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Methods of determination of organic compounds in air

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Abstract. Data published from 2005 to 2009 on the development of new methods and on improvement and application of the existing methods for determination of various organic compounds in atmospheric air, housing air, office air, occupational air and exhaled air are generalized. The attention is focused on the determination of the priority pollutants and establishment of new pollutants. Modern trends in optimization of air sampling stages and impurity preconcentration to reduce the detection limits are considered. The problems of miniaturization of analytical instruments and the reliability of the determination of organic compounds in air are touched upon. The bibliography includes 150 references.

I. Introduction

At present, more than 50 000 000 chemical substances are known, most of which are organic compounds.[1] The presence of organic compounds including toxic ones in air is one of the main reasons for deep concern of researchers throughout the world because many such compounds and products of their decomposition are hazardous for human health and environment.[2] They produce offensive odours, induce diseases in respiratory organs and lead to cancer.

The toxicity and other undesired properties of organic compounds can manifest themselves at concentrations of the order of 10^{-3} – 10^{-6} mg m^{-3} and lower and should therefore be controlled using the most sensitive methods of chemical analysis. Studies on the subject are mainly devoted to analysis of atmospheric air or workplace air. A smaller number of publications are concerned with analysis of indoor air (occupational, office and housing air).[3–5] Up to 1 600 000 untimely deaths per year and 4% of all diseases are due to toxic compounds present in housing air.[6] This is twice as large as the number of cases caused by toxic compounds in outdoor air; therefore, control of indoor air is a very important problem.[7] The number of studies on the determination of impurities in exhaled air also increases. A few thousands of impurities including hydrocarbons, aldehydes, organosulfur compounds, ethanol, acetone, aromatic compounds, saturated aliphatic acids, *etc.* were detected in air.[8,9] Analysis of exhaled air allows one to obtain important data on the development of such diseases as lung cancer, diabetes, hepatopathy, cardiovascular diseases and schizophrenia.[10,11] This offers unequivocal advantages over blood and urine analyses because in this case one deals with a simpler matrix (air), noninvasive sampling procedure and continuous control.

The main stages of determination of pollutants in air include sampling, efficient preconcentration and identification of impurities, reduction of detection limits and improvement of the reliability of detection. These and some other problems in analytical chemistry have been considered in a number of reviews and monographs.[3–5,8,12–34] Unlike the previously published reviews, here we will consider application of almost all highly sensitive (including spectral and biochemical) methods of determination of toxicants in atmospheric air, exhaled air, indoor air (housing and office air). Our attention will be focussed on the specific features of aerosol pollutants, on new methods of their determination, and on the reliability of analysis of air of different origin. The review generalizes the data published in 2005 – 2009.

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II. Methods of determination

Organic compounds present in air are determined by various methods. Simple organic compounds, such as formaldehyde, methane, ethane and acetylene absorb IR radiation and can therefore be determined by highly sensitive optoacoustic spectroscopy,[35] tunable-diode laser IR spectroscopy, Fourier-transform IR spectroscopy[36–39] and some other methods.[40,41] At optical path lengths of 0.25–170 m and data acquisition times in the range 1–100 s, the direct detection limits of various impurities are in the range $(0.9-1.4)\times10^{-4}$ mg m^{-3}. UV spectroscopy (150-W krypton lamp, optical path length 250 m) is used for the determination of formaldehyde, benzene and toluene[40] with the detection limits in the interval $(0.5-3.42)\times10^{-3}$ mg m^{-3}. Optical spectroscopy methods are fast and allow one to study changes in moving air flows and to carry out continuous monitoring of substances with simple structures in exhaled air.

Organic compounds with complex structures are determined by mass spectrometry (MS),[33] ion mobility technique,[8–18] as well as by gas chromatography and liquid chromatography.[3,4,21] To simplify the spectra of impurities and to reduce the impurity detection limits, mass spectrometric studies are carried out with chemical ionization (most often, proton transfer ionization as a result of the ion–molecule reaction with H_3O^+). H_3O^+ ions were chosen as reactants because organic compounds have higher proton affinities than water. The signal is formed over a period of a few seconds while the impurity detection limit is $(0.1-1.0)\times10^{-4}$ mg m^{-3} (Refs 42 and 43). Real-time analysis of exhaled air was also carried out by mass spectrometry with chemical ionization of impurity molecules.[44,45] The precursor ions were H_3O^+, NO^+ and $O_2^{+\bullet}$, which react with the compounds to be determined. The impurity detection limits were of the order of 10^{-3} mg m^{-3}. A less known ion mobility technique is based on the motion of ions in pure nitrogen or purified air at atmospheric pressure under the action of external electric field. The ion drift time and ion current characterize the nature of impurity and its concentration, respectively. Ionization of impurities is achieved by exposure to β- and UV-radiation or by electric discharge. The pollutant detection limits are of the order of 10^{-3} mg m^{-3} (Refs 8, 18, 46).

When analyzing complex mixtures, especially, mixtures of isomers, the use of various versions of MS and the ion mobility method is complicated. A much greater potential for the detection of various organic compounds belongs to gas chromatography (GC) with traditional mass-spectrometric, flame-ionization, electron-capture, thermoionic, flame photometric, photo-ionization, chemiluminescent and atomic emission detectors.[3,4] Gas chromatography with mass-spectrometric detection (GC–MS) is the most informative method. In addition to electron impact ionization, chemical ionization with selective formation of anions is used. The technique allows the pollutant detection limits to be reduced down to 5×10^{-5} mg m^{-3}, which is the lowest attainable value (see Refs 8 and 21). Combining the ion mobility and GC separation methods made it possible to determine the pollutant concentrations of the order of $(0.008-5.0)\times10^{-3}$ mg m^{-3} (Ref. 18). GC separation of impurities is usually carried out in capillary columns 20–50 m long. In addition, exhaled air was analyzed using polycapillary columns,[18] and low-volatile components of aerosols were determined using short 10-m capillary columns.[47] Also, high-performance liquid chromatography (HPLC) with mass spectrometric (HPLC–MS), fluorescence and UV detection is used.[21,22] Complex mixtures are analyzed by two-dimensional chromatography with isolation of a particular chromatographic fraction, which is then separated on a column with a more selective stationary phase.[48,49] In some cases, the selectivity is improved and the detection limits are reduced by using a tandem MS–MS detection.[21]

Immunochemical methods of determination of pollutants, based on the use of specific antibodies as reagents towards these substances, have a great potential (for more detail, see Ref. 41).

III. Sampling and preconcentration

Stringent requirements on the methods of sampling and preconcentration of impurities are due to low concentrations of impurities in air and to the fact that they are present in the molecular form and as aerosol particles.

The proportion of studies involving air sampling into containers and sealed bags followed by their transportation to analytical laboratories is small.[3,4,24,25] Most often, this concerns the sampling of exhaled air and workplace air. Samples are collected into containers by drawing air with a membrane pump or by passing air through an aspirator.[20,50] Containers are made of various materials including glass, polished stainless steel and polymers. The most reliable results were obtained with glass[20] and stainless steel covered with synthetic SiO_2 film.[19] Background delivery of organic substances from the glass surface is at most 10^{-5} mg m^{-3} per year.[50]. Metallic containers with inert SiO_2 coating are suitable for storage of air containing traces of organosulfur substances. Plastic bags made of teflon, tedlar [a poly(vinyl fluoride) polymer] and mylar (polyester) are used for sampling of exhaled air. It was established that the first 150 ml of exhaled air are transferred from the oral cavity and upper air passages while the next 300 ml of exhaled air are transferred from alveoles where substances indicating diseases are present. Recently, samplers of alveolar air have been reported.[8,51,52]

When air is sampled into polymeric bags, the impurity detection limits are usually of the order of 5×10^{-4} mg m^{-3} or higher. The is due to the solubility of organic substances in polymers, which predetermines the 'memory' effect of such containers and reduction of the impurity content. To reduce the permeation of impurities from atmospheric air into polymer films, they are laminated with aluminium coating.[22] It should be noted that all types of containers are unsuitable for the determination of organic compounds present in air in the form of aerosol particles because such particles are removed from the gas phase through collisions with walls and thus cannot be transferred to analytical instruments. Most often, plastic containers are 0.5–100 litres in volume (*cf.* 2.5–6 litres for glass or metallic ones). Usually, the pressure in containers is equal to atmospheric pressure or is 10%–20% higher. Samples in containers are sealed using polypropylene or glass taps and movable Teflon cylinders.[3,22] Having the sampling finished, air is analyzed directly or after preconcentration. In the latter case, a concentrator is attached to the container and air to be analyzed is passed through the concentrator. To avoid irreversible adsorption of impurities on the container walls when the volume of air sampled is of the order of hundreds of litres and more, the sampling and preconcen-

tration steps are combined. There are active (dynamic) and passive sampling – preconcentration methods.

1. Active sampling – preconcentration methods

Preconcentration of large samples. The method involves passage of large volumes of air through filters and columns filled with adsorbents. Filters for collection of aerosol pollutants consist of glass or quartz fibres; molecular impurities are accumulated on high-performance adsorbents made of styrene and divinylbenzene copolymers (XAD-2 and XAD-4),[53] polyurethane foam or their combinations. The air flow rate is 100 – 1000 litre min^{-1}, the sampling time varies from a few days to two weeks and the total air volume can reach a value of 13 680 m^3. Impurities are determined by analyzing the concentrate collected on a concentrator attached in series.[3,24] Preconcentration of impurities from large volumes of air is mainly used for analysis of atmospheric air.

Cryogenic preconcentration. The technique involves passage of air through a cooled tube filled with glass beads. Usually, the tube is cooled to −(170 – 150) °C with liquid nitrogen. Recently, Peltier elements have been used for cooling to -30 ± 10 °C.[54] In this case, cryogenic preconcentration can be accompanied by solid-phase extraction. The main difficulty of this method consists in the need for removal of water condensed from air. Water makes the impurity trapping procedure less efficient and causes the formation of side products. The method is most widely used for control of indoor air.[25]

Solid-phase extraction.[24,25] The method is used in dynamic preconcentration of pollutants from small air volumes with efficient sorbents including Tenax TA, Tenax GC, Chromosorb 106, Carbotrap B, Carbotrap C and silica gel with grafted octadecyl groups. Solid-phase extraction is suitable for collection of complex difficult-to-preconcentrate impurities, such as polar organophosphorus esters. Preconcentration of pollutants is followed by their extraction with a solvent (carbon disulfide, toluene, hexane, dichloromethane, *etc*.) or thermodesorption. A version of this method is solid-phase microextraction. From the standpoint of the sorption of impurities from air exhaled from patients, the technique can also be classified as active preconcentration method. Various sorption coatings of 'backbone' fibre may be nonpolar [polydimethylsiloxanes (PDMS)], of low polarity [PDMS – divinylbenzene (DVB)], polar [poly(ethylene glycol) – DVB] or be based on adsorbent and a polymer (PDMS – Carboxen).

Recently, highly efficient adsorption coatings were prepared using the sol – gel technology.[39,40] For instance, coatings based on quinoxalin derivatives allow the benzene detection limit to be halved. The total mass of sorbent in setups for solid-phase microextraction is at most a few milligrammes. The thickness of the coating sorbed ranges from 7 to 100 μm and the coated fibre can be up to 100 mm long. Reproducible results on the nonequilibrium preconcentration with PDMS coatings can be obtained 60 min after start of the procedure. Equilibrium preconcentration is attained after at least 6 h.[27,28] Preconcentration of impurities in needle-shaped microconcentrators 0.35 – 2 mm in diameter and 10 – 150 mm long with PDMS, Tenax TA, DVB, Carboxen as sorbents was reported. Impurities were concentrated from an air volume of 1 litre. Desorption of impurities is carried out at temperatures below 300 °C over a period of 1.5 – 2 min.

Chemisorption preconcentration. This preconcentration technique is used to collect unstable impurities, such as aldehydes, ketones[55,56] and aromatic amines.[57] 2,4-Dinitrophenylhydrazine supported on silica gel or on a filter is most often used as adsorbent. Unsaturated carbonyl compounds, *viz*., methyl vinyl ketone, aldehydes (crotonaldehyde, acrolein, benzaldehyde and methacrolein) poorly react with 2,4-dinitrophenylhydrazine. A chemisorption method based on the sorption of impurities by a sodium bisulfite solution followed by derivatization with 2,3,4,5,6-pentafluorobenzylhydroxylamine and determination by gas chromatography – mass spectrometry was proposed for preconcentration of these compounds. The detection limits of the carbonyl compounds appeared to be of the order of 10^{-5} mg m^{-3} (Ref. 56). Very often, the potential of the chemisorption methods is limited by the requirements of high-purity reagents; therefore, the use of such methods for the determination of concentrations lower than 5×10^{-3} mg m^{-3} is problematic.

2. Passive methods

Passive preconcentration.[29] In passive preconcentration, impurities are delivered to a concentrator by diffusion through an air gap or a semipermeable membrane. Therefore, usually passive preconcentration takes a longer time than active preconcentration. Air flow naturally delivered to a concentrator is 2.5 – 4 m^3 day^{-1}. There are samplers oriented at the maximum wind flow rate.[58] In this case, the sampler can collect 100 m^3 day^{-1}. The role of the collecting phase can be played by semipermeable membranes, PDMS films, polyurethane foam discs and Amberlite XAD supported on a developed surface. Semipermeable membrane are most often made of polyethylene. Fir needles[59] and silicon tubes[21] are also used for passive preconcentration of contaminants. The sampling media are protected from sunlight and large particles. Semipermeable membranes are successfully used for the determination of polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins, dibenzofurans and biphenyls. Polyurethane foam discs are suitable for preconcentration of polychlorobiphenyls and perfluorinated organic compounds.[60] The concentrations of contaminants in air are calculated using the amount of analyte collected, the analyte diffusion coefficient in air (diffusion sampling), the membrane permeability coefficient (membrane sampling), the diffusion path lengths and the effective cross-sections of the samplers. When using passive samplers, the diffusion parameters are usually determined experimentally by analyzing standard air mixtures and the amount of analyte collected.

Diffusion denuders. As mentioned above, a feature of the analysis of air is that impurities are present in the molecular form and as aerosol particles. Collection of a solid aerosol phase on a filter can cause partial sorption of molecular impurities and thus change the composition of the analyte sample. The aerosol and molecular impurities can be separated using so-called diffusiton denuders,[21] which became available recently. The operation of a denuder is based on diffusion of impurities taking into account the lower diffusion mobility of aerosol particles compared to molecules. In the case of a laminar flow of contaminated air along the denuder the contaminant molecules rapidly diffuse towards the sorbent surface and are thus trapped by the sorbent. Aerosol particles characterized by low diffusion coefficients are carried away by the air flow and collected on appropriate filters. The conditions for efficient operation of a

denuder are as follows: a stable laminar air flow at the inlet, no changes in analytes within the denuder, high efficiency of sorbent towards the gaseous compounds collected and the constant temperature and viscosity of the air flow. The advantages of denuders include a relatively short sampling time and a small volume of the solvent necessary for extraction of the collected pollutants. Denuders are used to collect the PAH impurities, polychlorobiphenyls and other low-volatile substances.[61,62]

3. Sample preparation

Sample preparation involves extraction of impurities from the concentrator and removal of undesired components.[1,13,24,25] To improve the selectivity of determination of aldehydes, ketones, tetrabromobisphenol A and alkylphenols, these compounds were derivatized in the course of sample preparation.[55,56,63,64] Medium- and low-volatile impurities are most often removed from filters and sorbents by extraction with a solvent. As a rule, such solvents (desorbers) have boiling points of at most 150 °C; in addition, their purity grade should be sufficiently high. Usually, extraction of contaminants is carried out in Soxhlet apparatuses; the process can be accelerated by exposure to UV radiation.[21] Efficient extraction of aerosol particles is achieved by microwave extraction.[24,25] Usually, sample preparation is accompanied by removal of undesired components. This stage of analysis is called 'purification of extracts' and carried out by column chromatography on silica, Fluorisil (magnesium silicate), alumina or their combinations. Dust particles are removed by filtering extracts through glass wool or cotton wool. The determination of medium-volatility contaminants (saturated hydrocarbons, chlorinated hydrocarbons, aromatic hydrocarbons, *etc*.) is often carried out by thermal desorption/extraction. This technique has the advantage of no dilution of the sample with a solvent; however, its drawback consists in the impossibility of qualitative isolation of low-volatile and thermally unstable substances.

IV. Identification and detection of contaminants

1. Identification of contaminants

Identification of contaminants is the most critical and difficult step of air analysis. Incorrect determination of the nature of impurities makes further analysis senseless.[12] The principles of identification of organic impurities have been considered in detail in monographs.[1,12] Preliminary identification is carried out using the chromatographic retention parameters of contaminants. The retention times are measured to an accuracy of 0.05%,[14] which allows one to use electronic databases for identification of contaminants. Reliable identification at a level of 10^{-3} mg m^{-3} can be attained using gas chromatography with multidetector systems (flame-ionization, photoionization, thermoionic, electron-capture, flame photometric, atomic emission) and the Hall detector. In some cases, one can use reaction chromatography with subtraction of the target components or their transformation to certain selectively detectable forms.[12]

Recently, yet another problem in the analysis of air has emerged, *viz*., the need for detection, at a level of 10^{-6} mg m^{-3}, of groups of toxic impurities including tens and hundreds of compounds against the background of even greater number of natural substances. The best method of multicomponent analysis is chromatography–mass spectrometry.[1,21,65] The identification criteria include the retention times, the total mass spectrum and the molecular masses of the substances under study. The sensitivity of this method is very high.[66] Its reliability is improved using tandem mass spectrometry, which is based on additional fragmentation of ions by collisions with neutral molecules or atoms.[1,14,67] The most complex problems in the identification and detection of such toxic compounds, as polychlorinated dibenzo-*p*-dioxins, dibenzofurans and biphenyls, are solved using high-resolution gas chromatography–mass spectrometry.[66] Great potential for suppression of electrical noise, separation of overlapping component peaks and identification of contaminants are offered by the AMDIS software used by domestic researchers and abroad.[68]

2. Reference samples for air analysis

Reference samples (calibration mixtures) are prepared using statistical or dynamic methods, which are described in detail in a monograph.[3] Traditional dynamic methods are based on the diffusion dosage of impurities moving through polymeric membranes, mixing of gas flows or exponential dilution. An original dynamic chromatography–membrane method for preparation of gaseous mixtures was proposed.[69] It is based on mass exchange between the gas and liquid phases in hydrophobic porous media. As a result of mass exchange, the gas phase is saturated with analyte whose concentration depends on its content in the liquid (aqueous) phase. The potential of the technique was demonstrated taking the determination of acetic acid impurity as an example. The lowest acetic acid concentration in the air sample was 10 mg m^{-3}.

Dynamic methods are more reliable than statistical ones but require complex, thermostatted equipment and are often characterized by long time taken to establish a stationary state. Statistical methods involve the introduction of microquantities of impurity and purified air or nitrogen into a vessel. The lifetime of the samples prepared by statistical methods depends on the inertness of the internal surface of sampling bottles. Best of all are glass, aluminium and stainless steel bottles whose surfaces are passivated with synthetic silica. The impurity concentrations in the samples prepared by the statistical or dynamic methods are in the range from 0.01 to 5 mg m^{-3}. Mixtures with lower impurity concentrations are prepared by additional dilution of commercially available samples. For instance, a number of 'Spectra Gas' reference samples containing about 1 mg m^{-3} of halogenated hydrocarbons were diluted with pure nitrogen to obtain the calibration mixtures with impurity content from 2×10^{-7} to 5×10^{-4} mg m^{-3} (Ref. 70). Dilution was carried out in passivated aluminium bottles. A significant drawback of synthetic reference samples is the lack of contaminants characteristic of real air. Undesired effects of such substances can lead to noticeable systematic errors in the analysis. Studies involving correctly prepared reference samples obtained by sampling real air and certified based on the results of analyses carried out in different laboratories were also reported.[71,72] The air samples were certified for alkyl nitrates at three laboratories by gas chromatography using not only flame-ionization, but also highly selective atomic emission detection. The results of laboratory analyses differed by at most 5%.

3. Determination of various contaminants in air

Benzene and its homologues. Methods of determination of benzene and its homologues by gas chromatography with mass-spectrometric and flame-ionization detection systems,[73–82] by Fourier transform IR spectroscopy[39] and by UV spectroscopy have been reported.[40] Both active and passive impurity preconcentration were used.[74,75] The former was done with a carbon sorbent Carbotrap, polymeric sorbents Tenax TA and HayeSep D (Ref. 39) and new sorbents prepared by the sol–gel technology.[78] Solid-phase microextraction was used,[75,76] as well as its version involving collection of impurities in a needle-shaped sampler.[79] The preconcentration time was 1.7 min. Passive preconcentration was performed with the Carbograph 4 sorbent and a Carbopack B + Carbosite III mixture.[65] The volume of the air sample was 1–12 litre. Impurities were removed from the sorbents by thermal desorption or with carbon disulfide.[74–76] The lowest detection limits for benzene, toluene, ethylbenzene, xylenes and trimethylbenzenes [$(1-4)\times10^{-5}$ mg m^{-3}] were achieved by GC–MS.[72,77]

Perfluorinated organic compounds. Impurities of perfluorinated organic compounds including perfluorinated alcohols and perfluorinated sulfamides are most often determined by GC–MS with positive and negative chemical ionization and columns with polar stationary phases.[83–85] Analysis requires large air volumes, samplers containing quartz fibrous filters (to isolate impurities as particles) and glass columns with fillers based on XAD resins for collection of gaseous contaminants. From 50% to 100% of impurities can be extracted. The best results were obtained for *N*-substituted perfluoroalkyl derivatives of sulfonamide ethanol. Extracts from the samples were purified by Fluorisil and glass wool. The detection limits for the perfluorinated compounds studied were $(0.001-3.5)\times10^{-9}$ mg m^{-3}. Ionic perfluorinated organic compounds in air samples were determined by liquid chromatography–mass spectrometry with quadrupole and time-of-flight mass analyzers.[86,87] The determination of ionic perfluorinated organic compounds is a very complicated problem because extractants are contaminated with components of fluoroplastic materials. For instance, methanol stored in a bottle is contaminated with impurities from the stopper bushing. Yet another source of contaminants is fluoroplastic containing in the nitrogen pressure regulator (nitrogen is used for solvent evaporation). This established the contaminant control limits. The detection limits for most ionic perfluorinated compounds are of the order of 1×10^{-9} mg m^{-3}; the highest values, $(2.2-5.6)\times10^{-8}$ mg m^{-3}, are characteristic of perfluorohexanoic, perfluorooctanesulfonic and perfluorononanoic acids.

Antipyrenes (fire retardant agents). Brominated organic compounds are used to impart the fire-retardant properties to various materials. Most often, these are polybrominated diphenyl ethers (PBDE). The concentrations of these low-volatile compounds in air are at most 10^{-9} mg m^{-3}. Therefore, dynamic preconcentration of aerosol particles on filters and gaseous impurities in cartridges filled with appropriate sorbents is usually carried out with a powerful aspiration pump.

Interesting studies on the determination of PBDE particles were conducted in the Arctic.[88] The volume of the air sample was 2051 m^3. Extraction in a Soxhlet apparatus was done with dichloromethane and acetone/hexane mixture. The extracts were purified using multilayer chromatographic columns filled with neutral alumina, neutral and alkaline silica and sodium sulfate. The degree of extraction of the lower PBDE isomers ranged from 85% to 114% (*cf.* 50% to 60% for the higher isomers). Probably, in the latter case the low degree of extraction is due to very strong binding to samplers or to the loss during purification.

A study of the negative chemical ionization mass spectra of PBDE revealed the lack of molecular ions and predominance of Br^- ions. Therefore, electron impact ionization was used for reliable identification of the compounds under study. Low detection limits $(1.6-5.0)\times10^{-10}$ mg m^{-3} were obtained in the negative chemical ionization mode. Contaminants collected in polyurethane foam sorbent were extracted by microwave extraction with hexane/acetone mixture.[89–91] The recovery was more than 75%. The determination was carried out by GC–MS–MS with separation of isomers in a wide quartz capillary column (10 m × 0.53 mm × 0.25 μm). The detection limits of PBDE varied in the interval $(0.4-7.0)\times10^{-10}$ mg m^{-3}. Using GC–MS with electron impact ionization, brominated organic compounds including tetrabromobisphenol A,[63] 1,2-bis(2,4,6-tribromophenoxy)ethane and 2,3,4,5,6-pentabromoethylbenzene were identified in the air samples in the negative chemical ionization mode and determined quantitatively.[92] To control the extraction recovery of tetrabromobisphenol A impurity, a ^{13}C-labelled analogue was introduced into the sorbent prior to sampling. A mixture of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (1%) was used for derivatization of this impurity. The detection limit of tetrabromobisphenol A was 4.0×10^{-11} mg m^{-3} at a sample volume of 1000 m^3.

Synthetic aromatizing agents including alkylated nitrobenzenes and polycyclic compounds based on tetralin or indan were collected in samplers with glass fibrous filters for particles and polyurethane foam (sorbent)/XAD-2 (XAD-4) resin filters for gaseous compounds.[93–97] Impurities were extracted using dichloromethane and hexane/diethyl ether or acetone/hexane mixtures. The extraction recovery of impurities was 56%–114%, being in most cases higher than 80%. Extracts were purified in a chromatographic column containing deactivated silica and silica gel with alumina. The determination of synthetic aromatizing agents was carried out by GC–MS with electron impact ionization. The loss of impurities in the course of sampling or sample preparation procedure was monitored using deuterated aromatizing agents as internal standards. In some cases, proton exchange can occur, which makes this approach inappropriate.[97] The detection limits of aromatizing agents are of the order of 10^{-9} mg m^{-3}. This is sufficient for the determination of the concentration of synthetic aromatizing agents in indoor air [about $(1.7-300)\times10^{-6}$ mg m^{-3}].[93]

Alkylphosphorus esters belong to a relatively new group of contaminants possessing fire-retardant properties; they are used as plasticizers. Methods of determination of alkylphosphorus esters were developed for analysis of indoor air.[98–101] Preconcentration was carried out using glass fibrous filters for aerosol particles and filters made of polyurethane sorbent, Chromosorb 106, silica and XAD-2 resin for gaseous components. Impurities collected were extracted with acetone, dichloromethane and a hexane/diethyl ether mixture. To accelerate the extraction of impurities, sonication was used.[101] The extraction recovery of contaminants was 34%–110%. Quantitative analysis was carried out by GC with thermoionic and flame-photometric detection systems and by HPLC–MS. The lowest

detection limits attained $(0.04-1.9)\times10^{-8}$ mg m^{-3} were reported in Ref. 98.

Alkylphenols.[64, 102] Air samples for the determination of alkylphenols were preconcentrated using glass fibrous filters and a combined sorbent based on polyurethane foam and XAD-2 resin. The concentrates were extracted with a hexane/diethyl ether mixture. The extracts were purified by column chromatography on silica gel. To reduce the loss of impurities due to adsorption on the internal surface of evaporator, to improve the peak shape and to enhance the sensitivity of GC–MS-detection, the alkylphenols were silylated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane. The extraction recovery of alkylphenols was 69%–105%; the largest variations of this parameter were observed for aerosol particles. Silylated derivatives were efficiently separated in a chromatographic column (30 m × 0.32 mm × 0.25 μm) filled with a HP-5 low-polarity phase. The detection limits in the case of electron impact ionization were $(0.6-8)\times10^{-9}$ mg m^{-3} (Ref. 64).

Polycyclic aromatic hydrocarbons. The determination of PAHs including the most toxic ones (benz[*a*]pyrene, benz[*b*]-fluoranthene and fluoranthene) in groups from 5 to 24 compounds was studied.[60, 103–117] Active preconcentration methods were used, the air volume varied from 0.42 to 13680 m^3. Also, denuders were used for preconcentration.[60] The aerosol components of PAHs were collected on fluoroplastic or quartz glass fibrous filters while the molecular components were collected on the XAD-2,[103, 108, 109, 111] XAD-4,[60] or Tenax TA [113] sorbents or on polyurethane foam.[109, 113] The collected contaminants were extracted in Soxhlet apparatus using methanol, toluene, dichlorometane and acetone. Often, extraction was accelerated by sonication [108–111, 113] and exposure to microwave radiation.[104, 107] The degree of extraction of PAHs was 80%–100%. Intermediate extracts were transferred to aqueous solutions and then final preconcentration was carried out by solid-phase microextraction.[103, 113] PAHs in the concentrates were determined by fluorescence spectroscopy,[115] GC–MS [60, 103, 108, 110, 112] and HPLC with fluorometric detection.[60, 105, 107, 111] Preconcentration of impurities by solid-phase microextraction involved sample dosage by thermal desorption. To reduce the detection limits to 2.6×10^{-10} mg m^{-3}, large samples (70 μl) were introduced into a temperature-programmed evaporator.[104] The lowest impurity detection limits were $(0.26-8.1)\times10^{-9}$ mg m^{-3} (Refs 104 and 108).

Studies [118–121] are devoted to the determination of PAH nitro, oxygen and chloro derivatives. The preconcentration of these impurities as well as the sample preparation stages are similar to those developed in the PAH studies. The impurities were determined by GC–MS with electron impact ionization and by negative chemical ionization (in the case of nitro derivatives). In some cases, the authors reported only the absolute detection limits (in units of mass). For instance, the absolute detection limits were $(0.1-2.6)\times10^{-9}$ mg for the PAH hydroxy derivatives, $(3-7)\times10^{-11}$ mg for the PAH nitro derivatives and $(0.007-5)\times10^{-6}$ mg for the PAH chloro derivatives.

Polychlorinated and polybrominated dibenzo-*p*-dioxins, dibenzofurans and biphenyls. Numerous studies are devoted to the determination of supertoxic substances, such as polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) [122–133] and their brominated analogues.[134–136] These substances are collected from air on glass or quartz fibrous filters [122–135] and using sorbents, *viz*., polyurethane foam [122–136] and XAD-2.[125] For active preconcentration, the air volume reached 7000–8000 m^3 and the sampling step took 20–24 days.[122] The duration of the passive preconcentration step took up to three months. The rate of passive preconcentration of air [123, 126, 128, 129, 131] was estimated at 0.4–7.2 m^3 day^{-1}. Polyurethane foam and, in a particular study, fir needles were used as collectors for passive sampling.[58] In all studies, contaminants were extracted in Soxhlet apparatuses with toluene,[123–125, 127, 130, 132, 133, 135] hexane [58, 126, 128, 131] and dichloromethane.[58] The extraction time was 8 to 48 h. The extracts were concentrated to 1–2 ml and then purified by liquid chromatography using silica gel, alumina, Fluorisil and Carboxen. The extraction recovery (51%–118%) was estimated from the data obtained for ^{13}C-labelled analogues of the analytes studied. In all cases, the analytical procedure was completed by gas chromatography–mass spectrometry with selective ion monitoring (the resolution of mass analyzers was at least 10^4). Difficulties in the determination of brominated dioxin-like compounds due to their partial decomposition in the extraction, injection and chromatographic separation stages were reported. Mass-spectrometric detection is complicated by the overlap of dibenzofuran fragment ions and ions of fragmentation products of polybrominated diphenyl ethers.[136] To reduce the probability of analyte decomposition in the course of GC–MS-analysis, thin-film (0.1–0.2 μm) capillary columns were used. The detection limits were estimated from the tenfold signal-to-noise ratio. The absolute detection limits were $(0.2-1.5)\times10^{-6}$ mg.[130, 133, 135] This made it possible to determine the concentrations of the polychlorinated dibenzo-*p*-dioxin and dibenzofuran impurities up to 6×10^{-14} mg m^{-3} (Ref. 122).

Organoelement compounds. Preconcentration of dimethyl mercury from air was carried out [137] using the Carbotrap adsorbent; subsequent determination of this highly toxic substance was done by GC with atomic fluorescence detection. The detection limit for dimethyl mercury was 1×10^{-8} mg m^{-3} at an air volume of 0.05 m^3. The determination of organosulfur compounds was reported.[138, 139] Preconcentration was carried out by vapour phase deposition and solid-phase microextraction. The determination was performed by GC with flame photometric [139] and mass-selective [138] detectors. The detection limits were $(1-8)\times10^{-5}$ mg m^{-3}. The determination of hydrazine and its derivatives was also reported.[140] Hydrazine, phenylhydrazine and 1,1-dimethylhydrazine were concentrated on silica gel coated with 5,7-dinitro-4-chlorobenzofurazan. Contaminants were determined by HPLC with a diode array detection system. The detection limits were 0.01–0.017 mg m^{-3}. A method [141] of determination of sarin and soman at a level of $(1-2)\times10^{-7}$ mg m^{-3} is based on sorption of analytes by an absorbing solution followed by extraction of contaminants by ethyl acetate and hexane. The determination was carried out by GC with flame photometric and thermoionic detectors.

Biologically active contaminants. After air sample preparation and transfer of contaminants into the aqueous phase they can be quantitatively detected by immunochemical methods, which are highly sensitive and specific and enable significant improvement of the performance of the determination procedure. For instance, up to 50 samples per hour can be tested for estrogens (ethylestradiol, estradiol and estrone) in the air of pharmaceutical plants.[142]

Procedures for control of air contamination by proteolytic enzymes were developed (detection limit of subtilizin enzyme in air is 5×10^{-9} mg m^{-3}). During the working day, analyte is sorbed from occupational air of pharmaceutical plants on strip membranes designed similarly to personal radiation dosimeters and then is determined by enzyme immunoassay (this takes a few minutes).[143] This method was used for the determination of allergens from some exotic species of wood in dust at woodworking plants. In aqueous extracts, the allergen detection limit is 3×10^{-5} mg litre^{-1}; this makes it possible to determine allergens in aerosol contaminants[144] at a level of 1.5×10^{-2} mg of allergen per gramme of dust. Probably, immunochemical methods (first of all, enzyme immunoassay technique) will be more widely used in the determination of biologically active contaminants in the indoor air (the air purity should be monitored continuously). Selected characteristics of the most sensitive methods of impurity determination in air of different origin are shown in Table 1.

Table 1. Characteristics of methods for the determination of impurities in air of different origin.

Impurity	Method of analysis	Air volume /m^3	Method of preconcentration	Detection limit /mg m^{-3}	Note	Ref.
Benzene, toluene, ethylbenzene, xylenes	differential absorption UV spectroscopy, 150-W krypton lamp, $L = 250$ m	—	none	$(0.5-2) \times 10^{-3}$	atmospheric air	40
Ethane	tunable-diode laser IR spectroscopy with frequency modulation, multipass cell, $L = 170$ m	$\leqslant 5 \times 10^{-3}$	"	1×10^{-4}	exhaled air	36, 37
Methane	optoacoustic spectroscopy with interferometric detection	not specified	"	1×10^{-3}	atmospheric air	35
Ethylestradiol, estradiol and estrone	enzyme immunoassay	1.2×10^{-3}	SPE with cellulose nitrate and polytetrafluoroethylene	10^{-5} mg of steroid	indoor air	142
Proteolytic enzyme subtilisin	the same	3.2×10^{-3}	SPE with strip membranes	5×10^{-9}	the same	143
Methanol, ethanol, benzene and alkylbenzenes, acetone, dimethyl sulfide	chemical ionization mass spectrometry	3×10^{-3}	none	$n \times 10^{-4}$	exhaled air	43
Alcohols, hydrocarbons, isoprene, acetone	ion mobility spectrometer with a ^{63}Ni source and polycapillary columns	1×10^{-5}	"	$10^{-3}-10^{-5}$	the same	18
Methyl mercaptan and ethyl mercaptan, dimethyl sulfide, carbon disulfide	GC – MS	$(1-3) \times 10^{-3}$	SPME, PDMS, carboxen	$(1-2) \times 10^{-4}$	"	145
Benzene, 2,5-dimethylfuran, toluene, xylenes	GC – MS	8×10^{-4}	SPME, combination of sorbents	$(1.6-4.3) \times 10^{-5}$	"	146
22 Substances including hydrocarbons C_5-C_{24}, aldehydes, benzene, acetone	GC – MS time-of-flight mass analyzer	5×10^{-3}	SPME, PDMS	$(0.04-8) \times 10^{-3}$	"	147
40 Substances including hydrocarbons C_5-C_{12}, aldehydes, alcohols, benzene homologues, terpenes	two-dimensional GC – FID, capillary columns	$(2.5-8) \times 10^{-4}$	SPE, Combination of sorbents	$(1.6-2.7) \times 10^{-4}$	"	48
Benzene and alkylbenzenes	GC – FID	passive sampling, 7 days	SPE, carbograph 4	$(1-4) \times 10^{-5}$	atmospheric air	75
Benzene	GC – MS	not specified	SPME, divinylbenzene/carboxen/PDMS	8×10^{-3}	exhaled air	77

Table 1 (continued).

Impurity	Method of analysis	Air volume /m^3	Method of preconcentration	Detection limit /mg m^{-3}	Note	Ref.
Benzene, styrene, propylbenzene, n-decane, n-undecane	GC – FID	0.005	SPME, PDMS	$(0.012 - 1.26) \times 10^{-3}$	exhaled air	78
Polybrominated diphenyl ethers PBDEs 28, 52, 101, 138, 153 and 180 isomers	GC – MS – MS	60 – 260	quartz filters, SPE, polyurethane sorbent	$(0.4 - 7) \times 10^{-10}$	atmospheric air	90
Tetrabromobisphenol A	GC – MS/NCI	1000	quartz filters, SPE, polyurethane and XAD-2	4×10^{-11}	the same	63
Perfluorinated alcohols and sulfamides	GC – MS – PCI, GC – MS – NCI, HPLC – MS – time-of-flight mass analyzer	20 – 1780	quartz filters, SPE, sorbents based on polyurethane and XAD-2	$(0.3 - 2.1) \times 10^{-9}$ $(0.03 - 3) \times 10^{-7}$	the same indoor air	84
54 Substances including hydrocarbons and aldehydes	GC – MS, HPLC – UV	4 – 144	SPE, silica gel	$(0.5 - 8) \times 10^{-5}$	atmospheric air, indoor air	79
Galaxolide, tonalide	GC – MS	not specified	SPE, polyurethane sorbent, XAD-2	1×10^{-9}	atmospheric air	93
Cashmeran, celestolide	GC – MS	72 – 524	SPE, polyurethane sorbent, quartz filters	–	atmospheric air, indoor air	96
Dimethyl mercury	GC with atomic fluorescence detector	0.002 – 0.2	SPE, Carbotrap TM	1×10^{-8}	the same	137
Organosulfur compounds	GC – FPD, GC – MS, GC – FID	0.002 – 0.003	vapour phase method and SPME	$(1 - 8) \times 10^{-5}$	atmospheric air	138, 139
Hydrazine, phenylhydrazine, 1,1-dimethylhydrazine	HPLC with diode array detector	0.012	SPE, silica gel with immobilized 4-chloro-5,7-dinitrobenzofurazan	$(1 - 1.7) \times 10^{-2}$	air-based model mixtures	140
Sarin, soman	GC – FPD, GC – TID	0.15 – 0.72	liquid absorbent – ethylene glycol in acidified water (1 : 5)	$(1 - 2) \times 10^{-7}$	atmospheric air, indoor air	141
Perfluorinated alcohols	GC – MS – PCI	300	quartz filters, SPE, sorbents based on polyurethane and XAD-2	$(0.001 - 3.5) \times 10^{-9}$	atmospheric air	85
Alkyphosphorus esters	HPLC – MS/MS/ electrospray ionization MS	14.4	SPE, C_{18} membranes	$(0.04 - 1.9) \times 10^{-8}$	the same	98
Organophosphorus and polybrominated fire retardants	GC – FPD(phosphorus) GC – AED(bromine)	14.4	quartz filters, SPE, C_{18} sorbent	$(0.24 - 9.9) \times 10^{-6}$	atmospheric air, indoor air	101
PCDD, PCDF, PCB	high-resolution GC – MS (at least 10000)	300 6000 – 8000	quartz filters, SPE, polyurethane-based sorbents	$(0.2 - 1.3) \times 10^{-9}$ (see [a]) 6×10^{-14}	atmospheric air	130, 122
PCDD, PCDF	the same	290	the same	$(1 - 5) \times 10^{-12}$	the same	133
PCDD, PCDF, polybrominated dibenzo-*p*-dioxins, polybrominated dibenzofurans	the same	1512	the same	$(0.5 - 5) \times 10^{-9}$ (see [a]) (chlorinated), $(0.25 - 1.5) \times 10^{-9}$ (see [a]) (brominated)	"	135
Tertiary octylphenol, 4-n-nonylphenol, 4-n-octylphenol	GC – MS	400 – 1000	quartz filters, SPE, polyurethane-based sorbents, XAD-2	$(0.6 - 8) \times 10^{-9}$	"	64

Table 1 (continued).

Impurity	Method of analysis	Air volume /m^3	Method of preconcentration	Detection limit /mg m^{-3}	Note	Ref.
16 EU priority PAHs	GC–MS	0.144–1296	SPE, sorbents based on polyurethane and polydimethylsiloxane; quartz filters and Tenax TA	4.5×10^{-7}–1.2×10^{-4}	atmospheric air	113
8 of 16 EU priority PAHs	GC–MS	0.42	XAD-2	2×10^{-8}–1×10^{-6} (see [a])	indoor air	103
PAH nitro derivatives	GC–MS–NCI	0.24–0.58	polyurethane-based sorbents, quartz filter	$(3-7)\times10^{-11}$ (see [a])	the same	118, 119
Products of partial oxidation of PAHs	GC–MS–NCI	not specified	the same	$(0.1-2.6)\times10^{-9}$ (see [a])	atmospheric air	119
PAH chloro derivatives	high-resolution GC–MS	1440	"	$(0.007-5)\times10^{-6}$ (see [a])	the same	120, 121

Note. Notatios are as follows: FID is flame-ionization detector, SPME is solid-phase microextraction, PDMS is poly(dimethylsiloxane), NCI is negative chemical ionization, PCI is positive chemical ionization, FPD is flame photometric detector, TID is thermoionic detector, AED is atomic emission detector, and SPE is solid-phase extraction. [a] The detection limits reported in original studies are given in milligrammes.

V. Reliability of determination of contaminants

Traditional methods for validation of the correctness of the results of analysis include variation of the sample volume and additives.[3,4,22,24] They are used if the concentrations of toxic substances are no lower than $(0.1-1)\times10^{-4}$ mg m^{-3}. Detection of lower concentrations by these methods faces some difficulties because very large air sample volumes and long-term preconcentration are required. To control the reliability of the determination of lower impurity concentrations, an element-by-element control of particular stages of analysis is carried out, as a rule, using ^{13}C- or ^{2}D-labelled analogues of the compounds to be determined.[3,21,22] This makes it possible to determine the extraction recovery of analytes from the sampling medium. The losses of analyte collected on transportation, storage and analysis are also controlled. The greatest uncertainty in the analysis comes from the extraction of impurities from air. Model experiments are usually carried out using standard mixtures with impurity concentrations of the order of 1 mg m^{-3}; the mixtures are diluted with nitrogen or pure air[70] to $(0.002-6)\times10^{-4}$ mg m^{-3} (no lower!). The control of preconcentration of aerosol particles is more difficult because one deals with even lower concentrations. Model experiments with air mixtures containing impurities at a level of 10^{-6}–10^{-8} mg m^{-3} are very complicated. Here, the correctness of analysis at concentrations in the range from 10^{-6} to 10^{-8} mg m^{-3} (and lower) can be controlled by interlaboratory comparative analysis. For instance, interlaboratory determination of toxic organohalogen compounds and dioxin derivatives[136,145–148] showed that the results obtained can differ by 24%–38%. Unfortunately, this approach is rarely used for validation of the quality of determination of contaminants in air.

Atmospheric water and ozone present in samples complicates the sampling and impurity preconcentration stages and affects the results of analysis. Ozone can be a source of systematic errors in the determination of PAHs, unsaturated hydrocarbons and organochlorine compounds.[50,60,148] For instance, an increase in ozone concentration may lead to an increase in propene concentration in air samples as well as underestimation of the results of PAH determination by 10%–20%. It was proposed to eliminate the effect of ozone by chemically binding it to potassium iodide.[60]

Water reduces the sorption capacity of adsorbents, which makes the preconcentration of impurities less efficient. In addition, impurities can dissolve in aqueous condensate and enter into chemical reactions resulting in other forms of contaminants. In the course of gas chromatography analysis, water can affect the separation of impurities and the detector response. Water can be removed using semipermeable films[149] or by condensation in the sampling stage.[50] Problems due to the effect of water and carbon dioxide are particularly topical in the analysis of exhaled air.[19]

The results of analysis may differ when using different preconcentration techniques. In the case of passive preconcentration, the impurity diffusion rate depends on the impurity concentration in air. For the simplest aromatic hydrocarbons, the decrease can vary from 14% to 30%.[74]

VI. Conclusion

At present, the concentrations of various classes of organic compounds in air can be determined at a level of 6×10^{-14}–1×10^{-10} mg m^{-3}. Taking into account a huge number of contaminants in air and a wide range of their concentrations, one should use selective methods of preconcentration and determination. The lowest impurity detection limits are characteristic of tunable-diode IR laser spectroscopy (simple compounds) and gas chromatography–mass spectrometry with negative chemical ionization. Low detection limits of non-electrophiles were attained by electron impact and positive chemical ionization of impurities and tandem mass spectrometry.

The determination of polycyclic aromatic hydrocarbons and dioxin-like compounds, as well as relatively new polybrominated organic fire retardants. Among PAHs, a large number of chloro and nitro derivatives were identified. When analyzing exhaled air, simple organic compounds, such as ethane, acetone and aldehydes are also of interest.

The corresponding detection limits in exhaled air are of the order of 10^{-4} mg m^{-3}. At present, the detection limits of phosphorus esthers in atmospheric air are 10^{-7}–10^{-8} mg m^{-3}, which allows these contaminants to be controlled only near the evolution sources.

Almost all highly sensitive methods of determination of contaminants enable preconcentration from large air volumes up to 13 680 m^3. Impurities collected on filters and sorbents are often extracted by microwave extraction, which allows one to save the solvent and to shorten the extraction time. The method can be treated as n alternative to conventional extraction of impurities. The selectivity of preconcentration of substances in solid-phase microextraction can be considerably improved by using nanocarbon sorbents, especially those obtained by the sol–gel technology. In the latter case, one can control the adsorbent polarity by modifying its structure with various fragments, such as crown ethers, β-cyclodextrins and poly(ethylene glycols).[25, 26] The thermal stability of the modified sorbents is very high, *viz*., they can be used up to 400 °C. Miniaturization of samplers for preconcentration in gas chromatography and liquid chromatography allows one to use solvent-free methods, to combine the sampling, preconcentration and dosage stages, to eliminate cryofocussing in the dosage step and to improve the separation of mixtures.

The problem of determination of impurities in exhaled air against the background of indoor air can be solved using purified air.[6, 20] However, this has not been implemented in clinical practice. Therefore, contaminants in exhaled air are determined from the difference between the results obtained in the analyses of initial and exhaled air. Separation of alveolar component in exhaled air is also a complicated task. In addition, individual features of patients introduce uncertainty into the results of determination. It should be noted that a standard exhaled-air sampling procedure has not been developed so far.

As earlier, improvement of the sensitivity of determination of contaminants in air of different origin and the design of mobile devices for field analysis still remain topical.[150]

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