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Short Communication

Development of a method for simultaneous determinations of nitrogen oxides, aldehydes and ketones in air samples

Andreas H.J. Grömping, Uwe Karst and Karl Cammann*

Lehrstuhl für Analytische Chemie, Anorganisch-Chemisches Institut, Westfälische-Wilhelms-Universität Münster, W-4400 Münster (Germany)

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ABSTRACT

Nitrogen oxides, aldehydes and ketones are important environmental toxins which frequently occur together (*e.g.* in automobile exhaust and in tobacco smoke). In this paper a convenient method for a simultaneous analysis of nitrogen oxides, aldehydes and ketones in air is presented for the first time. This method is based on the well-established and practical 2,4-dinitrophenylhydrazine method for the determination of aldehydes and ketones. Detection limits for the determination of nitrogen oxides were 10 ppb (v/v) using solid sorbents, 50 ppb (v/v) using impingers (sampling at 0.8 l/min for 15 min), and 150 ppb (v/v) using passive sampling devices (sampling for 4 h).

INTRODUCTION

Nitrogen dioxide as well as aldehydes and ketones often occur together in gaseous samples, *e.g.* automobile exhaust [1,2], gas-stove exhaust [3], and tobacco smoke [2,4]. Both are formed as combustion byproducts underlining the necessity of a method for their simultaneous determination. Recognition of their toxicity has stimulated a rapid development of new analytical techniques for these compounds.

The classical methods for the analysis of formaldehyde, such as the pararosaniline (PRA) method [5], the chromotropic acid (CTA) method [6] and the 3-methyl-2-benzthiazolonhydrazine (MBTH) method [7], are based on colorimetric techniques. Since some of the methods suffer from interferences, different methods using chromatographic separations have been proposed [8–10]. In recent years the 2,4-dinitrophenylhydrazine (DNPH) method has become the most important method for the analysis of aldehydes and ketones [11–17], since a large number of these compounds can be determined simultaneously.

Nitrogen oxides are determined with the Saltzman technique (see ref. 18) or the triethanolamine method [19], both of which are based on colorimetric techniques. As the simultaneous determination of nitrogen oxides, aldehydes and ketones is very important, Kaul-

* Corresponding author.

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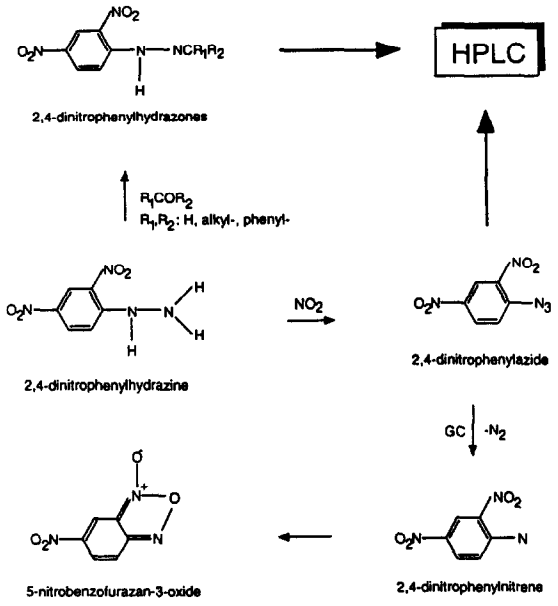

Fig. 1. Basic reactions mentioned in this paper.

bach [20] proposed a simultaneous determination of these compounds using two different colorimetric methods, the Saltzman method for the detection of nitrogen dioxide and the PRA method for the determination of formaldehyde. Unfortunately, two analytical procedures have to be performed to determine only formaldehyde and nitrogen dioxide which makes this method very time consuming.

The interferences of nitrogen dioxide with the determination of aldehydes and ketones using the DNPH method have been described recently [13]. In this paper the development of the first fast and convenient method for the simultaneous determination of aldehydes, ketones, and nitrogen oxides in gaseous samples using only one reagent [21] based on their reactions with DNPH (see Fig. 1) is described.

EXPERIMENTAL

Reagents

Formaldehyde (37%, w/v), methanol, hydrochloric acid and sulphuric acid were Merck analytical grade. Deionized, twice distilled water and methanol purified by distillation over a 1-m column filled with Raschig rings were used as eluents for HPLC. Acetonitrile (liquid chromatography grade) was purchased from Merck. Nitrogen monoxide (99.8% pure) and nitrogen dioxide (98% pure) were purchased from Messer-Griesheim.

Apparatus

Portable air sampling pumps, Models S 2500 and Alpha 1 from DuPont were used. The HPLC system used consisted of an Alltech Model 100 A pump or a Knauer HPLC pump and a Rheodyne Model 7125 injection valve or a Rheodyne Model 7126 pneumatic injection valve, both with 20-μl sample loops. Detectors used were a Zeiss Model PMQ 3 UV–visible absorbance detector with a Uvicon 6-μl cell or a Knauer UV–visible absorbance detector. As detection wavelength either 300 nm (absorbance maximum of dinitrophenylazide) or 345 nm (absorbance maximum of dinitrophenylhydrazones) was chosen. A Machery–Nagel Poligosil C_{18} (5 μm, 20 × 4 mm) guard column and a Machery–Nagel Poligosil C_{18} (5 μm, 250 × 4 mm) analytical column were used. Injections were done via a Knauer injection loop of 20 μl volume.

For the identification of the different formaldehyde derivatives a GC–MS system was used, which consisted of a Hewlett-Packard Model 5890 series II gas chromatograph, a Hewlett-Packard Ultra 2 column (50 m × 0.32 mm), and a Hewlett-Packard Model 5970 mass-selective detector.

Chromatographic separation

Karst *et al.* [13] solved the problem of the separation of dinitrophenylazide and formaldehyde–dinitrophenylhydrazone which have a similar chromatographic behavior using a complex gradient for baseline separation. We used an isocratic solvent system to separate the two compounds. Typically, the chromatographic separation was carried out at a flow-rate of 1.0 ml/min, with acetonitrile–water (60:40) as eluent.

Formaldehyde standard solution

The formaldehyde standard solution was prepared by diluting 1 ml of commercial formaldehyde solution (37%, w/v) to 100 ml with purified water. A final concentration of 0.124

mol/l was determined according to the method used by Harris [22].

Air sampling

Impingers were filled with solutions of DNPH in organic solvents. Using a personal sampling pump, an air stream of 0.8 l/min was drawn through the impinger. A trap filled with methanol–dry ice prevented the solvents from vaporizing into the pump. Sampling of candle smoke was carried out as described in a previous paper [23].

Sampling with solid sorbents coated with DNPH was investigated as well. Coating of Chromosorb P with DNPH, preparation of the sampling tubes, and desorption utilized the procedure of Binding *et al.* [24] with the modifications described below. This technique was applied to the sampling of nitrogen oxides as well as aldehydes and ketones. In order to reduce the blank, the DNPH was recrystallized twice from 6 *M* hydrochloric acid and then twice from acetonitrile. Next, 5 g DNPH were suspended in 20 ml acetonitrile (instead of dissolving in dimethylformamide [24]) and 6 g Chromosorb P added. The suspension was treated for 5 min in an ultrasonic bath. The next modification of the procedure of Binding *et al.* [24] was to remove all acetonitrile with a rotavapor without any remaining solvent. This solid sorbent was used to prepare sampling tubes as described below.

Finally, the possibilities of diffusive sampling were studied. For this purpose diffusive samplers as described by Levin *et al.* [25] were used. Elution was done by shaking the filter for a few minutes with 5 ml acetonitrile in a 10-ml glass vial. In each case, 20 μl of the absorbing or desorbing solution were analyzed after sampling by means of HPLC.

Synthesis of the hydrazone standards

A solution of 5 m*M* 2,4-dinitrophenylhydrazine in 15 ml of 40% (w/v) sulphuric acid was diluted with 25 ml ethanol. To this solution 5 m*M* of the carbonyl compound were added as 10% (w/v) solution. The precipitate was washed with water and recrystallized from ethanol. Characterization of the hydrazones was performed using spectroscopic methods and mass spectrometry.

Synthesis of the azide standard

Gaseous nitrogen dioxide was passed into an acidified (0.1 ml of concentrated hydrochloric acid) solution of DNPH in 60 ml acetonitrile. The color of the solution changed from orange to yellow. The progress of the reaction was monitored by HPLC. The solvent was removed in vacuo, and the residue was dried and characterized using spectroscopic methods and MS [13].

RESULTS AND DISCUSSION

Identification of the reaction product between nitrogen oxides and DNPH

The identification of the reaction products of nitrogen oxides and DNPH has been described in a previous paper [13]. The main reaction product could be identified as 2,4-dinitrophenylazide (see Fig. 1); an important by-product is 2,4-dinitrochlorobenzene. Spectroscopic data of the 24,-dinitrophenylazide: IR (KBr): 3050 (s, C–H), 2100 (s, C–N), 1600 9s), 1500, (s), 1320 (s), 1270 (s), 905 (m), 825 (m). MS (GC) (see bottom of Fig. 1) 181 (100%) [M^+], 165 (12%) [M − O], 105 (9%), 104 (10%), 77 (27%), 75 (47%), 74 (37%). UV (methanol): maximum at 300 nm. ^{1}H NMR (C^2HCl_3): 8.82 (s, 1H), 8.47 (d, 1H), 7.49 (d, 1H).

Air sampling with impingers

Nitrogen dioxide was diluted in a gas-tight flask (volume 1 l). This was connected to two impingers in series with a personal air sampling pump. The impingers were filled with a solution of 1.5 mg DNPH in 2.5 ml acetonitrile. Because of the hydrophilicity of NO_2, for a better solubility the solution was diluted with 1 ml water and acidified with 0.1 ml 1 *M* HCl to allow an efficient sampling of nitrogen dioxide. Finally, an air stream of 0.5 l/min was drawn through the gas-tight flask and the impingers for 15 min.

To study the reproducibility, ten 8-l samples (each corresponding to 0.5 ml pure NO_2) were taken. The data have a standard deviation of 6%. This corresponds to a deviation of 14% at

the 95% confidence level. The correlation between the peak height of dinitrophenylazide and the quantity of NO_2 added was studied injecting eight different amounts of NO_2 (0–1.0 ml) into the gas-tight apparatus. The linear regression has a correlation coefficient of 0.998.

Air sampling of aldehydes and ketones is usually done without addition of water to the absorbing solution. To work under the same conditions for nitrogen dioxide measurements, a solution of 1.5 mg DNPH in 2.5 ml acetonitrile and 0.1 ml HCl was used without addition of water. Again a linear correlation was observed with the same correlation coefficient. In blank measurements no dinitrophenylazide could be detected. Therefore, the limit of detection (LOD) for NO_2 was determined corresponding to a signal-to-noise ratio of 3:1 to be 50 ppb (v/v) for a 7.5-l sample.

Nitric oxide was detected by oxidation to nitrogen dioxide using potassium dichromate. A tube (100 × 4 mm) was filled with 200 mg potassium dichromate and acidified with 2–3 drops of concentrated phosphoric acid (see Fig. 2). This tube was inserted in line before the impingers. Different quantities of nitric oxide were then drawn through this oxidation layer and the impinger as was done for the nitrogen dioxide. A linear correlation between peak height of dinitrophenylazide and addition of nitric oxide was observed, injecting seven different volumes of NO (0–0.7 ml) into the apparatus. A correlation coefficient of 0.996 was obtained for the linear diagram of signal *vs.* volume. Thus, it is possible to determine the sum of nitric oxide and nitrogen dioxide (NO_x) by connecting the impinger to a tube containing an oxidation layer of acidified $K_2Cr_2O_7$. For the determination of nitric oxide, the difference of a measurement with an oxidation layer and without an oxidation layer can be determined. Because potassium dichromate oxidizes alcohols to aldehydes and ketones [26], formaldehyde and higher homologues cannot be analyzed with this method.

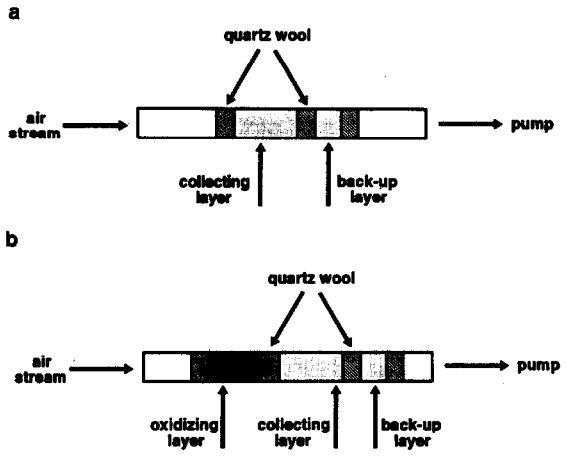

Fig. 2. Sampling with solid sorbents. (a) Determination of nitrogen oxide, aldehydes and ketones; (b) determination of the sum of nitrogen dioxide and nitric oxide (NO_x).

Air sampling with solid sorbents

Using solid sorbent tubes, prepared according to Binding *et al.* [24], nitrogen dioxide could not be detected. The reproducibility was very poor and linear calibration curves could not be obtained. In order to allow an efficient sampling of the hydrophilic nitrogen dioxide, 0.5 ml demineralized water were added to 2.5 g of the dry solid sorbent. Once again, different quantities of nitrogen dioxide were drawn through tubes filled with this solid sorbent. A linear calibration curve was obtained with a correlation coefficient of 0.997 for more than three orders of magnitude (see Fig. 3a). Addition of 0.2 μl pure NO_2 (diluted with nitrogen to 8 l) corresponds to an LOD of 10 ppb (v/v) NO_2.

For sampling of aldehydes and ketones these sampling phases are used without addition of water. To study the possibilities for the determination of NO_2 of this dry sampling phase another calibration curve was taken (see Fig. 3b). In the lower concentration range its linearity is better than that of the wet sampling phase ($r > 0.999$). But its capacity is restricted so that sampling above a concentration of 10 ppm (v/v) is not recommended.

Using the procedure described above, the sampling of NO with solid sorbents was tested as well. For this purpose the tubes were filled with an oxidation layer of 200 mg potassium dichromate acidified with 2–3 drops of concentrated phosphoric acid in front of the sampling layer. The calibration curve is linear with a correlation coefficient of 0.994. Fig. 4 shows the difference

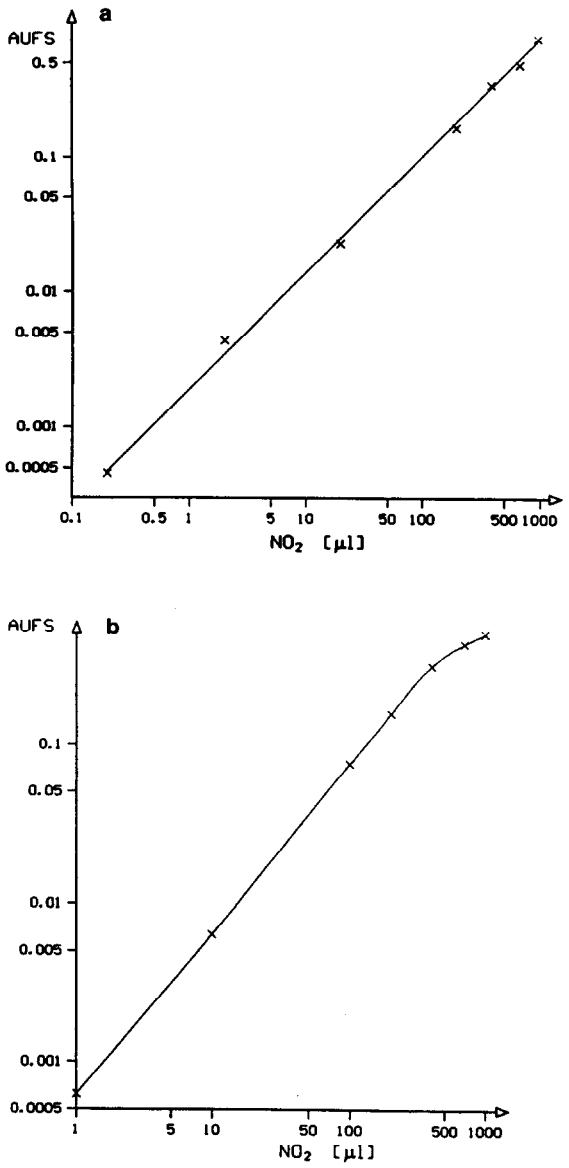

Fig. 3. Correlation between peak height of dinitrophenylazide and addition of NO_2; sampling with solid sorbents. (a) Wet sampling phase, (b) dry sampling phase. Column: Polygosil C_{18} (5 μm, 250 × 4 mm); flow-rate: 1.0 ml/min; eluent: acetonitrile–water (60:40); detection wavelength: 300 nm; injection volume: 20 μl.

between sampling with and without an oxidation layer. Because of different alcohols which had been oxidized (see Fig. 4b) to aldehydes/ketones, several peaks besides the dinitrophenylazide peak emerged.

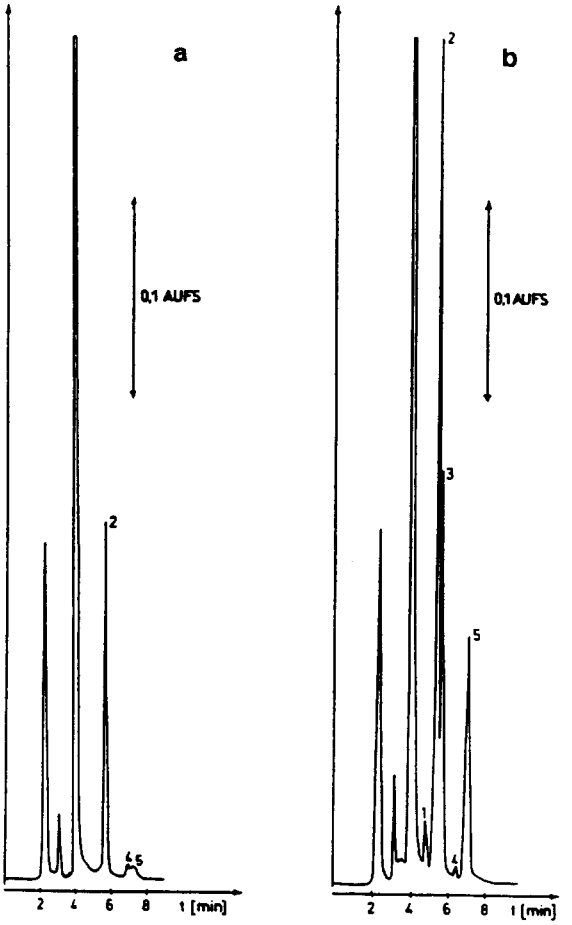

Fig. 4. Chromatogram of automobile exhaust (a) without and (b) with oxidation layer. Column: Polygosil C_{18} (5 μm, 250 × 4 mm); flow-rate: 1.0 ml/min; eluent: acetonitrile–water (60:40); detection wavelength: 345 nm; injection volume: 20 μl. Peaks: 1 = dinitrophenylazide; 2 = formaldehyde–dinitrophenylhydrazone; 3 = unknown; 4 = acetaldehyde–dinitrophenylhydrazone; 5 = acrolein–dinitrophenylhydrazone.

Air sampling with passive samplers

For measurements in working areas, passive samplers are often used. Therefore, the suitability of passive samplers based on the reaction with DNPH was studied for the determination of nitrogen dioxide. A passive sampler was placed in the middle of a 144-l plexiglas box. Five different volumes of nitrogen dioxide (0–1.0 ml) were injected through a septum. A linear calibration curve with a correlation coefficient of 0.999 was obtained. The LOD corresponds to

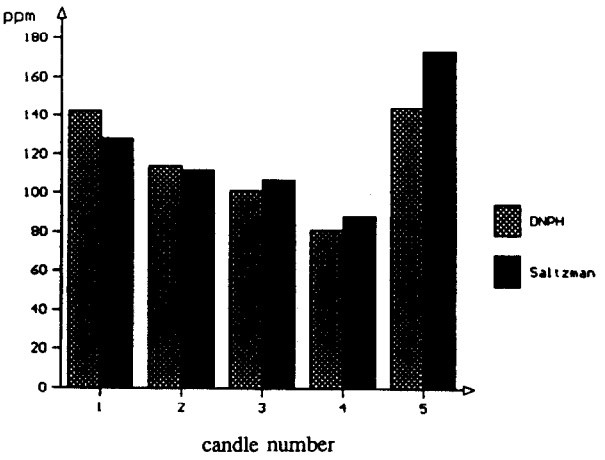

Fig. 5. Comparison of DNPH and Saltzman methods by analyzing smoke of different candles. Sampling with impingers; DNPH method: column: Polygosil C_{18} (5 μm, 250 × 4 mm); flow-rate: 1.0 ml/min; eluent: acetonitrile–water (60:40); detection wavelength: 300 nm; injection volume: 20 μl.

150 ppb (v/v) NO_2 for a signal-to-noise ratio of 3:1.

Comparison to the Saltzman method

A widely used procedure for the determination of nitrogen oxides in air is the collection of a sample in an impinger filled with water followed by spectrophotometric determination using the Saltzman method [27,28]. In order to compare the methods, the DNPH impinger techniques and the Saltzman method were applied to the analysis of candle smoke. Similar values were obtained with both methods (see Fig. 5). The observed deviations were not greater than those observed with one single method during several repetitive measurements. According to Wiederholt *et al.* [28] the LOD for the Saltzman method is 200 ppb (v/v). Since an LOD of 50 ppb (v/v) for the impinger techniques and an LOD of 10 ppb (v/v) with solid sorbents was obtained in this study the detection of nitrogen oxides was improved by at least a factor of 4.

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