity of having the gaseous analytes sources,</td>
<td>▪ time-consuming and inaccurate procedure</td>
</tr>
<tr>
<td>▪ necessity of controlling the flow rate of stream of diluting gas</td>
<td>▪ losses of analytes due to adsorption and condensation on the walls of the chambers,</td>
</tr>
<tr>
<td>▪ difficulties arising from stopping of generation of standard gas mixture</td>
<td>▪ impossible to storage in amounts sufficient to reuse,</td>
</tr>
<tr>
<td></td>
<td>▪ stratification during the stage of storage,</td>
</tr>
<tr>
<td></td>
<td>▪ unsuitable for unstable and reactive compounds</td>
</tr>
</tbody>
</table>
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 defined porosity
   - Mechanical strength

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
<table>
<thead>
<tr>
<th>Year</th>
<th>Milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td>• Preparation of matrix free reference material of ethene in the form of glass fibers covered with thin layer of aluminum – CERTIFICATION OF MATERIAL</td>
</tr>
<tr>
<td>2008</td>
<td>• Trials with GLASS FIBERS COVERED WITH ALUMINUM for preparation of standard gas mixtures of methyl chloride and ethene</td>
</tr>
<tr>
<td>2007</td>
<td>• PATENT modified silica gel for preparation of standard gas mixtures</td>
</tr>
<tr>
<td>2006</td>
<td>• Carrier: SILICA GEL; standard gas mixture – ACETONE,</td>
</tr>
<tr>
<td>2004</td>
<td>• Use of TRIMETHYLAMINE for chemical modification, Carrier: SILICA GEL; standard gas mixture – ETHENE, METHYL CHLORIDE;</td>
</tr>
<tr>
<td>2001</td>
<td>• Carrier: POROUS GLASS</td>
</tr>
<tr>
<td>2000</td>
<td>• Carrier: SILICA GEL; standard gas mixture – ETHENE;</td>
</tr>
<tr>
<td>1997</td>
<td>• Carrier: SILICA GEL; standard gas mixture – AMMONIA, METHYLAMINE, DIETHYLAMINE, TRIETHYLAMINE;</td>
</tr>
<tr>
<td>1996</td>
<td>• Development of calibration technique for TD-GC-MS system</td>
</tr>
<tr>
<td>1992</td>
<td>• Carrier: SILICA GEL; standard gas mixture – n- PROPANETHIOL;</td>
</tr>
<tr>
<td>1991</td>
<td>• Carrier: SILICA GEL; standard gas mixture – ISOTHIOCYANATE;</td>
</tr>
<tr>
<td>1991</td>
<td>• Concept of application of appropriate surface compounds for obtained reference materials; Carrier: SILICA GEL; standard gas mixture – THIOLES;</td>
</tr>
</tbody>
</table>
APPARATUS SET UP FOR THE THERMAL DECOMPOSITION OF SURFACE COMPOUNDS

TD-GC-FID

Thermal desorber

Glass fibers modified by surface compound

Four-port valve

Carrier gas

GC - FID

Temperature driver
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 REFERENCE MATERIALS

Different matrix

<table>
<thead>
<tr>
<th>Different matrix</th>
<th>Wide range of analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. soil</td>
<td>1. WWA</td>
</tr>
<tr>
<td>2. sediment</td>
<td>2. PCB</td>
</tr>
<tr>
<td>3. biological tissues (FISHES, BIRDS)</td>
<td>3. Heavy metals</td>
</tr>
</tbody>
</table>
THE RESULTS OBTAINED DURING THE PRODUCTION OF MATRIX FREE REFERENCE MATERIALS OF BTX COMPOUNDS

TOLUENE

BENZENE

O-XYLENE

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

Review papers

Original papers
Department of Analytical Chemistry
Chemical Faculty
Gdańsk University of Technology

http://chem.pg.edu.pl/katedra-chemii-analitycznej/strona-glowna
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
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
Thank you for your attention!