N-Methyl-4-hydrazino-7-nitrobenzofurazan as a New Reagent for Air Monitoring of Aldehydes and Ketones

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The synthesis of *N*-methyl-4-hydrazino-7-nitrobenzofurazan (MNBDH) and its application as a new reagent for the determination of aldehydes and ketones are described. MNBDH reacts with carbonyl compounds in acidic media to the corresponding MNBD-hydrazones. In contrast to the established reagent 2,4-dinitrophenylhydrazine (DNPH), MNBDH is oxidized by both ozone and nitrogen dioxide quantitatively to only one product, *N*-methyl-4-amino-7-nitrobenzofurazan (MNBDA). This can easily be separated from the hydrazones of lower aldehydes by means of HPLC. Due to larger molar absorptivities and absorption maxima at wavelengths over 470 nm, selectivity is higher and limits of detection are lower for the new reagent compared to DNPH. MNBDH reacts slightly faster than DNPH with carbonyl compounds and significantly faster than other N-alkylated hydrazine reagents.

Air monitoring of aldehydes and ketones frequently employs derivatization with an aromatic hydrazine reagent. Stable hydrazones are formed, which are separated by HPLC and detected by UV/visible spectroscopy. Among these reagents, 2,4-dinitrophenylhydrazine (DNPH) is the most widely used. Several national and international standardization bodies suggest this reagent for the analysis of aldehydes and ketones in gaseous samples. Sampling of carbonyl compounds in air can be performed using solutions of DNPH in impingers[1,2] or solid sorbents coated with DNPH, including test tubes for pumped sampling[3] and passive sampling devices.[4,5] However, problems with respect to the determination of aldehydes and ketones in complex matrixes were described recently. Oxidants such as nitrogen dioxide or ozone frequently occur in conjunction with carbonyl compounds, e.g., in ambient air or in automobile exhausts.[2,6] The presence of these substances[7−9] causes problems regarding an exact deter-mination of aldehydes and ketones in air samples due to oxidative decomposition of the reagent and the hydrazones, respectively. In case of ozone, several products are formed, but only some of those have been identified so far.[10] The reaction of DNPH with nitrogen dioxide leads to 2,4-dinitrophenyl azide (DNPA). The above-mentioned problems are caused by coelution of these reaction products with the hydrazones in chromatography.

An approach to overcome this problem was described in ref 11. *N*-Methyl-2,4-dinitrophenylhydrazine (MDNPH) was used as a new derivatization reagent with reduced interferences, because the reaction of MDNPH with both nitrogen dioxide and ozone led to only one defined product, *N*-methyl-2,4-dinitroaniline (MDNA). This compound could be separated from the hydrazones by liquid chromatography. However, a major disadvantage of this new reagent is its reduced reactivity compared to that of DNPH.

For this reason, a new hydrazine reagent should be developed which combines the above-mentioned advantages concerning the more defined reactivity toward nitrogen dioxide and ozone with a fast derivatization reaction known from the DNPH method.

EXPERIMENTAL SECTION

Chemicals. All chemicals were purchased from Aldrich Chemie (Steinheim, Germany) in the highest quality available. Acids were Merck (Darmstadt, Germany) analytical grade. Triethylamine was from Fluka (Neu-Ulm, Germany). Acetonitrile for HPLC was Merck gradient grade.

Instrumentation for Product Identification. ^{1}H NMR measurements were performed with an AC 200 spectrometer (200.13 MHz) from Bruker (Bremen, Germany). The solvent for all NMR measurements was CDCl₃. All peaks are given as δ in ppm. FT-IR spectral information was obtained for the products in KBr pellets by using an IFS48 instrument from Bruker. Mass spectra were recorded on a MAT 212 from Varian. Elementary analyses were performed with a Heraeus (Hanau, Germany) CHN-O-Rapid

(1) Grosjean, D.; Fung, K. *Anal. Chem.* **1982**, *54*, 1221−1224.

(2) Lipari, F.; Swarin, S. J. *J. Chromatogr.* **1982**, *247*, 297−306.

(3) Beasley, R. H.; Hoffmann, C. E.; Rueppel, M. L.; Worley, J. W. *Anal. Chem.* **1980**, *52*, 1110−1114.

(4) Levin, J. O.; Andersson, K.; Lindahl, R.; Nilson, C.-A. *Anal. Chem.* **1985**, *57*, 1032−1035.

(5) Levin, J. O.; Lindahl, R. *Analyst* **1994**, *119*, 79−83.

(6) Swarin, S. J.; Lipari, F. *J. Liq. Chromatogr.* **1983**, *6*, 425−444.

(7) Karst, U.; Binding, N.; Cammann, K.; Witting, U. *Fresenius' J. Anal. Chem.* **1993**, *345*, 48−52.

(8) Arnts, R. R.; Tejada, S. B. *Environ. Sci. Technol.* **1989**, *23*, 1428−1430.

(9) Smith, D. F.; Kleindienst, T. U.; Hudgens, E. E. *J. Chromatogr.* **1989**, *483*, 431−436.

(10) Achatz, S. Diploma Thesis, Technical University of Munich, 1996.

(11) Büldt, A.; Karst, U. *Anal. Chem.* **1997**, *69*, 3617−3622.

instrument. The analytical data for the reagent and its derivatives are provided as Supporting Information.

Syntheses. (1) *N*-Methyl-4-hydrazino-7-nitrobenzofurazan (MNBDH). A 2.24 mL sample of methylhydrazine (0.04 mol) in 100 mL of methanol was added dropwise to a solution of 1 g (0.005 mol) of 4-chloro-7-nitrobenzofurazan in 80 mL of chloroform. After being heated at reflux for 20 min, the solution was cooled, and MNBDH precipitated as a red crystalline material. The precipitate was filtered off and washed with methanol. The yield was 48%. The purity of the product was examined by means of HPLC. The product was fully characterized by means of ^{1}H NMR, IR, UV, MS, and elemental analysis. These data are provided as Supporting Information.

(2) Aldehyde and Ketone MNBD-Hydrazones. The derivatives were prepared according to a procedure published by Behforouz et al.[12] for the synthesis of DNPH derivatives. A 100 mg sample of *N*-methyl-4-hydrazino-7-nitrobenzofurazan (4.8×10^{-4} mol) was dissolved in 0.7 mL of water, 0.5 mL of sulfuric acid, and 2.5 mL of 95% ethanol. A 50% molar excess of the aldehyde or ketone (7.2×10^{-4} mol) was added. The hydrazones precipitated as reddish crystalline material. The precipitate was filtered off and washed first with a 5 mass % aqueous solution of sodium bicarbonate until no further development of carbon dioxide was observed and then with distilled water. If necessary, the products were recrystallized from ethanol. Yields ranged from 70% to >95% depending on the degree of purification required for the individual hydrazones. The reaction products were fully characterized by means of ^{1}H NMR, IR, UV, MS, and elemental analysis. These data are available as Supporting Information.

(3) *N*-Methyl-4-amino-7-nitrobenzofurazan (MNBDA). (a) Synthesis by Reaction with Nitrogen Dioxide or Ozone. A 100 mg sample of *N*-methyl-4-hydrazino-7-nitrobenzofurazan (4.7×10^{-4} mol) was dissolved in 2.5 mL of distilled water, 0.8 mL of sulfuric acid, and 0.3 mL of acetonitrile. Nitrogen dioxide gas was produced by adding 10 mL of concentrated nitric acid to 2 g of copper wire and transported into the reagent solution by nitrogen carrier gas. Alternatively, ozone from an ozone generator was transported into the reagent solution by oxygen carrier gas. After the reaction, nitrogen was blown into the solutions to remove unreacted oxidant. The precipitate was filtered off and washed with sodium bicarbonate solution (5%) as well as with distilled water.

(b) Synthesis According to a Procedure Published by Clusius and Schwarzenbach.[13] A 200 mg sample of *N*-methyl-4-hydrazino-7-nitrobenzofurazan (9.4×10^{-4} mol) was dissolved in 30 mL of ethanol and 5 mL of concentrated hydrochloric acid. While the mixture was cooled with ice, a solution of 70 mg of sodium nitrite (1×10^{-3} mol) in 5 mL of distilled water was added. After the reaction solution was allowed to stand for 0.5 h at room temperature, 50 mL of distilled water was added. Afterward, the solution was left at room temperature again for 1 h. The product precipitated as a yellow material. This was filtered off and washed with ice-cold water. The yield was 67%. The reaction product was

fully characterized in the same way as MNBDH and its hydrazones. These data are available as Supporting Information.

Preparation of the MNBDH Sampling Tubes. A 8×10^{-3} mol/L MNBDH solution was prepared by adding 100 mg of MNBDH to 2 mL of concentrated sulfuric acid in 60 mL of acetonitrile. The used sampling tubes (cartridge lengths 7.4 cm), filled with 350 mg of silica gel (chromatographic quality; particle size $150-250$ μm, $60/100$ mesh), were purchased as a special order (part no. 8-54122) from Supelco (Deisenhofen, Germany). These tubes were conditioned first with 3 mL of acetonitrile. Afterward, the silica gel was coated with MNBDH by allowing 3 mL of the reagent solution to seep through the tubes. Subsequently, the material was dried in a nitrogen stream.

Air-Sampling Procedure and Analysis. Air sampling was performed using a personal air sampler pump (Buck I. H. Pump) from A. P. Buck (Orlando, FL) with the corresponding calibrator also from A. P. Buck. For all measurements, a collecting tube and a controlling tube were connected in series to identify incomplete recovery on the collecting tube. The sampling rate was 1 L/min. Sampling of the car exhaust was performed by locating the collecting tube directly at the end of the exhaust pipe of the car for 1 min. During the sampling of the air of the disinfected room, the tubes were located in the middle of the room for 2 min. The simulated air sampling with a defined amount of the analyte was performed by pipetting 50 μL of a 5.8×10^{-3} mol/L solution of formaldehyde in acetonitrile onto quartz wool that was placed in front of the collecting layer. Afterward, a constant air stream was pumped through the tube for 4 min. After sampling, the tubes were eluted with 10 mL of a 1% solution of sulfuric acid in acetonitrile. A 10 μL portion of this solution was injected into the HPLC system.

Photometer. An HP 8453 diode array spectrophotometer (Hewlett-Packard, Waldbronn, Germany) with HP Chem Station 845x-biochemical UV/VIS-system software was used.

UV/Visible Absorption Measurements. All UV/visible measurements were performed in the concentration range from 8.1 $\times 10^{-5}$ to 5.3×10^{-5} mol/L for MNBDH, MNBDA, and the hydrazones in acetonitrile. The spectra were recorded in the range from 290 to 600 nm.

Spectrofluorophotometer. An RF-5301 PC spectrofluorophotometer (Shimadzu, Duisburg, Germany) with software version 1.10 was used.

HPLC Instumentation and Analysis. A high-performance liquid chromatograph consisting of the following components was used: two LC-10AS pumps (Shimadzu, Duisburg, Germany), SPD-M10Avp diode array detector (Shimadzu), SIL-10A autosampler (Shimadzu), Class LC-10 version 1.6 software (Shimadzu), and CBM-10A controller unit (Shimadzu). The injection volume was 10 μL. The column material was Merck LiChroSpher RP-18 (Merck, Darmstadt, Germany) in ChromCart cartridges (Macherey-Nagel, Düren, Germany): particle size 5 μm; pore size 100 Å; column dimensions 250 mm $\times$ 3 mm; guard column 8 mm $\times$ 3 mm.

For separation, binary gradients consisting of acetonitrile and a mixture of water/triethylamine/acetic acid (preparation: 500

(12) Behforouz, M.; Bolan. J. L.; Flynt, M. S. *J. Org. Chem.* **1985**, *50*, 1186−1189.
(13) Clusius, K.; Schwarzenbach, K. *Helv. Chim. Acta* **1958**, *41*, 1413−1416.

Table 1. UV/Visible Spectroscopic and Chromatographic Data for a Series of MNBD-Hydrazones, MNBDH, and MNBDA

| MNBD-hydrazone of	$10^{-3}\epsilon$ (474 nm)	$10^{-3}\epsilon$ (514 nm)	ϵ(474 nm)/ϵ(514 nm)	A(474 nm)/A(514 nm)	λ_{max} (nm)	$10^{-3}\epsilon(\lambda_{max})$
formaldehyde	24.7	6.48	3.9	2.5	474	24.7
acetaldehyde	25.7	20.0	1.3	1.0	488	29.0
propanal	25.0	20.3	1.2	1.0	492	28.5
acetone	18.4	21.3	0.9	0.8	500	24.6
acrolein	23.0	25.6	0.9	0.7	499	28.8
butanal	24.0	19.9	1.2	1.0	492	27.7
2-butanone	21.2	25.2	0.8	0.7	501	28.6
crotonaldehyde	19.9	31.6	0.6	0.6	511	31.8
pentanal	27.8	23.6	1.2	1.1	492	31.7
hexanal	24.9	21.3	1.2	1.1	492	28.9
heptanal	25.3	21.7	1.2	1.1	493	29.5
octanal	25.2	21.6	1.2	1.2	494	27.6
nonanal	23.4	20.5	1.2	1.2	493	27.3
decanal	26.3	22.5	1.2	1.2	493	30.7
glutaraldehyde	38.2	32.2	1.2	1.2	492	44.2
benzaldehyde	24.5	36.1	0.7	0.5	508	33.9
p-tolualdehyde	20.2	35.2	0.6	0.5	514	34.4
MNBDH	20.2	11.1	1.8	1.1	486	21.6
MNBDA	20.0	1.0	20.0	10.6	459	23.3

mL of water with 2415 μL of triethylamine and 975 μL of acetic acid, pH $\approx$ 7.5) were chosen with the following profile:
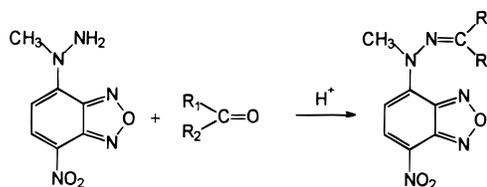
gradient A

time (min)	0	1.5	13.5	17.5	18.5	20.5 (stop)
c (CH₃CN) (%)	45	45	100	100	45	45
flow (mL/min) 0.62						

gradient B

time (min)	0	1.5	8.5	10.5	11.5	12.5 (stop)
c (CH₃CN) (%)	45	45	100	100	45	45
flow (mL/min) 0.62						
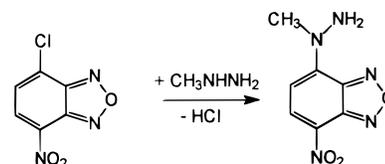
The carbonyl compounds react with MNBDH in the presence of sulfuric acid, forming the corresponding hydrazones:

with R_1, R_2 = -H, -Alkyl, -Alkenyl, -Aryl

RESULTS

The derivatization of carbonyl compounds with 4-hydrazino-7-nitrobenzofurazan[14,15] is known from the literature. Although a UV/visible detection at significantly longer wavelengths compared to those of the DNPH method is possible, the reagent has yet found only limited use. This is, on one hand, due to the formation of a hydrazine adduct of the reagent during synthesis. On the other hand, only the analysis of longer-chained aliphatic aldehydes starting with C_3 has been described in the literature and not the analysis of the most important aldehydes, especially formaldehyde.

To use the excellent chromophoric properties of these compounds, the N-methylated hydrazine appeared to be an attractive alternative. N-Methyl-4-hydrazino-7-nitrobenzofurazan (MNBDH) was synthesized in a nucleophilic substitution reaction of N-methylhydrazine with 4-chloro-7-nitrobenzofurazan:

(14) Gübitz, G.; Wintersteiger, R.; Frei, R. W. *J. Liq. Chromatogr.* **1984**, *7*, 839–854.
(15) Uzu, S.; Kanda, S.; Imai, K.; Nakashima, K.; Akiyama, S. *Analyst* **1990**, *115*, 1477–1482.

Neither the reagent nor any of the respective hydrazones have been described in the literature before and are now applied to the determination of aldehydes and ketones in air samples. The hydrazones are separated by means of high-performance liquid chromatography (HPLC) and detected by UV/visible spectroscopy at wavelengths which depend on the absorption maxima of the relevant hydrazones. In Table 1, the UV/visible spectroscopic data measured photometrically are shown for MNBDH and a series of hydrazones. Compared to the spectra of the DNPH derivatives, a shift of the absorption maxima of 100–150 nm is observed. This large shift may lead to higher selectivity of the new method especially in the presence of colored matrix constituents. Furthermore, the molar absorptivities of the derivatives are higher compared to those of the derivatives of DNPH, thus resulting in lower limits of detection. Table 2 shows the comparison of the detection limits of several MNBD-hydrazones with those of DNP-hydrazones that have been obtained by means of HPLC with UV/visible detection under identical elution conditions but using the respective absorption maxima for quantification. A fluorimetric detection after HPLC separation is possible for the MNBD-

Table 2. Comparison of the Detection Limits of Several MNBD-Hydrazones with Those of DNP-Hydrazones

	detection limit (10^{-8} mol/L)			detection limit (10^{-8} mol/L)	
	using DNPH	using MNBDH		using DNPH	using MNBDH
formaldehyde	6	3	acetone	4	2
propanal	5	3	p-tolualdehyde	4	2
crotonaldehyde	4	2			

Figure 1. Chromatogram of a series of aldehyde and ketone MNBD-hydrazones, MNBDH, and MNBDA at the detection wavelengths $\lambda = 474$ nm (solid) and 514 nm (dotted) using gradient A. The concentration range of the compounds dissolved in acetonitrile was $(1.1-4.5) \times 10^{-5}$ mol/L.

hydrazones as well. They show an excitation maximum of about 470 nm, an emission maximum of about 560 nm, and a resulting Stokes shift of 90 nm. Unfortunately, the fluorimetric detection does not lead to improved limits of detection compared to the UV/visible detection due to the weak fluorescence of the hydrazones. However, fluorescence detection may provide higher selectivity when carbonyls are determined in complex matrixes.

The reaction of MNBDH with ozone and nitrogen dioxide was investigated. MNBDH reacts with both oxidants, resulting in almost quantitative formation of one single product, N-methyl-4-amino-7-nitrobenzofurazan (MNBDA):
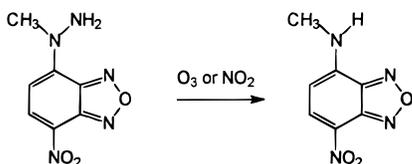
As a very positive aspect, MNBD-hydrazones are not decomposed by nitrogen dioxide or ozone as long as an excess of MNBDH is present. The UV/visible spectroscopic properties of MNBDA are similar to those of MNBDH and the MNBD-hydrazones and are listed in Table 1.

The differences concerning the absorption maxima of the substances can be used to identify groups of aldehyde and ketone hydrazones by dual-wavelength detection after the HPLC separation. As the absorption spectra of formaldehyde MNBD-hydrazone and p-tolualdehyde MNBD-hydrazone are rather different, the respective absorption maxima at $\lambda = 474$ and 514 nm are selected for this purpose.

Figure 1 presents a chromatogram of several MNBD-hydrazones, MNBDH, and MNBDA recorded at these wavelengths. While MNBDH and the aliphatic aldehyde MNBD-hydrazones exhibit a ratio ($(\epsilon(\lambda = 474 \text{ nm})/\epsilon(\lambda = 514 \text{ nm}))$) of approximately 1, it is obvious that the ratio for formaldehyde MNBD-hydrazone as well as for MNBDA is much larger than 1. The ketone and unsaturated aldehyde hydrazones show a ratio slightly smaller than 1. Furthermore, it is obvious that the aromatic aldehyde hydrazones are characterized by a ratio much smaller than 1. These differences show very clearly that the dual-wavelength detection can be a very helpful tool for the identification of different groups of carbonyl compounds in HPLC. The quotients of the peak areas at these two wavelengths are listed in Table 1 besides the results given by photometric investigations. In most cases, the values obtained by UV/visible spectrophotometry and by
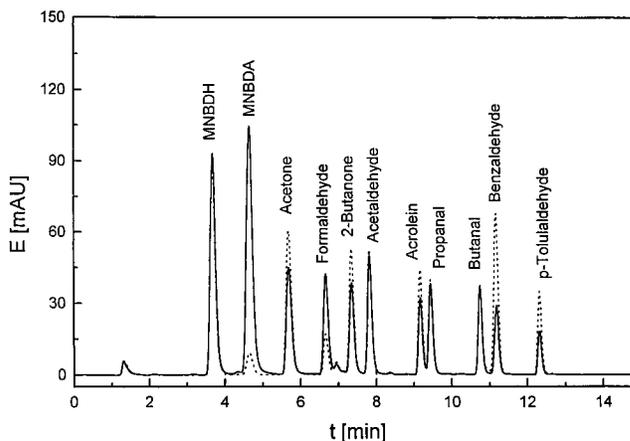
HPLC coincide well. The variations may be traced back to the reasons discussed in ref 16 and to the use of different mobile phases.

Another interesting aspect regarding the chromatogram in Figure 1 is the elution order of the hydrazones. It corresponds to the elution order of other N-alkylated hydrazones as described in ref 11 and exhibits significant differences compared to the elution order observed for the DNP-hydrazones. The hydrazones of the aliphatic aldehyde hydrazones elute in order of increasing alkyl chain lengths, while the ketone hydrazones elute significantly in advance of aldehyde hydrazones with even shorter alkyl chain lengths. Furthermore, it should be noted that MNBDA can easily be separated from the MNBD-hydrazones, thus avoiding interferences from a coelution as in case of DNPH.

First, HPLC chromatograms of the new reagent on reversed-phase columns with a binary water/acetonitrile gradient yielded not one but several peaks in the chromatogram. After addition of a carbonyl compound, all of these peaks disappeared and only one new peak of the hydrazone was formed. This indicated that equilibria between the reagent and solvent molecules or between at least two reagent molecules lead to the formation of stable intermediates which may be separated in HPLC. To suppress these equilibria, acetic acid and triethylamine (for concentrations, see Experimental Section) were added to the aqueous eluent. As can be seen in Figure 2, significant differences are observed: If only pure water and acetonitrile are used for the gradient, several peaks appear in the chromatogram. If the additives are used, only one peak appears in the chromatogram. It should be noted that the areas of the reagent peaks without using the additives varied strongly between different chromatograms, even when these were recorded within only a short time span. All separations should therefore be carried out using the additives to avoid misinterpretations of the additional peaks.

As the major drawback of the only known N-alkylated hydrazine reagent MDNPH was its slow reaction with the carbonyl compounds, special focus should be directed to the reactivity of

(16) Pötter, W.; Karst, U. *Anal. Chem.* **1996**, *68*, 3354−3358.
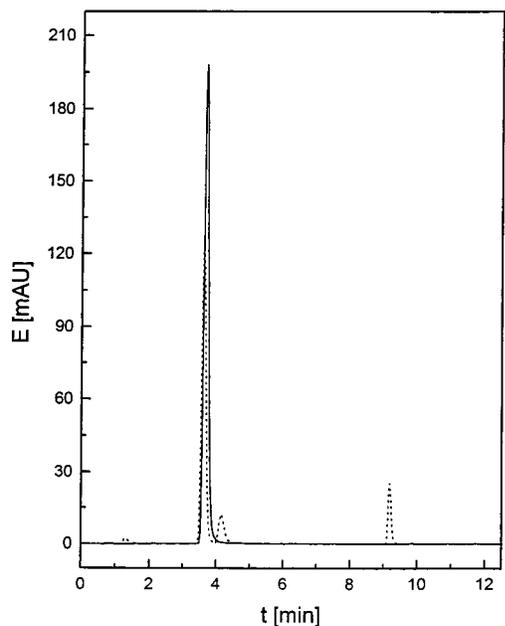
Figure 2. Chromatogram of MNBDH analyzed with different mobile phases using gradient B: acetonitrile and water (dotted) and aceto-nitrile and water/triethylamine/acetic acid (solid). The concentration was 9.7×10^{-5} mol/L in acetonitrile.
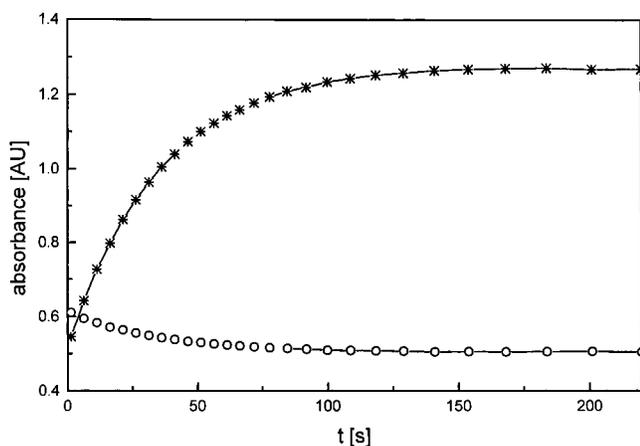

Figure 3. Absorbance/time curves for the formation of formaldehyde MNBD-hydrazone in acetic solution (5.8×10^{-7} mol of MNBDH in a mixture of 1.4 mL of H_2SO_4, 1.9 mL of H_2O, and 6.7 mL of ethanol) at the wavelength of 474 nm (star) and the consumption of MNBDH at 400 nm (circle).

Figure 4. Absorbance/time curves for the formation of formaldehyde DNP-hydrazone in acetic solution (6.5×10^{-7} mol of DNPH in a mixture of 1.4 mL of H_2SO_4, 1.9 mL of H_2O, and 6.7 mL of ethanol) at the wavelength of 355 nm (star) and the consumption of DNPH at 295 nm (circle).

Figure 5. Chromatogram of a car exhaust sample at the detection wavelength $\lambda = 474$ nm using gradient A: sampling layer (dotted); controlling layer (solid).

the new reagent MNBDH. The investigations were carried out with UV/visible spectroscopy. Special experimental conditions had to be chosen according to the reasons mentioned in ref 11. For the measurements, an excess of the carbonyl compound was added directly to an acidified reagent solution in a cuvette. Figure 3 shows the absorbance/time curves of the reaction of MNBDH with formaldehyde. The consumption of the protonated reagent can be observed at $\lambda = 400$ nm, while the formation of formal-dehyde MNBD-hydrazone is recognized at its absorption maxi-mum ($\lambda = 474$ nm). The reaction is completed after 150 s. To compare these results with those for DNPH, the reaction of DNPH with formaldehyde, carried out under the same conditions, is shown in Figure 4. The consumption of protonated DNPH is observed at $\lambda = 295$ nm and the formation of the hydrazone at $\lambda = 355$ nm. This reaction is completed after 250 s. The quantitative
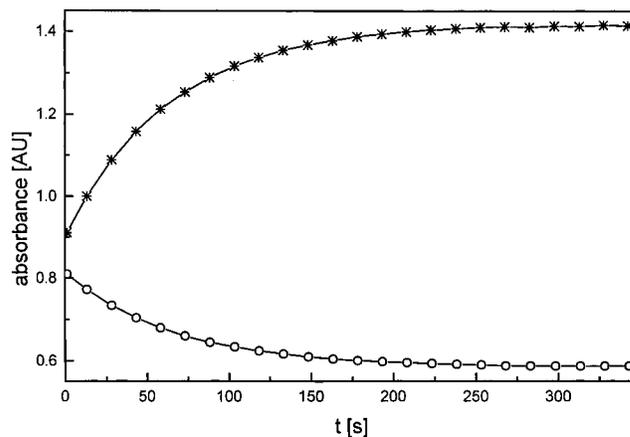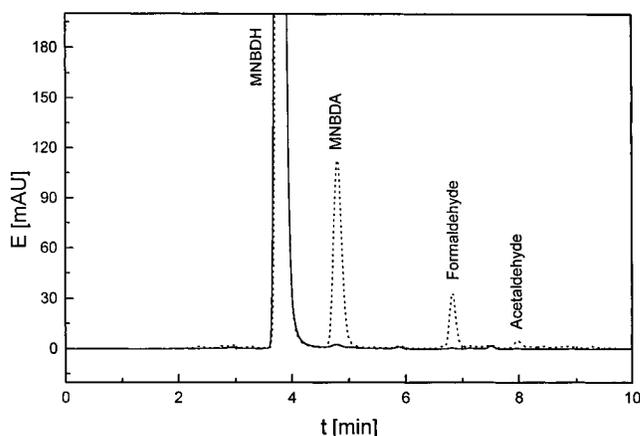
reaction of MDNPH with formaldehyde, however, requires several hours. Therefore, MNBDH can be considered to be an excellent alternative to DNPH with regard to reactivity.

In the following, MNBDH was used to prepare test tubes for air sampling of the carbonyls as stated above. The recovery rate of formaldehyde was determined by pipetting a solution with a defined amount of formaldehyde in acetonitrile (50 μL of a 5.8×10^{-3} mol/L solution) onto quartz wool which was placed in front of the collecting layer. Afterward, a constant air stream of 1 L/min was pumped through the tubes. Two test tubes were connected in series to observe possible incomplete recoveries on the collecting tube. Both collecting and controlling tubes were analyzed by means of HPLC. This way, the recovery rate of formaldehyde was determined 10-fold with a formaldehyde amount of 8.7 μg. In all cases, no breakthrough of the analyte in the controlling layer could be observed. The average recovery was 97.5% with a standard deviation of 1.5%. These investigations prove the suitability of MNBDH-coated test tubes for the determination of carbonyl compounds in gaseous samples.

Next, real samples were analyzed using the MNBDH-coated test tubes. A car exhaust sample was selected as an example for a matrix with a very high content of nitrogen dioxide. Figure 5
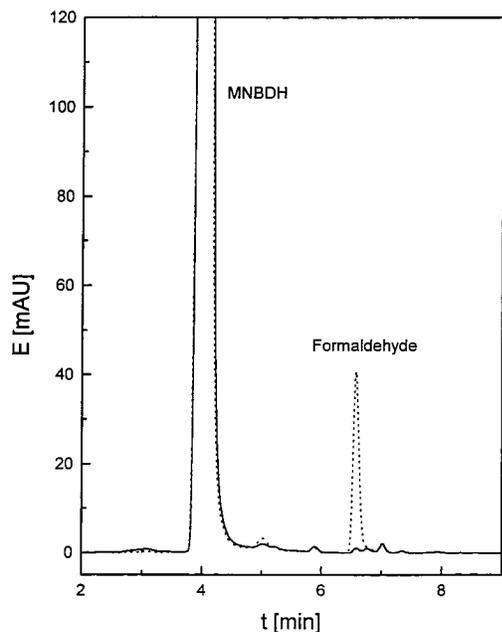
Figure 6. Chromatogram of an air sample of a disinfected room at the detection wavelength of $\lambda = 474$ nm using gradient B: sampling layer (dotted); controlling layer (solid).

shows the corresponding chromatogram of the car exhaust with a volume of 1 L from a diesel-fueled car. Data for both collecting and controlling layers are presented in this figure. Again, there was no breakthrough of the analytes in the controlling layer. As is obvious from the large MNBDA peak, the exhaust contains significant amounts of nitrogen dioxide. Other constituents of the exhaust are formaldehyde and acetaldehyde. The measurement was carried out twice. The concentrations of the pollutants found in these two measurements were 11.2 and 11.3 ppm of nitrogen dioxide, 2.0 and 2.1 ppm of formaldehyde, and 0.32 and 0.33 ppm of acetaldehyde, respectively. It should be noted that the data represent only the concentrations of the pollutants in the exhaust sample. As the total exhaust volume is not known, this cannot be correlated to the total amount of emitted aldehydes from the automobile. The calculations concerning the amount of nitrogen dioxide are only allowed on the supposition that the MNBDA peak is exclusively caused by reaction of MNBDH and nitrogen dioxide.

Additionally, an air sample was taken from a room which had been subjected to disinfection with a formaldehyde-containing disinfectant. An air volume of 2 L was pumped through the tubes as described above. In Figure 6, the chromatograms of both the collecting layer and the controlling layer are presented. Again, no breakthrough of the aldehydes in the controlling layer was observed. The sample contained 1.4 ppm of formaldehyde im-

mediately after disinfection. This value agrees very well with the amount of formaldehyde found by means of the DNPH method (1.4 ppm).

The investigations of the car exhaust sample and the disinfected room sample prove the suitability of the new reagent MNBDH for the determination of carbonyl compounds and nitrogen dioxide in real air samples.

CONCLUSIONS

MNBDH has been synthesized and applied as a new reagent for the determination of aldehydes and ketones with several advantages compared to the well-known DNPH method. Reagent and derivatives are characterized by high absorption maxima and molar absorptivities. Due to this fact, the selectivity is higher and the limits of detection are lower compared to those of the established reagent. The reaction of MNBDH with both nitrogen dioxide and ozone leads to only one product, MNBDA, which offers the possibility of determining carbonyl compounds simultaneously with nitrogen dioxide in real samples. MNBDH, MNBDA, and the hydrazones can be separated easily by means of reversed-phase HPLC using UV/visible detection. The reaction of MNBDH with carbonyl compounds has been investigated by means of UV/visible spectroscopy and found to be even slightly faster compared to the reaction of DNPH with the respective carbonyl compounds.

SUPPORTING INFORMATION AVAILABLE

Text presenting ^{1}H NMR, MS, IR, and elemental analysis data for *N*-methyl-4-hydrazino-7-nitrobenzofurazan, formaldehyde MNBD-hydrazone, acetaldehyde MNBD-hydrazone, propanal MNBD-hydrazone, butanal MNBD-hydrazone, pentanal MNBD-hydrazone, hexanal MNBD-hydrazone, heptanal MNBD-hydrazone, octanal MNBD-hydrazone, nonanal MNBD-hydrazone, decanal MNBD-hydrazone, acetone MNBD-hydrazone, 2-butanone MNBD-hydrazone, acrolein MNBD-hydrazone, crotonaldehyde MNBD-hydrazone, glutaraldehyde MNBD-hydrazone, benzaldehyde MNBD-hydrazone, *p*-tolualdehyde MNBD-hydrazone, and *N*-methyl-4-amino-7-nitrobenzofurazan. This material is available free of charge via the Internet at http://pubs.acs.org.