Determination of benzene in ambient air

1. Introduction

Air pollution is defined as a presence of toxic compounds in atmosphere at levels that pose a health risk. This term may describe the condition in which air is contaminated by foreign substances, or the substances themselves.

Air pollution may be divided in two fundamental groups: anthropogenic and natural. Sources of natural air pollution include volcanic activity (ash, sulfur, chloride), digestion of food by animals (methane) and natural forest fires (sulfur dioxide). Anthropogenic air pollution is caused mainly by exhausts from industry, burning of fossil fuels and mining operations.

Particularly dangerous pollutants due their high toxicity are a volatile organic compounds (VOCs), such as benzene and its substituted derivatives. Benzene (C\textsubscript{6}H\textsubscript{6}) is a transparent, volatile, flammable liquid with a characteristic gasoline-like odor.

Benzene is released to the atmosphere by both man-made and natural processes:

<table>
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<th>Natural sources of benzene:</th>
<th>Anthropogenic sources of benzene:</th>
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<tr>
<td>- forest fires</td>
<td>- combustion of fuels / processing of petroleum products</td>
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<td>- volcano eruptions</td>
<td>- cigarette smoke</td>
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<td>- building materials (for example paints)</td>
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<td>- industry (for example rubbers and plastic production, petroleum refining)</td>
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The exposure to benzene is a subject of regulations and has to be monitored. Despite restrictions on its use in the industry, benzene is still used for example as a component of gasoline, dyes, lubricants and in the chemical industry to obtain it’s useful derivatives (for example nitrobenzene).

Chronic exposure to benzene causes leukemia and may promote the formation of mutagenic effects. Short-term exposure to high levels of benzene results in narcotic effects and disturbances in the central nervous system and can cause irritation of mucous membranes.

After entry into the human organism, benzene is accumulated in fat-rich tissues owing to its lipophilic nature. In addition, the accumulation of benzene in umbilical and placental blood is also particularly dangerous.

According to the report of Wojewódzki Inspektorat Ochrony Środowiska w Gdańsku, there was no excess benzene concentration in the air (it means $\geq 5$ $\mu$g/m\textsuperscript{3} of atmospheric air) in 2016 in
the Tri-City agglomeration. The highest benzene concentration was recorded in Starogard Gdański (approx. 4.2 µg/m³ of atmospheric air) - this might be the consequence of the presence of a large pharmaceutical plant in this area.

Analytical chemistry uses a variety of techniques and devices for sampling and for measuring the concentrations of certain types of constituents of atmospheric air pollution.

The results of pollution measurements can refer to real time or to selected time interval. The concentration of analytes (compounds of interest) in environmental samples is often below limit of detection. Therefore, it is necessary to use a suitable method for analyte enrichment. A popular way used for sampling of atmospheric air is the use of adsorption tubes. The essence of the method is to pass an air sample through the sorption tube (fig. 1). The sorption tube contains special sorbent capable to selectively retain the analytes on its surface. Tubes filled with activated charcoal or Tenax (porous polimer based on 2,6-diphenyl-p-phenylene oxide) are frequently used for determination of benzene in the air.

![Fig. 1. Scheme of adsorptive sampling of the atmospheric air.](image)

The sorbent tube with "trapped" analytes is located in the thermal desorber. Thermal desorption is one of the techniques used for introducing samples into gas chromatograph. The essence of this method is to heat the adsorbent to a high temperature. Under the influence of heat, desorption of "trapped" analytes takes place. Gas flowing through the tube transports released compounds to the chromatographic column where their separation and detection takes place.

**Principle of the gas chromatography**

Chromatography is a technique which allows for separation of mixtures. In each chromatographic technique, the mixture is separated first and then the individual components are detected. The separation takes place inside a column filled with some kind of sorbent (stationary phase). The sample (mixture) under the study is dissolved in a fluid (so called eluent or mobile phase), which carries it through the column. Components of the mixture are carried by the mobile phase (eluent) and migrate through the column at different speeds. Different travel speeds are the results of differences in analytes’ affinity towards mobile or stationary phase.

According to the type of the mobile phase, we can distinguish two kinds of chromatographic
techniques: liquid chromatography (LC) and gas chromatography (GC). In LC, the mobile phase is a liquid. This technique is preferred for analyzing non-volatile components or components with lower thermal stability. It is widely used for the analysis of biological and environmental samples, as well as polymers, chiral compounds etc. In GC, the mobile phase is a gas. Chemical compounds which are analyzed using this method must have sufficient thermal stability and adequate volatility.

A high purity gas or gases (mobile phase) are delivered to the gas chromatograph (fig. 2). The mobile phase (carrier gas) flows through the injector, the column and then goes to the detector. The sample is introduced into the injector with a chromatographic syringe or external injection device. The injector is heated to evaporate the volatile components of the sample. The evaporated components are transported to the column by a carrier gas. Inside the column separation of sample components takes place.

![Diagram of GC system](image)

Fig. 2. Scheme of GC system; 1 – tanks (generators) of the carrier gas, 2 – flow meter, 3 – injector, 4 – column, 5 – GC oven (thermostat), 6 – detector, 7 – data recording equipment.

Each component that leaves the column enters the detector. The detector reacts to the individual analyte and generates the corresponding electronic signal which is recorded by the data system and then plotted in the chromatogram. The magnitude of the signal is proportional to the amount of analyte. Chromatogram shows the intensity of the detector’s response (peaks) at a given time (fig. 3).
Gas chromatography is one of the analytical techniques that are able to perform qualitative and quantitative analysis in one process. The amount of substance in the mixture can be calculated from the analyte’s peak area.
2. Experimental

Labware and reagents:
- syringe (volume: 50 ml)
- tube with sorbent (Tenax)
- gas chromatograph
- thermal desorber
- methanol
- benzene

Laboratory procedure

1) Calibration
- mount the sorption tube in a stand,
- turn on the gas flow through the tube (He, 50 mL/min),
- inject the standard solution of benzene onto the sorption tube and wait 5 min.,
- mount the sorption tube in thermal desorber,
- perform thermal desorption and GC analysis
Repeat operations for 5 different concentrations of benzene (in the range 1 ÷ 100 µg/mL)

2) Air samples
   a) atmospheric air:
- pass an air sample (2 dm$^3$) through the sorption tube,
- mount the sorption tube in thermal desorber,
- perform thermal desorption and GC analysis
   b) air from the underground garage:
- pass an air sample (1 dm$^3$) through the sorption tube,
- mount the sorption tube in thermal desorber,
- perform thermal desorption and GC analysis

Report

Report must contain:
- introduction (properties of benzene; analytical techniques used for determination of benzene in ambient air),
- description of experiment,
- calculation of benzene concentration (in µg/m$^3$) and comparison obtained result with the report of Wojewódzki Inspektorat Ochrony Środowiska,
- conclusions.
Students are obliged to prepare report within one week after laboratories.