Determination of Nitrophenols and Nitrocresols in Gaseous Samples

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A procedure for determination of nitrophenols and nitrocresols in gaseous samples was proposed. The analytes from samples were absorbed in NaOH solution. The alkaline solution was extracted with dichloromethane to remove the neutral and basic interfering compounds. After acidification of the absorption solution the analytes were extracted into dichloromethane and analyzed by gas chromatography on capillary column with polydimethylsiloxane stationary phase. Detection limits of individual analytes 0.1—1.4 mg m^{-3} in gaseous samples were achieved.

Nitrophenols and nitrocresols are present in the emissions from various technological processes (dyes, pharmaceuticals, plastics) where they are usually used as reagents [1]. Moreover, they are found where phenols or cresols and nitrogen oxides are simultaneously present [1—3]. Due to their photochemical stability, nitrophenols present in atmosphere are degraded very slowly [2].

Nitrophenols belong to the hazardous pollutants because of their strong phytotoxic activity [1, 2].

They are regularly monitored in water samples. However, only few papers dealing with their determination in gaseous samples have been published [2—5].

There is a large number of possible congeners of nitrophenols. Not all of them are equally important considering the probability of their constitution and their toxicity. Congeners with the nitro group in the positions 2, 4, and 6 of the benzene ring are preferably constituted. The 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, and 6-methyl-2,4-dinitrophenol belong to the priority pollutants [6].

The nitrophenols and nitrocresols are relatively strong acids [7] with pK_a value from 4 to 8.

Several types of polymer sorbents have been found to be suitable for solid phase extraction of nitrophenols from water samples [1, 3, 8—14]. Some authors propose liquid-liquid extraction with dichloromethane [9, 15, 16] or a mixture of pentane and diethyl ether (1 1) as extraction agent. According to *Chen* [16] the matrix has negligible effect on the extraction recovery. *Graves* [17] has proposed to extract the alkalized water sample with dichloromethane and subsequently after acidification with diethyl ether. This procedure allows to remove some of the possible interfering components as the extraction recoveries of the majority of compounds with basic and neutral character from basic aqueous solution are usually very high.

Various stationary phases were investigated for the gas chromatographic analysis of nitrophenols and nitrocresols. *Williams et al.* [18] have compared six types of stationary phases. The best results were obtained on nonpolar and slightly polar stationary phases. Similar conclusions have been made by other authors [19—23].

Due to the molecular structure of nitrophenols and nitrocresols a comparatively broad range of detectors can be used to detect them with a high sensitivity. Electron capture detector (ECD) [9, 24, 25], mass-spectral detector (MSD) [4, 8, 12, 14, 18, 24], nitrogen-phosphorus detector (NPD) [4, 24], Fourier transform infrared detector (FTIR) [18], and flame ionization detector (FID) [22] were used as detectors for gas chromatographic determination of nitrophenols and nitrocresols.

The aim of this work was to find a procedure for determination of nitrophenols and nitrocresols in gaseous samples, including sampling and preseparation.

EXPERIMENTAL

For all measurements HP 5890 Series II (Hewlett—Packard, Germany) gas chromatograph equipped by split/splitless injector and flame ionization detector was used. The injector was operated in splitless mode. Both injector and detector temperature was set to 250 °C. Hydrogen was used as carrier gas.

After preliminary experiments 10 m fused silica capillary column with internal diameter 0.53 mm was selected for all analyses. The column was coated with nonpolar polydimethylsiloxane stationary phase of the film thickness of 1.2 μm (RSL-150, RSL, Belgium). A 10 mm^3 syringe (Hewlett—Packard, USA) was used for all injections.

The measured signal was processed by HP ChemStation 3365 (Hewlett—Packard, USA) chromatographic software.

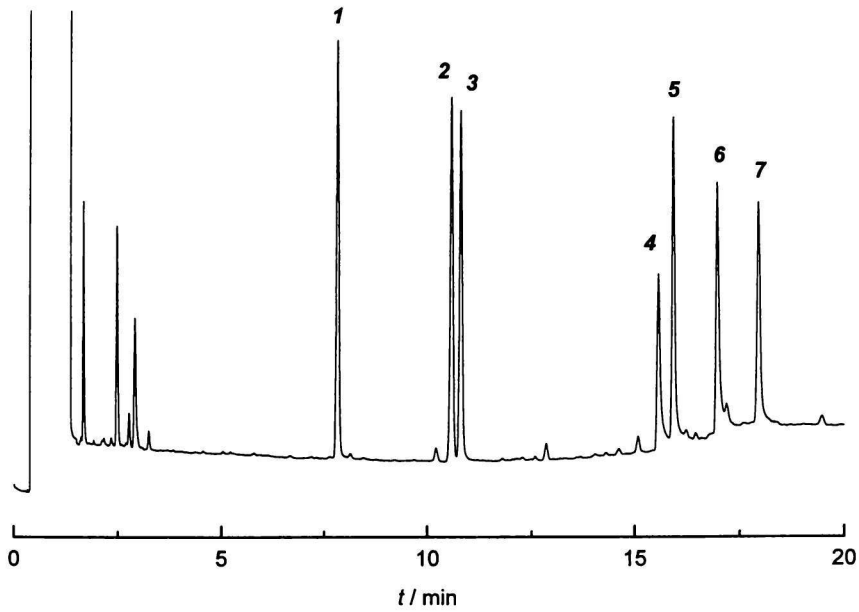

Fig. 1. Chromatogram obtained by analysis of the calibration solution of nitrophenols and nitrocresols; 1 mm^3 of dichloromethane solution containing 20 ng of each analyte was injected by splitless technique; detector FID. *1.* 2-Nitrophenol, *2.* 3-methyl-4-nitrophenol, *3.* 2-methyl-4-nitrophenol, *4.* 2,4-dinitrophenol, *5.* 3-nitrophenol, *6.* 4-nitrophenol, *7.* 2-methyl-4,6-dinitrophenol.

Dichloromethane, diethyl ether, NaOH, H_2SO_4, NaCl, and anhydrous Na_2SO_4 (all supplied by Lachema, Czech Republic) were used for experiments. All chemicals were of the analytical grade.

The apparatus used for the model sampling of gas consisted of gas cylinder with nitrogen (carrier), needle valve for adjusting the gas flow through the system, vaporizer (heated to 250 °C) with septum injection port, main and checking bubblers both filled with 50 cm^3 of NaOH solution (0.1 mol dm^{-3}). For sampling of the analytes 100 cm^3 bubblers with fritted glass stem were used. For protection of the flow meter, a bubbler with H_2SO_4 solution (0.1 mol dm^{-3}) followed by a drying tube (filled with anhydrous $CaCl_2$) was coupled after the two sampling bubblers.

The flow rate of the nitrogen carrier was set to 500 cm^3 min^{-1}. Various amounts of the mixtures of analyzed compounds were injected by microliter syringe into the vaporizer as solutions in dichloromethane. (The amount of each analyte in the mixture was equal.) The evaporated analytes were transferred by 15 dm^3 of carrier gas into the bubblers. The bubblers were cooled by immersing into ice-water bath to prevent losses caused by evaporation.

The liquid-liquid extractions were performed in 100 cm^3 extraction funnels.

RESULTS

Chromatographic Separation

The temperature program was optimized with respect to the optimal resolution of analytes and minimum analysis time. The initial temperature was set to 40 °C to enable using of splitless injection technique with dichloromethane as solvent. The temperature rate (6 °C min^{-1}) was determined so as to achieve minimum analysis time at sufficient separation of analytes. The final temperature of the temperature program was set to 140 °C.

The chromatogram of the separation of the studied nitrophenols and nitrocresols under the aforementioned conditions is shown in Fig. 1.

Detection Limits

The detection limits of the analytes were determined by consecutive analyses of solutions with decreasing concentrations of the analytes in dichloromethane. The obtained detection limits are listed in Table 1. They were calculated according to procedure recommended by IUPAC [26].

Linearity

The linearity of the detector response was determined in the range 2 ng—2 μg. A set of calibration solutions was prepared – the most concentrated by weighting of 100 mg of each analyte and filling up to 5 cm^3 in volumetric flask by dichloromethane. The other solutions (ρ/(mg cm^{-3}): 2, 0.2, 0.02, 0.002, and 0.0002) were prepared by consecutive dilution. The calibration curves for all analytes are shown in Fig. 2. In the range from the detection limit up to 2 μg per injection the calibration curves are linear for all analyzed compounds with intercept not significantly dif-

Table 1. Detection Limits (for FID) and Extraction Recoveries Determined for the Analyzed Nitrophenols and Nitrocresols

Analyte	Detection limit ng	Extraction recovery %
2-Nitrophenol	0.13	100
3-Nitrophenol	0.20	100
4-Nitrophenol	0.27	100
2,4-Dinitrophenol	1.40	100
3-Methyl-4-nitrophenol	0.11	91
2-Methyl-4-nitrophenol	0.12	82
2-Methyl-4,6-dinitrophenol	0.32	96

The reported extraction recoveries correspond to the concentration of analytes in gaseous samples 20 mg m^{-3}.

ferent from zero. The zero intercept allows to plot the calibration lines in a log—log scale. An exception is 2,4-dinitrophenol for which a minor irreversible absorption in the column was observed.

Preseparation

Nitrophenols and nitrocresols were absorbed in aqueous solution at model sampling, thus before analysis they had to be transferred into solvent suitable for gas chromatographic separation. Both dichloromethane and diethyl ether were investigated as the extracting phases for the liquid-liquid extraction. 50 cm^3 of the aqueous solution containing the analytes was measured by pipette into extraction funnel together with 5 cm^3 of extraction agent. After 1 min of shaking the organic layer was drained to a vial containing 0.5 g of anhydrous Na_2SO_4 and subsequently analyzed by gas chromatography.

The analytes were extracted by extraction agents from basic (pH = 12.5—13.0) and acidic (pH = 1.5—2.0) aqueous solutions. The extraction recoveries from the basic aqueous solution were approximately zero for all analytes under study. This could have been expected considering the acidic character of the analytes.

By contrast, the recoveries of the analytes from acidic aqueous solution were high enough, as shown in Table 1. To increase the extraction efficiencies 10 g of NaCl was added to the aqueous phase before extraction. This had an additional effect – the two phases were separated in a shorter time.

No difference was observed between the recoveries for dichloromethane and diethyl ether. The dichloromethane is more convenient for the subsequent gas chromatographic analysis because of high volatility of diethyl ether. (However, in the case of ECD as detector the diethyl ether has to be used.)

According to these observations and the results published in cited papers the following extraction procedure was proposed: The absorption solution (around 50 cm^3) was quantitatively transferred from the bubbler into the separation funnel. 10 g of NaCl and 5 cm^3 of dichloromethane were added to the funnel. The funnel was shaken for 1 min. After the separation of the phases the bottom (dichloromethane) layer was drained to the waste. The extraction of possible interfering components was repeated with two additional portions of dichloromethane. 1.5 cm^3 of 20 % H_2SO_4 solution was added to the funnel. The pH value of the solution in the funnel was checked by indicator paper (must be less than 2). 5 cm^3 of dichloromethane were measured by pipette and added to the funnel. The funnel was shaken for 1 min. After separation of the phases the dichloromethane layer was drained to a vial. The extraction was repeated with two additional portions of dichloromethane. (All three dichloromethane portions were drained to the same vial.) 0.5 g of anhydrous Na_2SO_4 was added to the vial to remove the residues of water from the extract. The vial was tightly capped and stored in a cold place prior to gas chromatographic analysis.

The content of the checking bubbler was treated by the same way.

Sampling

Various sampling experiments were performed using the above described apparatus. The analytes in the checking bubbler were determined to check whether their absorption efficiencies in the main bubbler were satisfactory. The results of these experiments are summarized in Table 2. It is evident that the absorption efficiencies were not different from 100 % within experimental errors. In checking bubbler a small amount of analytes (less than 2 % of the total amount) was found only for the highest quantity of analytes injected into the vaporizer.

Table 2. Results of the Model Sampling

Number of the series of measurements	1	2	3
The amount of each analyte in vaporizer/μg	150	750	1500
The total amount of analytes in vaporizer/μg	1050	5250	10500
Number of repetitions	6	6	6
Relative standard uncertainty of determination/%	5.5	6.2	5.3
Total amount of analytes determined in the main bubbler/μg	1042	5236	10410
Total amount of analytes determined in the checking bubbler/μg	< 30*	< 30*	211

*Below the detection limit. For more details see the text.

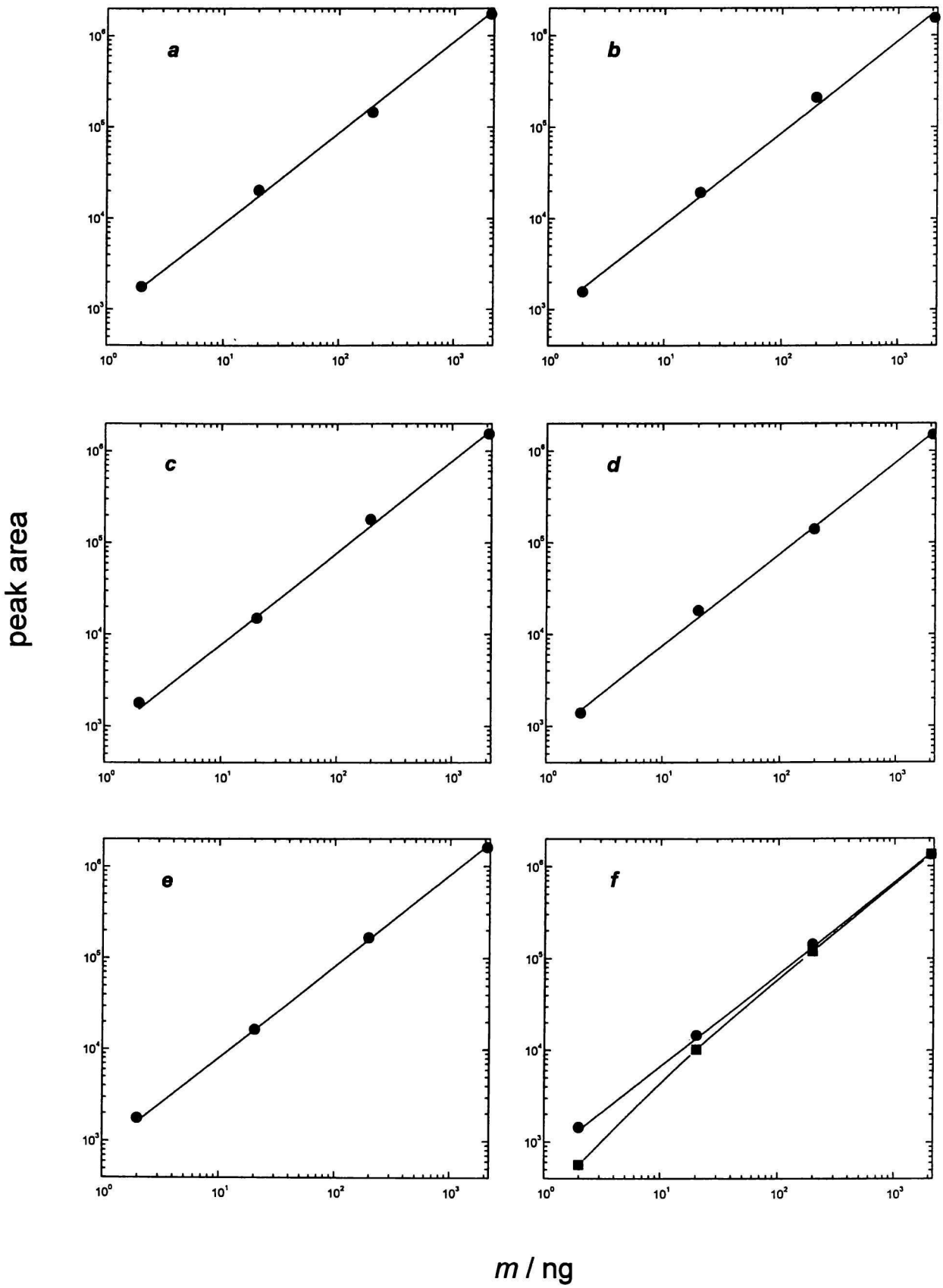

Fig. 2. Calibration curves of analyzed nitrophenols and nitrocresols. *a*) 2-Nitrophenol, *b*) 3-methyl-4-nitrophenol, *c*) 2-methyl-4-nitrophenol, *d*) 3-nitrophenol, *e*) 4-nitrophenol, *f*) 2-methyl-4,6-dinitrophenol (●) and 2,4-dinitrophenol (■).

DISCUSSION

The proposed method is simple and free of time-consuming operations. It does not require expensive chemicals or equipment.

The absorption efficiencies of the majority of non-polar as well as basic organic compounds in basic aqueous solutions can be expected to be very low. Thus the absorption can be expected to be very selective. The probability of interference is furthermore reduced by the pre-extraction of the absorption solution prior to its acidification. Thus the overall selectivity of the method is very high even if nonselective flame ionization detector is used. However, for particular application of the proposed method the presence of actual interfering compounds should be checked and possible interference should be eliminated (preferably by using selective detection technique).

The detection limits achieved allow to determine nitrophenols and nitrocresols in gaseous samples in concentration levels of 0.3—4.2 mg m^{-3} (if 15 dm^3 of sample is passed through the bubblers and if the above described preseparation procedure is used). These limits are by far sufficient for the purposes of determination of nitrophenols and nitrocresols in gaseous samples such as gaseous emissions.

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