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Impinger sampling coupled to high-performance liquid chromatography by a modified autoinjector interface

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Abstract

This work describes a device that permits the use of a small glass impinger for the automatic sampling and enrichment of air pollutants "on-line" with high-performance liquid chromatographic separation. The impinger is mounted in a modified autoinjector instead of in the vial rack which, using appropriately modified software, permits the automatic sampling of the pollutants by bubbling air through an adequate reaction solution. This solution with the trapped/reacted compounds is then transferred by the autosampler syringe from the impinger to a high-performance liquid chromatography (HPLC) column. After several steps to clean the impinger, using the mobile phase or a specially chosen solvent, the impinger is ready for a new analysis. With a tandem configuration, which allows the first sample to be analysed during the sampling of a second one, a higher analysis frequency is obtained. The technique was tested by determining ng/l concentrations of aldehydes and ketones in an urban environment, sucking air through solutions of 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid in triethylphosphate. The resulting DNP-hydrazones were injected automatically into a 250×4.6 mm I.D. reversed-phase C_{18} HPLC column (3 μm) and were separated using an isocratic acetonitrile–water (70:30, v/v) mobile phase and then they were detected with a UV monitor at 360 nm. All sampling parameters, such as DNPH and acid concentrations, impinger air flow, sampling time, derivatization speed, blank values, etc., are discussed.

Keywords: Sample preparation; Instrumentation; Environmental analysis; Injection methods; Aldehydes; Ketones; Dinitrophenylhydrazine

1. Introduction

The sensitivity of analytical methods currently available for the determination of organic trace pollutants, is often insufficient to measure low environmental concentrations directly and, therefore, a preliminary enrichment step is required.

Many enrichment techniques have been described in the literature, which vary according to the type of pollutant and the analysis method. For gas chromatographic (GC) analysis, adsorption on porous materials followed by thermal desorption, preconcentration in a cryotrap and following flash-heating into the GC column or by solvent elution and the subsequent injection of an aliquot of the solution are, for instance, used to analyse volatile organic substances in air. Pollutants adsorbed on solid matter are desorbed by Soxhlet or supercritical fluid extraction and concentrated by evaporation of the solvent before analysis.

Another preconcentration method consists of trapping volatile air pollutants in a reaction liquid containing a derivatization agent. Many reactions are described in the literature [1] that may be used for the selective preconcentration/derivatization of well-defined pollutant groups. Some of them are shown in the Table 1.

As early as 1972, Papa and Turner [2] used the

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Table 1
Preparation of derivatives

Derivative for ...	Type of Derivative
Acids	Phenylhydrazides
Alcohols	Substituted urethanes
Aldehydes	2,4-Dinitrophenylhydrazones
Aldehydes	Semicarbazones
Amides	9-Acylamidoxanthenes
Amines (I+II)	Sulfonamides
Amines (III)	Quarternary ammonium salts
Esters	3,5-Dinitrobenzoates
Ethers (aliphatic)	3,5-Dinitrobenzoates
Ethers (aromatic)	Picrates
Aromatic hydrocarbons	Aroylbenzoic acids
Ketones	Oximes
Phenols	Phenylurethanes
Diisocyanates	1-(2-Pyridyl)piperazine

dinitrophenyl hydrazine (DNPH) reaction to enrich trace concentrations of aldehydes and ketones in car exhaust fumes by passing large volumes of air through impingers. Later on, the impinger was substituted by a cartridge [3–5] that was filled with a porous stationary phase and impregnated with DNPH (Sep-Pak, Millipore). Both methods are very time consuming and need manual work, resulting in high analysis costs. In 1994, Grömping and Cammann [6] proposed an automated method that combined impinger-sampling of nitrogen oxides, aldehydes and ketones with HPLC separation.

This paper describes a modified mini-impinger method that allows full automation by placing a small glass impinger in the open space of an autoinjector where sampling, enrichment and separation are combined into a unique procedure.

2. Experimental

2.1. The new analytical instrument/procedure

A computer-controlled, commercially available autoinjector for HPLC analysis (Shimadzu model SIL-9A) has been modified by replacing the sample vials by a newly developed, conical mini-impinger (Fig. 1). By means of an air flow pump (Zambelli Chronos), a flow controller (Brooks model 5850) and a valve, sample air is drawn through the mini-impinger (3 ml) containing the DNPH reaction solution at preselected time intervals. A computer programme has been written for the autoinjector which allows it to (a) inject and extract a cleaning

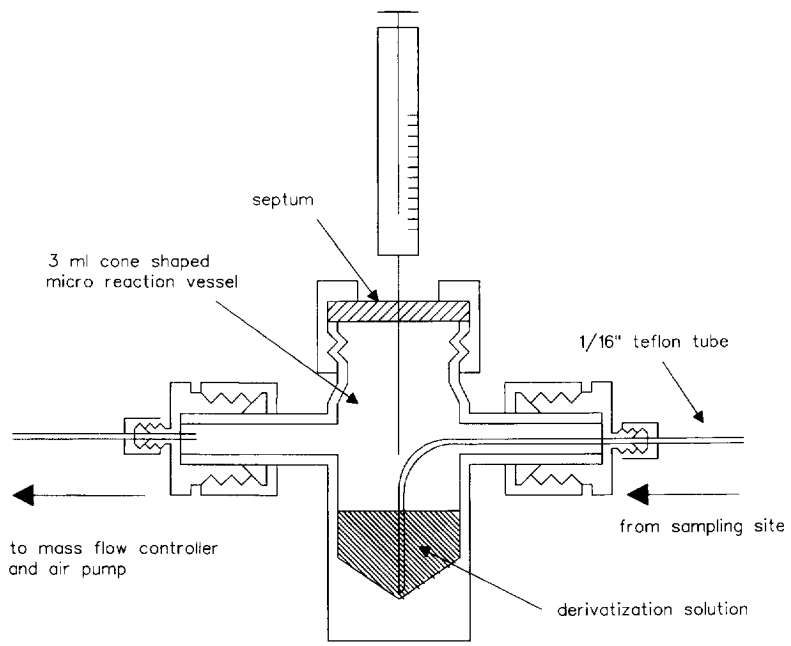

Fig. 1. Schematic diagram of the impinger with connection tubes and the reaction solution.

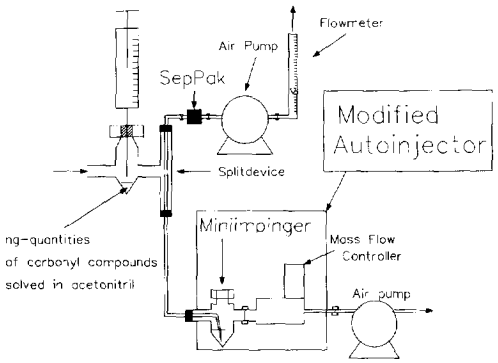

Fig. 2. Splitting device, designed to assure sampling of identical concentrations of carbonyl compound with the mini-impinger device and the Sep-Pak cartridge.

fluid and the reaction solution into/from the mini-impinger in consecutive, appropriately timed steps, (b) start and stop air sampling, (c) inject the reacted solution into the HPLC column and (d) start and stop the analysis. It is also possible to use two mini-impingers in parallel to increase the number of measurements. The computer program allows all experimental parameters within useful ranges to be controlled. A commercial version of the described instrument will be available in the near future, which will be small and light enough to be easily transported to field sites.

Because of its low vapour pressure and chemical reactivity (see blank values below), triethylphosphate (TEP) was chosen (after several trials) as the solvent

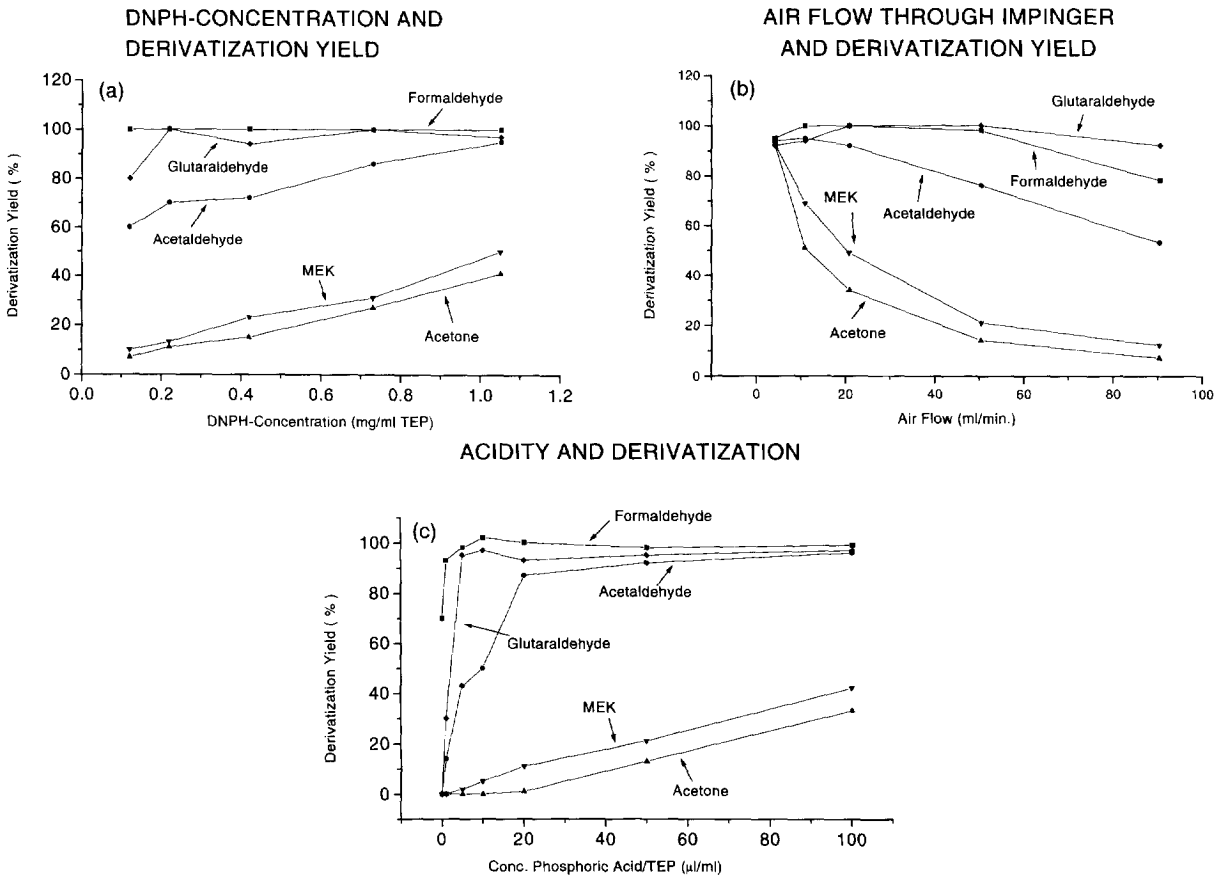

Fig. 3. Influence of the air flow-rate (a) and the concentrations of DNPH (b) and H_3PO_4 (c) on the derivatization yield of formaldehyde, acetaldehyde, acetone, MEK and glutardialdehyde. (a) 1 mg DNPH and 0.1 ml H_3PO_4/ml TEP; (b) air-flow of 20 ml/min and 0.1 ml H_3PO_4/ml TEP; (c) air flow of 20 ml/min and 1 mg DNPH/ml TEP.

for DNPH and phosphoric acid (H_3PO_4), which together constitute the reaction solution. The use of TEP as the injection solvent has no effect on the peak shape.

2.1.1. HPLC analysis

HPLC analysis is performed using a Bischoff (Leonberg, Germany) HPLC column (250×4.6 mm I.D.), packed with Spherisorb ODS II (3 μm particles) and a Brownlee RP-18 precolumn. The chromatographic conditions were as follows: 0.5 ml/min of CH_3CN–water (70:30, v/v), 10 μl test loop, about 100 bar, UV monitor at 360 nm.

2.1.2. Splitting device

A splitting device (see Fig. 2) was used to assess the influence of the sample air flow-rate and the DNPH and H_3PO_4 concentrations on the derivatization yield. Several carbonyl compounds were vapourized from an acetonitrile solution into an (ozone free) air flow, which was split in a controlled way between a Sep-Pak cartridge and the new mini-impinger for simultaneous concentration measurements. The splitting ratio of the air flows (1500 and 50 ml/min) was adjusted to be the same as the ratio of the solvent volume (3 ml) needed to elute the hydrazones from the solid-phase extraction cartridge and the volume of the reaction solution in the mini-impinger (0.1 ml). Therefore, the same hydrazone concentrations and amounts of hydrazone should be found in both liquids, if equal amounts of the two liquids are used for analysis. Air samples were collected over periods of 20 min. Based on long-term experience [7], at the flow-rate of 1500 ml/min, the Sep-Pak values can be assumed to correspond to a derivatization yield >95% and are taken as reference values (note that acrolein was not among the test compounds).

2.1.3. Blank values

Blank values are a critical feature of the DNPH method. The three components of the reaction solution, i.e. DNPH, TEP and phosphoric acid, contain carbonyl compound impurities which, after mixing, react with the corresponding derivatives. These are stable and can be subtracted easily from the samples' values. Unfortunately, there are other impurities in the components of the reaction solution (precursors), which form increasing quantities of carbonyl compounds and therefore increasing quantities of derivatives, only after mixing DNPH and phosphoric acid. This background value, which grows with time, cannot be subtracted easily.

For this reason, two solutions, DNPH in TEP and phosphoric acid in TEP, are prepared. Each solution contains small, but stable, traces of carbonyl compounds. We checked both solutions over weeks, without finding any increase in blanks. These solu-

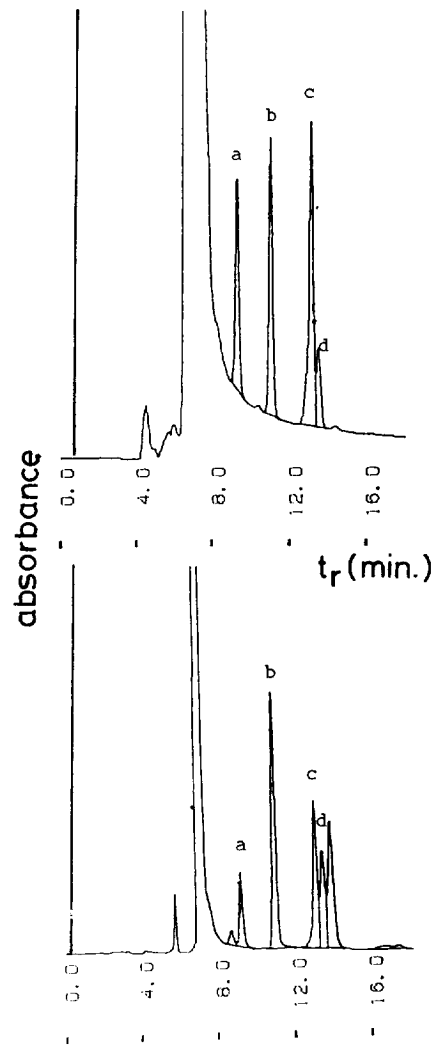

Fig. 4. Comparison of an air sample (spiked with acrolein) derivatized in the liquid phase (impinger), above, and on the solid phase (SEP-Pak/DNPH cartridges), below. Peaks: a= formaldehyde, b=acetaldehyde, c=acrolein and d=acetone.

tions are injected separately by the autoinjector software into the mini-impinger and are mixed by bubbling with air. The reaction of the precursors to hydrazones is so slow that the background resulting from mixing of the reaction solution and analysis of an air sample is negligible.

3. Results and discussion

3.1. Influence of the sample air flow-rate and the concentrations of DNPH and H_3PO_4 on the derivatization yield

Fig. 3 shows the dependence of the derivatization yield on these parameters. Quantitative sampling of formaldehyde and glutaraldehyde was performed previously at low DNPH and acid concentrations and with high air flows. To derivatize more than 90% of acetaldehyde however, (a) the air flow should not exceed 10 ml/min, (b) the DNPH concentration should be >0.9 mg/ml in TEP and (c) the H_3PO_4 concentration should be >50 μl/ml in TEP.

The speed of derivatization of ketones is still lower. To quantitatively trap acetone and methyl ethyl ketone (MEK), the air flow should not exceed 5 ml/min with a DNPH concentration of 1 mg/ml and a H_3PO_4 concentration of 100 μl/ml, in TEP.

3.1.1. Blank values

Blank values are negligible with the exception of formaldehyde, acetaldehyde and acetone. However, for formaldehyde, acetaldehyde and acetone, stable values of 2.4, 4.5 and 6.7 ng/100 μl, respectivley, could be achieved. Automatic correction of these blank values is possible.

3.1.2. Liquid phase derivatization in impingers

Liquid phase derivatization in impingers reduces problems with acrolein that are encountered using the dry phase derivatization on Sep-Pak plus DNPH. Fig. 4 shows the results obtained for an indoor air

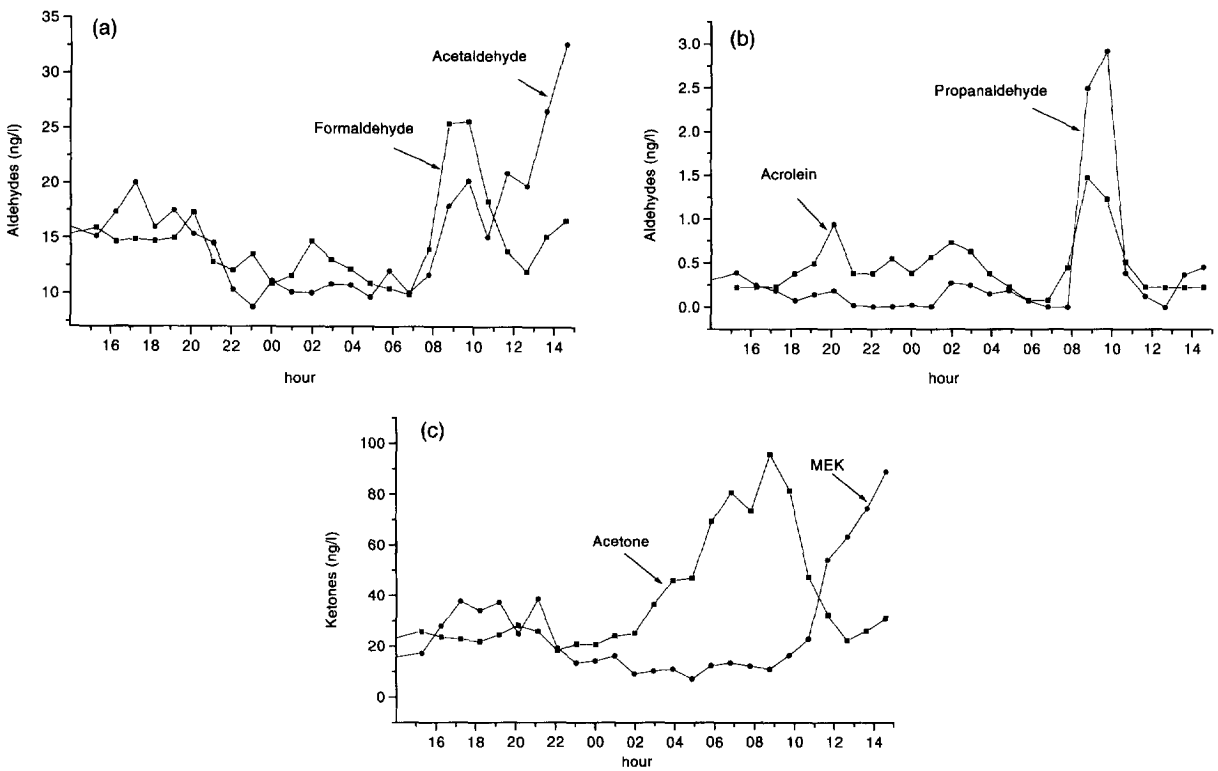

Fig. 5. Automatic monitoring of aldehydes (a) and (b) and ketones (c) in urban air over 24 h.

sample spiked with acrolein and split between a cartridge and the mini-impinger using the splitting device described above. Whereas the methods give comparable results if acrolein is not present, the differences shown in Fig. 4 suggest that dry derivatization leads to a loss of acrolein and the appearance of new compounds.

3.2. Use of method for monitoring urban air.

In order to test the performance of the system, a series of measurements were carried out in Milan near the municipal monitoring station for airborne pollutants. Samples were collected at 44 min intervals, at a distance of 5 m from a street with intense traffic and at a height of 2 m above street level. The results obtained over 24 h are shown in Fig. 5.

From Fig. 5a–b shows clearly that the aldehyde concentration pattern is caused by the morning rush-hour traffic. Only the concentration of acetaldehyde seems to be attributable to other sources, as it continues to increase after 10:00 h. The behaviour of acetone is completely different from that of the other carbonyl compounds. The relatively low daily concentration of 20 ng/l increases at night, to 95 ng/l, and decreases rapidly in the morning, while the MEK pattern seems completely independent of traffic.

This shows that the new instrument allows the automatic detection of environmental concentrations of aldehydes down to about 0.2 ng/l.

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