Portable Continuous Aerosol Concentrator for the Determination of NO$_2$ in the Air

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Abstract—The paper deals with the development of portable aerosol concentrator and its application for the determination of nitrites and nitrates. The device enables the continuous trapping of pollutants in the air. An extensive literature search has been elaborated which aims at the development of samplers and the possibilities of their application in the continuous determination of volatile organic compounds. The practical part of the paper is focused on the development of the portable aerosol concentrator. The device using the Aerosol Enrichment Unit has been experimentally verified and subsequently realized. It operates on the principle of equilibrium accumulation of pollutants from the gaseous phase using absorption liquid polydisperse aerosol. The device has been applied for monitoring nitrites and nitrates in the air. The chemiluminescence detector was used for detection; the achieved detection limit for nitrites was 28 ng/m^3 and for nitrates 78 ng/m^3.

Keywords—aerosol enrichment unit, air pollution, NO$_2$, portable aerosol concentrator

I. INTRODUCTION

THE Ministry of Health mentions in its annual statistical reports that a lot of patients living especially in large urban conglomerations and treated in public medical centres suffer from nasal allergy, URD (upper respiratory disease), chronic bronchitis, asthma and other respiratory tract diseases.

These diseases are related to the quality of the air in cities. Therefore, the measuring of air pollutants as possible causes of high occurrence of respiratory diseases in cities is implemented. NO$_2$, SO$_2$, O$_3$, the concentration values of which range between 14.82-27.86 and 16.58-43.43 and 18.25-35.80 μg/m^3 are main monitored pollutants [1].

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To determine them passive sampling devices which are small, reliable, don´t need electricity and are cheap are often used. They may be used for both internal and external monitoring of the atmosphere quality under various climatic conditions [2]. Samplers are also suitable for the determination of spatial distribution of gaseous pollutant concentration [3]-[5].

II. VIEW OF THE PROBLEMS

A. Passive samplers

Passive samplers can simplify the analytical procedure in sampling even if it is necessary to minimize the decomposition of a sample during transport and storage. Low sampling rates require long times of sampling in low concentrations as well, so that the time-weighted averages of analyte concentrations of subsequent obtained samples can provide considerably different values of substances. The results of analyses obtained through passive sampling may also be affected by the air temperature, humidity and velocity. The detection limit is dependent on the sampling rate, sampling time and especially on the sensitivity of selected detection systems [6].

Since the first sampler which was described by Palmes for collecting sulphur dioxide [7], several samplers have been developed by the Swedish Environmental Research Institute, Rupprecht and Patashnick Company (USA), Laboratory of Aerology in Toulouse (France), CSISRO (Australia), Radiello, and others. They generally rely on diffusion of contaminant molecules across concentration gradients defined by Fick's first law of diffusion. Diffused contaminants are trapped on filters impregnated with reagents consisted of NaOH, triethanolamine, Na$_2$CO$_3$, tetrachloro-mercurate, TEA, NaI + Na$_2$CO$_3$, citric acid, or phosphoric acid for trapping SO$_2$, NO$_2$, or NH$_3$ [8].

Ogawa´s passive samplers have been extensively used in monitoring SO$_2$, NO$_x$, O$_3$, and other gases by the American Environmental Protection Agency and Harvard School of Public Health. They were used in monitoring urban O$_3$ in national parks [9] and NO$_2$ emissions from highway traffic [10]. Good agreements between results from Ogawa's samplers and continuous gaseous analyzers were obtained [11].

A poorly sensitive spectrophotometric method for determining NO$_2$ in the air based on converting NO$_2$ into nitrite ions which was subsequently coupled with azodyes was reported [12]. Chemiluminescence sensitive methods based on catalytic reduction of NO$_2$ to NO which was subsequently reacted with ozone or luminol were also reported [13]-[14].

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Laser-induced fluorescence detection was used in determining NO_2, but its high cost prevented it from popular use [15]-[16]. NO_2 was also determined using optical sensors [17], electrochemical sensors [18], and passive sampling methods [19].

Currently, it is possible to find out that inorganic gaseous pollutants are trapped in denuders which are also suitable for separation of gaseous pollutants in the gaseous phase from those which occur in the atmosphere in the condensed phase. It has been proved repeatedly [20]-[22] that the reliability of results obtained through different types of denuders is much better than the reliability of results obtained through the abovementioned traditional techniques. The oldest type of diffusion denuder is the so-called AU dry denuder, the walls of which are provided with a suitable sorbent. The AU denuder [23] with oxalic acid as a sorbent was mentioned as the first one. This denuder was developed for determining ammonia in the ambient air. Unfortunately, preparing the sorbent covering the internal wall of the denuder tube together with liberating the compound already adsorbed were time-consuming and labour-intensive, therefore, this application was used only restrictedly.

Thermodenuders have also been used for enriching the samples of inorganic trace pollutants in the air [24]-[27]. This type of denuders also uses dry sorbents which absorb pollutants; however, as opposed to conventional dry denuders, the trapped pollutants are desorbed thermally at increased temperatures. Measurements using thermodenuders can be automated; however, they usually show unsatisfactory selectivity [25]-[27]. This is their principal disadvantage. It is true, in general, that enrichment techniques for volatile organic compounds (VOCs) in gaseous media are based on sorption on solid materials. From the viewpoint of the degree of enrichment the adsorption is much more effective than the absorption process as stated in literature [28]-[30]. The adsorption procedure is used for the concentration increase of organic compounds in the air in trace concentrations in the range from units of ppt up to tens of ppb (v/v). However, high values of the adsorption distribution constant complicate the liberation of the analyte. Other problems are caused by variable content of water vapours in the air [31]-[32].

In the analysis performed by this method the sorbent, after sampling, is stored and transported to the laboratory where the analyte is analyzed using gas chromatography or the combination of gas chromatography and mass spectrometry after thermal desorption or extraction. This relatively simple procedure fails when thermolabile organic compounds (e.g. organic compounds which contain sulphur in their molecules or biogenic substances such as terpenes) are determined. In these compounds it has been discovered that monoterpenes adsorbed on a sorbent can undergo catalytic reactions, e.g. they can react with ozone in the course of ambient air sampling, which subsequently leads to the diminishing of analyte concentration due to the formation of reaction oxidation products [33].

Activated carbon, Tenax or various compounds of silicon were used for the determination of volatile organic compounds (VOCs) in the atmosphere using dry denuders.

After the taking samples of organic compounds these were usually thermally desorbed or extracted using a suitable solvent and analyzed.

The discontinuity of determination is a common methodological disadvantage of all abovementioned procedures. That means that only integrated information values of the analyte content in the atmosphere in a given time interval was received.

B. Continuous Determination

Only a few methods which enable the continuous enrichment of a sample by a pollutant and on-line analyses have been described. Common condensation of organic trace analytes with solvent vapours [34] or absorption of gases and vapours in the water film in absorption liquid is characteristic of them. Admittedly, some methods have been published, but they have not been realized in practice [35]. The diffusion scrubber (DS) contains a semipermeable membrane in the denuder which separates the liquid and gaseous phase. This determination has been developed by Dasgupta [36]. He was the first who realized the continuous method of enrichment and the on-line analysis of gaseous pollutants in practice. In the diffusion scrubber (DS) with reverse-flow arrangement the running absorption liquid is separated from the air by a semipermeable microporous membrane. The diffusion scrubber (DS) was used for continuous, fully automated measurements of concentration of water-soluble inorganic gases [37]-[41]. Unfortunately, the porous material restricts the use with regard to time in case of long-term analyses when membrane pores clog.

III. PRACTICAL PART

Wet denuders where absorption liquid is in direct contact with the analyzed air provide much more effective enrichment of gaseous samples than the diffusion scrubber (DS) and do not enable the clogging of membrane pores. The simplest version of wet effluent diffusion denuder (WEDD) illustrated in figure 1 is formed by a cylindrical borosilicate tube with the internal wall modified with the layer of porous soft glass [42].

The internal wall of this tube is lined with the layer of porous soft glass which is highly wettable. The absorption medium runs down the wall in a thin layer owing to gravity while the analyzed air moves up countercurrentwise under conditions of laminar flow. The rotating denuder is a more complicated WEDD [43]-[45]. This type of denuder rotates around its longitudinal axis and the absorption liquid is maintained on the "active" denuder wall with the aid of centrifugal force and adhesion. The disadvantage is that the rotating wet annular denuder contains a comparatively large amount of liquid (up to 15 ml), the result of which is decreasing the detection limit of compounds determined in the air.
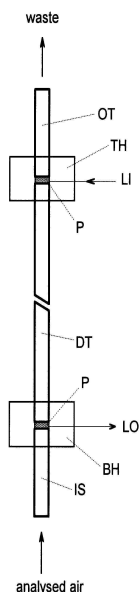
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Fig. 1 Scheme of the Wet Effluent Diffusion Denuder – WEDD
DT – denuder tube, IS – inlet subduction zone, OT – outlet tube, P - porous O-ring (PTFE), LI - liquid inlet, LO – liquid outlet, TH – top head, BH – bottom head

The Aerodisperse Enrichment Unit (AEU) [46] is another enrichment device we have proposed (figure 2) with the direct contact of the absorption liquid and the analyzed air. This device works on the principle of equilibrium accumulation of pollutants from the gaseous phase using polydisperse aerosol. The polluted air is sucked through a tube in which stainless steel capillaries supplying absorption liquid are positioned. The sorption liquid is dispersed in the form of aerosol using air ejection. The polydisperse aerosol forms a pencil beam which condenses in the next part of the AEU due to the quasiadiabatic expansion and the collision with an inclined barrier. The sampling procedure enables automatic measuring.
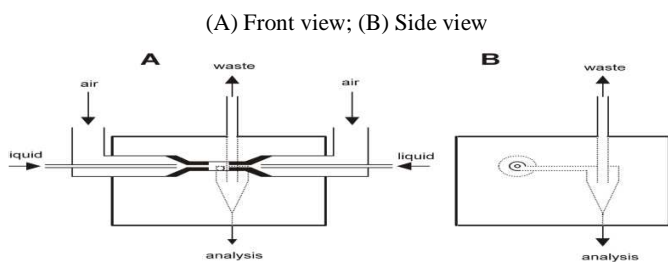
(A) Front view; (B) Side view

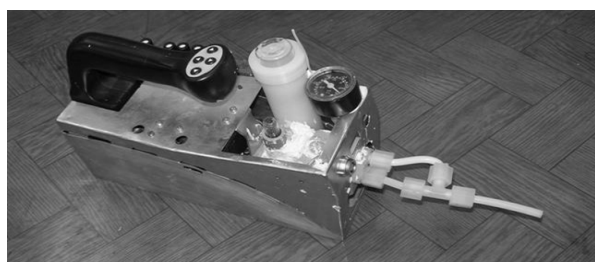Fig. 2 Proposed design of double-flow Aerosol Enrichment Unit – AEU

Fig. 3 Implementation of the portable continuous aerosol concentrator operating on the principle of double-flow Aerosol Enrichment Unit – AEU

IV. PRACTICAL APPLICATIONS OF THE AEROSOL ENRICHMENT UNIT FOR THE DETERMINATION OF NO_2 IN THE AIR

The principle of the Aerosol Enrichment Unit (figure 2) was used for monitoring nitrogen oxides. In the determination the chemiluminescence detector was used [47] which takes advantage of the reaction of nitrogen dioxide and luminol alkaline solution. The achieved detection limit for nitrogen dioxide was 0.01 ppb (v/v). The calibration graph was linear up to the concentration of 400 ppb (volume).

After the replacement of luminol by a solution containing eosine Y with gallic acid it was possible to monitor ozone concentration in the ambient air [48]. The detection limit for ozone was 0.3 ppb (v/v); the detector response was linear for ozone up to 349 ppb (volume). No significant interference from other gaseous pollutants incident in usual concentrations in the atmosphere was observed.

The AEU was used for constructing the device for continuous measurements of the soluble fraction of atmospheric aerosol [49]. A sample of the circulating air at the high linear rate flows through two jets of the Venturi tube (two flows of polydisperse aerosol are formed) (figure 2), two flows of drops collide and after condensation they are collected. Under optimum conditions of air circulation at the rate of 5 l/min and the rate of flow of 2 ml/min aerosols are trapped quantitatively. The operation of this device in combination with the on-line detection enables the in situ determination of water-soluble aerosols containing e.g. nitrites or nitrates. The detection limit for nitrites or nitrates was 28 or, if need be, 78 ng/m³.

V. CONCLUSION

Concentrations of nitrogen dioxide were determined over a year using the continual sampling with chemiluminiscence detections. It has been confirmed that the AEU is a structurally simple, mechanically resistant and suitable for the determination of feasible concentrations in water-soluble aerosols containing nitrates and nitrites. The developed AEU principle has also been used for the device structure enabling continuous measurements of the soluble fraction of atmospheric aerosols.

It has been confirmed that wet enrichment techniques based on the trapping of the analyte in the absorption liquid aerosol as an enrichment technique enable particular determinations or the on-line analysis of organic as well as inorganic gaseous pollutants in the air.

These techniques of wet concentration increase can be also used for the monitoring of trace substances, i.e. for their measuring at high sensitivity. Further, with regard to the higher sensitivity of measurement and more resistant device structure, the AEU has been selected for our application. The AEU has been miniaturized and the prototype – the portable continuous aerosol concentrator - has been built

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