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1-Methyl-1-(2,4-dinitrophenyl)hydrazine as a New Reagent for the HPLC Determination of Aldehydes

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The synthesis and first application of an N-alkylated hydrazine reagent for the HPLC determination of aldehydes and ketones is described. 1-Methyl-1-(2,4-dinitrophenyl)hydrazine (MDNPH) reacts with aldehydes to give the corresponding hydrazones in the presence of an acid as catalyst. In contrast to other hydrazine reagents, MDNPH is oxidized by both ozone and nitrogen dioxide quantitatively to *N*-methyl-2,4-dinitroaniline (MDNA), which can be separated from the hydrazones of the lower aldehydes by means of HPLC. Unexpected elution orders are observed for the 1-methyl-1-(2,4-dinitrophenyl)hydrazones compared to those of 2,4-dinitrophenylhydrazones. Dual-wavelength detection is employed as a means for identification of different groups of the hydrazones and MDNA.

Hydrazine reagents have been used for the determination of aldehydes and ketones in liquid and air samples for decades. Hydrazines react with these carbonyl compounds, forming the corresponding hydrazones. Among a large series of other hydrazines, 2,4-dinitrophenylhydrazine (DNPH) has become the most popular, and several standardization bodies have published standard procedures based on the derivatization of aldehydes and ketones with DNPH and subsequent HPLC separation. The DNPH method is employed with a large variety of sampling procedures for liquid[1,2] and gas samples,[3−7] including impingers,[3,4] test tubes,[5] and passive sampling devices.[6,7] In recent years, problems have become apparent with the DNPH method due to reaction of the reagent with ozone[8,9] and nitrogen dioxide[10] in air samples. In the case of ozone, several products are formed and have not been identified yet. Nitrogen dioxide yields one product with DNPH. This product has been identified as 2,4-dinitrophenyl azide, which may eliminate nitrogen and react further to 5-nitrobenzofurazan 3-oxide under cyclization.[10]

The reaction products of both ozone and nitrogen dioxide may interfere with the aldehyde determination by coelution with the hydrazones in chromatography, which requires measures to unambiguously identify the hydrazones and indicate the absence of coeluting interferents in complex samples. Dual-wavelength detection has been described as a rapid and convenient tool for this purpose.[11] Further problems may arise from the consumption of the reagent, thus reducing the capacity of the sampling device. Additionally, it should be considered that the oxidizing agents may react not only with the reagent but also with the hydrazones and therefore reduce the recovery rate for the carbonyl compounds. Similar problems have been described for the use of 5-(dimethylamino)-1-sulfonylhydrazide (dansylhydrazine) in ozone-contaminated gaseous samples.[12]

An approach to overcome these problems is the development and use of new hydrazine reagents with reduced or more defined reactivity toward ozone and nitrogen dioxide.

EXPERIMENTAL SECTION

Chemicals. All chemicals were purchased from Aldrich Chemie (Steinheim, Germany) in the highest quality available. Acids were Merck (Darmstadt, Germany) analytical grade. Acetonitrile for HPLC and TLC was Merck gradient grade. Stationary phases for thin-layer chromatography were also from Merck.

Instrumentation for Product Identification. ^{1}H NMR measurements were performed with the AC 200 spectrometer (200.13 MHz) from Bruker (Bremen, Germany), and ^{13}C NMR measurements were done with the unity plus (600 MHz) from Varian (Darmstadt, Germany). Solvent for all NMR measurements was $CDCl_3$. All peaks are given with δ in ppm. COSY spectra of MDNPH, MDNA, and the MDNP hydrazones of acetaldehyde, propanal, 2-butanone, and acrolein were recorded to confirm C−H correlation on the unity plus instrument from Varian. FT-IR spectral information was obtained for the products in KBr pellets by using the IFS48 from Bruker. Mass spectra were recorded on the MAT 212 from Varian. All spectroscopic data are included as Supporting Information.

Synthesis. *1-Methyl-1-(2,4-dinitrophenyl)hydrazine (MDNPH).* According to a procedure suggested by Allen,[13] 6 mL of methylhydrazine (0.11 mol) in ethanol (30 mL) was added to a solution of potassium acetate (10.8 g, 0.11 mol) in deionized water (50 mL). After the mixture was heated to reflux, a solution of 2,4-dinitrochlorobenzene (20.2 g, 0.1 mol) in ethanol (100 mL) was

(1) Takami, K.; Kuwata, K.; Sugimae, A.; Nakamoto, M. *Anal. Chem.* **1985**, *57*, 243−245.
(2) Ogawa, I.; Fritz, J. S. *J. Chromatogr.* **1985**, *329*, 81−89.
(3) Grosjean, D.; Fung, K. *Anal. Chem.* **1982**, *54*, 1221−1224.
(4) Lipari, F.; Swarin, S. J. *J. Chromatogr.* **1982**, *247* (2), 297−306.
(5) Beasley, R. H.; Hoffmann, C. E.; Rueppel, M. L.; Worley, J. W. *Anal. Chem.* **1980**, *52*, 1110−1114.
(6) Levin, J. O.; Andersson, K.; Lindahl, R.; Nilson, C.-A. *Anal. Chem.* **1985**, *57*, 1032−1035.
(7) Levin, J. O.; Lindahl, R. *Analyst* **1994**, *119*, 79−83.
(8) Arnts, R. R.; Tejada, S. B. *Environ. Sci. Technol.* **1989,** *23*, 1428−1430.
(9) Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E. *J. Chromatogr.* **1989,** *483*, 431−436.
(10) Karst, U.; Binding, N.; Cammann, K.; Witting, U. *Fresenius J. Anal. Chem.* **1993,** *345*, 48−52.
(11) Pötter, W.; Karst, U. *Anal. Chem.* **1996,** *68*, 3354−3358.
(12) Rodier, D. R.; Nondek, L.; Birks, J. W. *Environ. Sci. Technol.* **1993**, *27*, 2814−2820.
(13) Allen, C. F. H. *Org. Synth.* **1933**, *13*, 36−37.

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added dropwise under stirring. The solution was cooled to 0 °C after a reaction time of 8 h. The precipitate was filtered off, washed with warm ethanol (60 °C) to remove unreacted 2,4-dinitrochlorobenzene and finally washed with hot water. The product was obtained as a yellow-orange solid. The yield was 84%. The progress of the reaction was monitored using thin-layer chromatography (stationary phase, silica gel; mobile phase, toluene/acetonitrile 7:3 (v/v)). The purity of the product was examined by means of HPLC (conditions see below, $\lambda = 360$ and 300 nm). The product was fully characterized by means of ^{1}H NMR, ^{13}C NMR, IR, MS, elementary analysis, and its melting point. These data are available as Supporting Information.

1-Methyl-1-(2,4-dinitrophenyl)hydrazones. None of these derivatives has been subject to a full spectroscopic characterization yet. Only some of the derivatives have been described in literature.[14,15] The derivatives were prepared according to a procedure published by Behforouz et al.[16] for the synthesis of DNPH derivatives: 1-methyl-1-(2,4-dinitrophenyl)hydrazine (100 mg, 4.7×10^{-4} mol) was dissolved in 0.5 mL of concentrated sulfuric acid and then added to a solution of 0.7 mL of water in 2.5 mL of 95% ethanol. A 50% molar excess of the aldehyde or ketone (7.1×10^{-4} mol) was added as solution in ethanol (10−20 mass %). The hydrazones precipitated as yellow or orange 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. The progress of the reaction was monitored using thin-layer chromatography (conditions as with MDNPH, see above). Yields ranged from 72% to >95%, depending on the degree of purification required for the individual hydrazones.

Notes for the preparation of particular hydrazones:

(i) Acetone MDNP hydrazone is formed after heating of the solution to 80 °C for 3 h.

(ii) The hydrazones of the aldehydes and ketones with chain lengths of more than four carbon atoms precipitated only after the addition of ice to the reaction mixture.

(iii) Pentanal MDNP hydrazone was isolated as an oil, as the crystallization of the substance could not be achieved.

(iv) For the preparation of glutaraldehyde hydrazone, the stoichiometric amount of only 3.5×10^{-4} mol of the dicarbonyl compound was used.

The reaction products were fully characterized by means of ^{1}H NMR, ^{13}C NMR, IR, MS, elementary analysis, and their melting points. These data are available as Supporting Information.

N-Methyl-2,4-dinitroaniline. First, 100 mg of 1-methyl-1-(2,4-dinitrophenyl)hydrazine (4.7×10^{-4} mol) was dissolved in 0.5 mL of concentrated sulfuric acid. Next, 3 mL of distilled water was added to obtain a reagent solution. 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. In both cases, a yellow-orange precipitate was formed, and nitrogen was blown into the solutions after the reaction to remove unreacted oxidant. The precipitate was filtered off, washed with sodium bicarbonate solution (5 mass %) and then with water, and finally dried in vacuo. TLC control of the reaction was performed as described above. The yield was 76% in both cases. The identities of the products of both approaches were confirmed by complete spectroscopic and HPLC analysis. The reaction product was fully characterized in the same way as MDNPH and its hydrazones. These data are available as Supporting Information.

Preparation of the MDNPH Solution for Real Sample Analysis. A 5×10^{-3} mol/L MDNPH solution was prepared by adding 105 mg of MDNPH to 0.5 mL of concentrated sulfuric acid in 99.5 mL of acetonitrile. Of this solution, 80 mL was transferred into an impinger. After sampling, acetonitrile was added to a total volume of 100 mL.

Air Sampling Procedure and Analysis. Air sampling was performed using a personal air sampler pump (A. P. Buck, Inc., Orlando, FL) with the impinger located directly at the end of the exhaust pipe of the car. The sampling rate was 0.25 L/min, and the sampling time was 2 min.

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

UV Absorption Measurements. All UV/visible measurements were performed within a concentration range from 2.3×10^{-5} to 1.3×10^{-4} mol/L of the reagent and the hydrazones in acetonitrile. The spectra were recorded in the range from 250 to 470 nm.

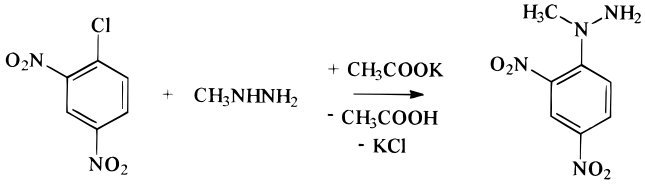
HPLC Instrumentation and Analysis. A high-performance liquid chromatograph consisting of the following components was used: two LC-10AS pumps (Shimadzu, Duisburg, Germany), SPD-10AV detector (Shimadzu), SIL-10A autosampler (Shimadzu), Class LC-10 Version 1.4 software (Shimadzu), and CBM-10A controller unit (Shimadzu). The injection volume was 10 μL. The column consisted of Deltabond AK reversed-phase C_{18} material (Keystone, Bellefonte, PA): column dimensions, 150 mm × 4.6 mm; particle size, 5 μm; pore size, 300 Å.

For separation, a binary gradient consisting of acetonitrile and water was selected with the following profile:

	time (min)						
	0	1	6.5	9.5	10	12	13 (stop)
$c(CH_3CN)$ (%)	30	30	42	100	100	30	
flow (mL/min)	1.5						

RESULTS

MDNPH was synthesized by a nucleophilic substitution reaction of *N*-methylhydrazine with 2,4-dinitrochlorobenzene:



The reagent has been described before in the literature for the preparation of pharmaceutical products,[17] but has not been applied for any analytical purposes yet. The corresponding hydrazone standards of a series of aldehydes and ketones were prepared by

(14) Bohlmann, F. *Chem. Ber.* **1951**, *84*, 490−504
(15) Rappoport, Z.; Sheradsky, T. *J. Chem. Soc. B* **1968**, 277−291.
(16) Behforouz, M.; Bolan, J. L.; Flynt, M. S. *J. Org. Chem.* **1985,** *50*, 1186−1189.
(17) Popp, F. D. *J. Heterocycl. Chem.* **1984**, *21*, 617−619.

Table 1. UV/Visible Spectroscopic and Chromatographic Data for a Series of 1-Methyl-1-(2,4-dinitrophenyl)hydrazones, MDNPH, and MDNA

compound	ϵ (L mol^{-1} cm^{-1}) × 10^3 368 nm	290 nm	ϵ(368 nm)/ ϵ(290 nm)	A(368 nm)/ A(290 nm)	λ_{max}	$\epsilon(\lambda_{max})$ (L mol^{-1} cm^{-1}) × 10^3
N-methyl-2,4-dinitrophenylhydrazone of						
formaldehyde	14.7	1.7	8.6	9.7	368	14.7
acetaldehyde	15.7	1.4	11.2	10.1	380	16.6
propanal	15.1	1.2	12.6	10.8	384	16.4
acetone	14.9	1.6	9.3	9.1	384	16.4
acrolein	16.7	6.0	2.8	2.2	393	19.9
butanal	15.1	1.5	10.1	10.9	384	16.5
2-butanone	14.5	1.2	12.1	9.2	386	17.2
octanal	14.4	1.3	11.1	10.7	385	15.0
decanal	15.3	1.3	11.8	12.1	385	16.1
glutaraldehyde	33.1	3.2	10.3	8.8	385	36.3
benzaldehyde	14.4	9.2	1.6	1.7	401	19.6
p-tolualdehyde	13.8	11.1	1.2	1.2	405	20.6
MDNPH	15.9	1.5	10.6	9.7	373	16.1
MDNA	12.1	1.6	7.6	6.5	351	15.8

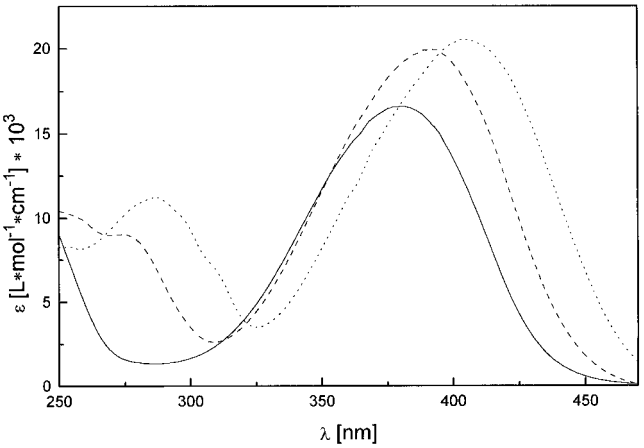
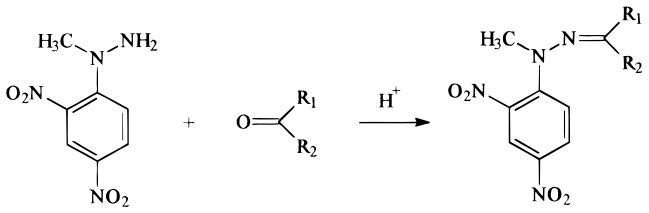


Figure 1. UV/visible spectra of the 1-methyl-1-(2,4-dinitrophenyl)-hydrazones of acetaldehyde (—), acrolein (- - -), and *p*-tolualdehyde (···).

reacting MDNPH with the carbonyl compounds in the presence of sulfuric acid as catalyst:



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

UV/visible spectra of the reagent and of the hydrazones were recorded to determine the optimum wavelengths for HPLC detection. It is known from the literature that different groups of aldehydes (aliphatic, olefinic, and aromatic) yield products with significantly different UV/visible spectra when reacting with DNPH. To demonstrate that these differences, which can be used to identify groups of aldehydes by means of dual-wavelength detection,[11] occur in a similar way for the MDNPH derivatives, the UV/visible spectra of the MDNP hydrazones of acetaldehyde, acrolein, and *p*-tolualdehyde are presented in Figure 1. Each of these hydrazones is representative for its group of aldehydes (aliphatic, olefinic, and aromatic, respectively) in terms of UV/visible absorption maxima and minima and their molar absorptivities. The spectroscopic data of related hydrazones are listed in Table 1. Compared to the spectra of the nonalkylated DNPH derivatives,[15] a general shift of the maxima to longer wavelengths is observed. Bohlmann[14] has interpreted this shift as the result of the missing interaction between the α-N-based hydrogen atom of the hydrazine group with the nitro group in the 2-position of the aromatic ring. This shift, however, is advantageous for HPLC detection, as selectivity toward other aromatic compounds is enhanced. In analogy with the DNPH derivatives, the absorption maxima and minima of the saturated aldehyde hydrazones are located at lower wavelengths compared to unsaturated hydrazones, as can be seen in Figure 1. The aromatic hydrazones exhibit their absorption maxima at the longest wavelengths.

Reactivity of MDNPH with aldehydes and ketones was investigated by means of UV/visible spectroscopy. Special experimental conditions have to be chosen for this purpose, because MDNPH exhibits its UV/visible absorption maximum in the same region as most aliphatic hydrazones. Even if the reagent is protonated by strong acids, a significant absorption of MDNPH remains at the location of the absorption maxima of the hydrazones. UV/visible spectroscopic observation of the reaction is, therefore, only useful when MDNPH reacts quantitatively. For this reason, an excess of the carbonyl compounds was added to an acidified reagent solution. The hydrazones are, in contrast to MDNPH, only weak bases and are, therefore, not protonated, even in strongly acidic solution. In Figure 2, the reaction of MDNPH with acetaldehyde in sulfuric acid is presented. The band of the protonated MDNPH disappears, and the product band is formed at a longer wavelength. Note the isosbestic point, indicating a direct reaction of protonated MDNPH with the aldehyde to the hydrazone. In Figure 3, the time dependence of this reaction is displayed. Quantitative reaction is observed after slightly more than 20 min. Compared to DNPH, reactivity was reduced for all carbonyl compounds investigated but could be enhanced significantly by using the strong Lewis acid boron trifluoride hydrate instead of sulfuric acid as catalyst in the same concentration. For both catalysts, aliphatic aldehydes with chain lengths from C_2 to C_{10} reacted faster than formaldehyde. *p*-Tolualdehyde reacted as fast as acetaldehyde, while acetone and 2-butanone exhibited very slow reactions with MDNPH, even under catalysis of a Lewis acid.

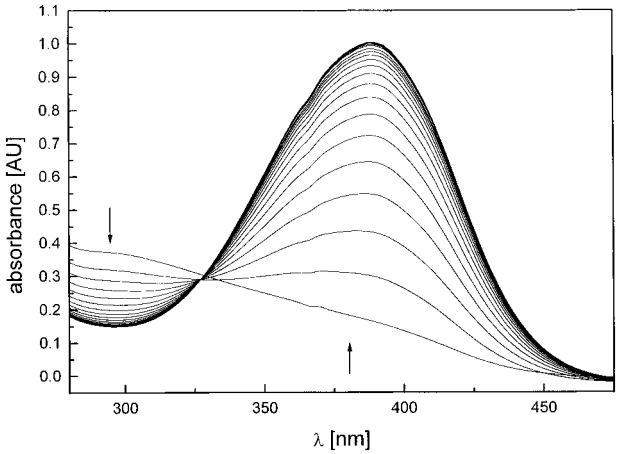


Figure 2. UV/visible spectroscopic investigation of the formation of acetaldehyde 1-methyl-1-(2,4-dinitrophenyl)hydrazone in acidic solution (6.5×10^{-7} mol of MDNPH in a mixture of 1.4 mL of H_2SO_4, 1.9 mL of H_2O, and 6.7 mL of ethanol) (↑) and of the consumption of 1-methyl-1-(2,4-dinitrophenyl)hydrazine (↓). The time interval between the measurements was 1 min.

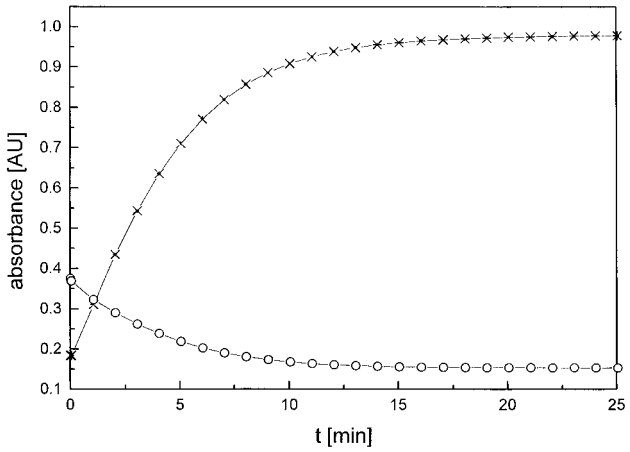


Figure 3. Absorbance/time curves for the formation of acetaldehyde 1-methyl-1-(2,4-dinitrophenyl)hydrazone at the wavelength of 380 nm (×) and the consumption of MDNPH at 290 nm (○). Concentrations are given in see Figure 2.

Therefore, MDNPH sampling tubes for gas analysis were prepared, applied, and analyzed by HPLC according to DNPH tubes as described in refs 11 and 18, and the recovery rate for different aldehydes was investigated depending on the flow rate of the gaseous sample. *p*-Tolualdehyde and acetaldehyde were recovered quantitatively at flow rates of up to 1 L/min, while formaldehyde was recovered only at flow rates up to 0.25 L/min. The order of reactivity was identical to the order obtained using the UV/visible spectrophotometric measurements.

Surprisingly, both ozone and nitrogen dioxide react with MDNPH under formation of *N*-methyl-2,4-dinitroaniline (MDNA) as the single product in high yields:

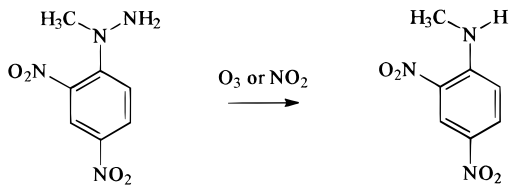


Figure 4 shows the chromatogram of an acidified solution of an excess of MDNPH with formaldehyde and acetaldehyde MDNP hydrazone before and after oxidation by nitrogen dioxide. The peak of MDNPH decreases and the one of MDNA increases appropriately, while the amounts of formaldehyde and acetaldehyde MDNP hydrazones remain constant. Therefore, no hydrazones are decomposed by nitrogen dioxide to MDNA as long as a MDNPH excess is present. However, the pure hydrazones are decomposed to MDNA after consumption of MDNPH. Only one significant product is formed during these reactions.

MDNA exhibits chromatographic properties similar to those of formaldehyde MDNP hydrazone and acetone MDNP hydrazone (see below). The UV/visible spectra of MDNA, MDNPH, acetone MDNP hydrazone, and formaldehyde MDNP hydrazone are presented in Figure 5, and additional data are provided in Table 1. It is obvious that acetone MDNP hydrazone is characterized

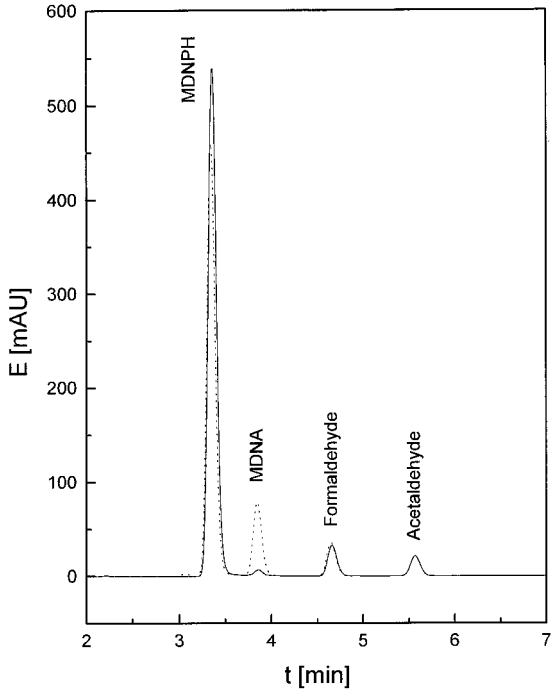


Figure 4. Chromatogram of a solution of an MDNPH excess (6×10^{-3} mol/L), formaldehyde 1-methyl-1-(2,4-dinitrophenyl)hydrazone (3.3×10^{-4} mol/L), and acetaldehyde 1-methyl-1-(2,4-dinitrophenyl)-hydrazone (2.6×10^{-4} mol/L) before (—) and after (- - -) addition of nitrogen dioxide.

by UV/visible properties similar to those of the aliphatic aldehyde MDNP hydrazones. Formaldehyde MDNP hydrazone and MDNPH are very similar in terms of their UV/visible maxima and minima and even their molar absorptivities. MDNA shows its absorption maximum at shorter wavelengths than the MDNPH derivatives.

Therefore, dual-wavelength detection is a useful tool to identify the different groups of aldehyde or ketone hydrazones. The ratio of the absorptions at two selected wavelengths is chosen for this purpose. As formaldehyde is the most important analyte among the aldehydes, its hydrazone absorption maximum and minimum at $\lambda = 368$ and 290 nm, respectively, are selected. The molar absorptivities of all synthesized hydrazones, MDNPH, and MDNA at these wavelengths determined on a spectrophotometer are

(18) Binding, N.; Thiewens, S.; Witting, U. *Staub-Reinhalt. Luft* **1986**, *46*, 444–446.

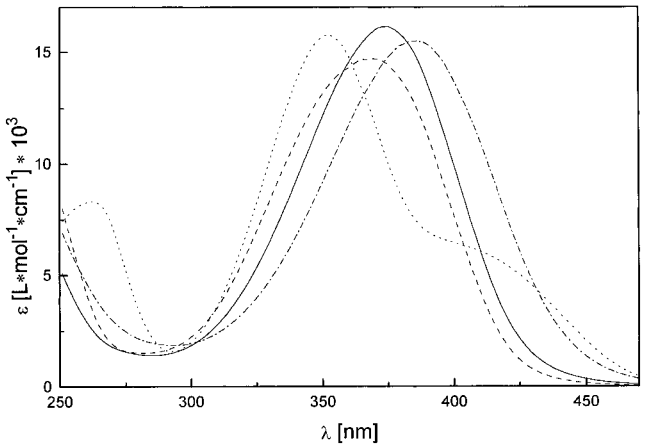


Figure 5. UV/visible spectra of MDNPH (—), MDNA (···), and the 1-methyl-1-(2,4-dinitrophenyl)hydrazones of formaldehyde (- - -), and acetone (-·-).

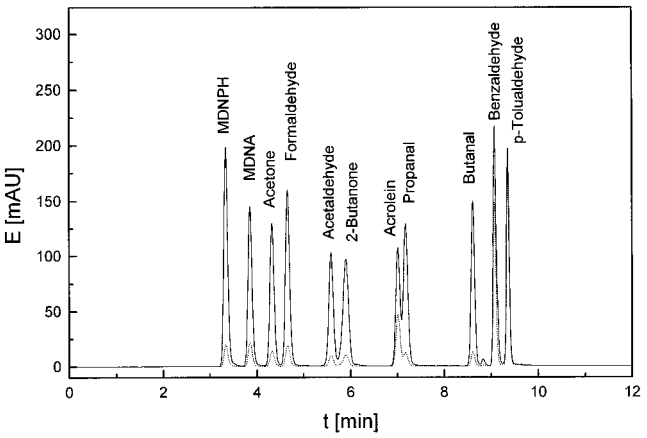


Figure 6. Chromatogram of a series of aldehyde and ketone 1-methyl-1-(2,4-dinitrophenyl)hydrazones, MDNPH, and MDNA at the detection wavelengths $\lambda = 368$ (—) and 290 nm (···). The concentration range of the compounds dissolved in acetonitrile was 1.1×10^{-4}–2.1×10^{-4} mol/L.

listed in Table 1. For comparison, the quotient of the peak areas at these two wavelengths obtained in HPLC with dual-wavelength detection is listed as well. Characteristic absorption ratio ranges for different groups of hydrazones and MDNA can be obtained from Table 1. It is obvious that the wavelength ratios (λ(368 nm)/λ(290 nm)) are larger for the hydrazones of aliphatic aldehydes than for those of unsaturated aldehydes or even aromatic aldehydes. MDNPH exhibits wavelength ratios similar to those of aliphatic aldehyde hydrazones, and MDNA is characterized by a slightly smaller ratio compared to those of aliphatic aldehyde hydrazones. The ratios determined using the two methods coincide well when considering the typical sources of variations as listed in ref 11.

In Figure 6, a chromatogram of a mixture of hydrazone standards, MDNPH, and MDNA at both selected detection wavelengths is presented. It should be noted that the aliphatic aldehyde MDNP hydrazones elute in the order of increasing alkyl chain length, as could be expected by comparison with the data of the corresponding DNPH derivatives when using the same chromatographic conditions (compare to Figure 7). Surprisingly, and in contrast to the DNPH derivatives, the MDNP hydrazones of acetone and 2-butanone elute significantly in advance of the aliphatic aldehyde MDNP hydrazones with shorter alkyl chain lengths. It should be noted in Figure 6 that the separation of

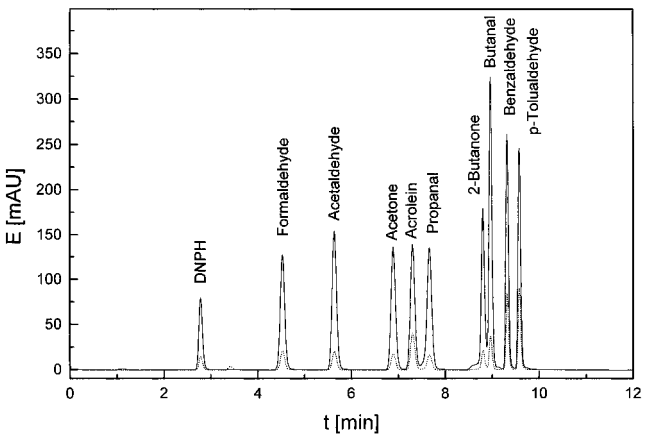


Figure 7. Chromatogram of a series of aldehyde and ketone 2,4-dinitrophenylhydrazones and DNPH at the detection wavelengths $\lambda = 368$ (—) and 290 nm (···). The concentration range of the compounds dissolved in acetonitrile was 9.2×10^{-5}–1.7×10^{-4} mol/L.

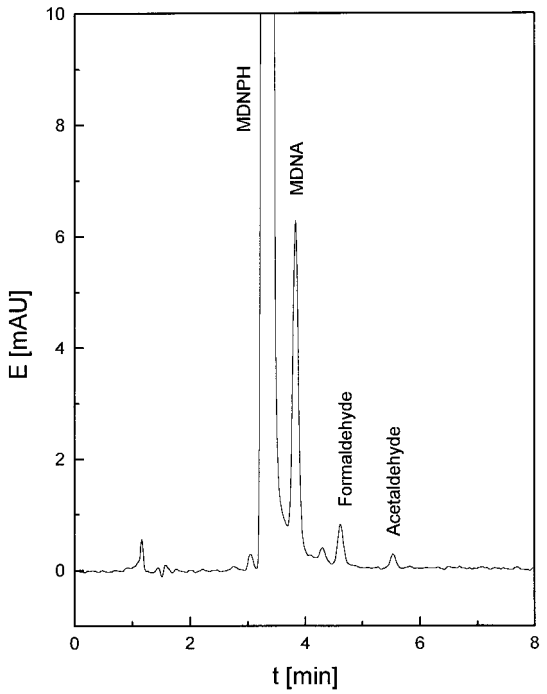


Figure 8. Chromatogram of a car exhaust sample at the detection wavelength $\lambda = 368$ nm.

MDNA and the acetone MDNP hydrazone succeeds without problems when the selected chromatographic conditions are used.

To examine if the new reagent is suitable to analyze real samples, an exhaust sample was taken from a cold-started car by pumping the exhaust through an impinger filled with MDNPH solution (for sampling conditions, see Experimental Section). The corresponding chromatogram is shown in Figure 8. The product of MDNPH with nitrogen dioxide, MDNA, is formed as well as formaldehyde MDNP hydrazone and acetaldehyde MDNP hydrazone. Since the total exhaust volumes per time scale may vary with different cars, the total amount of each analyte cannot be directly calculated from this information. Nevertheless, the chromatogram proves the suitability of the new reagent for the determination of aldehydes and nitrogen dioxide in real air samples.

CONCLUSIONS

MDNPH has been synthesized as a new reagent for the determination of aldehydes and ketones with interesting properties concerning its reactions with nitrogen dioxide and ozone, both of which form MDNA. MDNPH is suitable to determine aldehydes and nitrogen dioxide in real air samples by means of impingers. The MDNP hydrazones can be detected by UV/visible spectroscopy at longer wavelengths compared to the respective DNPH derivatives. MDNA, the hydrazones, and the reagent can be separated easily using reversed-phase HPLC. The elution orders of the corresponding ketone hydrazones in reversed-phase HPLC differ significantly from those of the DNP hydrazones.

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SUPPORTING INFORMATION AVAILABLE

Characterization data of 1-methyl-1-(2,4-dinitrophenyl)hydrazine, formaldehyde 1-methyl-1-(2,4-dinitrophenyl)hydrazone, acetaldehyde 1-methyl-1-(2,4-dinitrophenyl)hydrazone, propanal 1-methyl-1-(2,4-dinitrophenyl)hydrazone, butanal 1-methyl-1-(2,4-dinitrophenyl)hydrazone, pentanal 1-methyl-1-(2,4-dinitrophenyl)hydrazone, octanal 1-methyl-1-(2,4-dinitrophenyl)hydrazone, decanal 1-methyl-1-(2,4-dinitrophenyl)hydrazone, acetone 1-methyl-1-(2,4-dinitrophenyl)hydrazone, 2-butanone 1-methyl-1-(2,4-dinitrophenyl)hydrazone, acrolein 1-methyl-1-(2,4-dinitrophenyl)hydrazone, glutaraldehyde bis[1-methyl-1-(2,4-dinitrophenyl)hydrazone], benzaldehyde 1-methyl-1-(2,4-dinitrophenyl)hydrazone, *p*-tolualdehyde 1-methyl-1-(2,4-dinitrophenyl)hydrazone, and *N*-methyl-2,4-dinitroaniline, including ^{1}H NMR, ^{13}C NMR, IR, MS, elementary analysis, and melting points (5 pages). Ordering information is given on any current masthead page.

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