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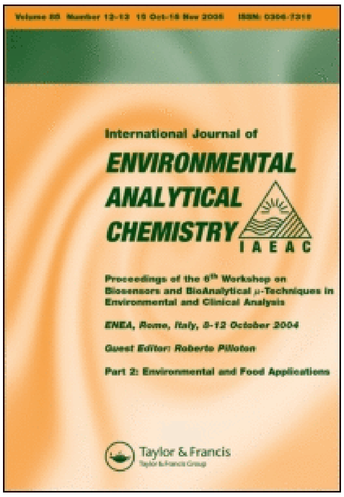

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Generation of Test Atmospheres of 2,4-Dinitrophenol and Evaluation of Sampling Methods for its Determination in Air

M. T. Oms-molla[a][b]; D. Klockow[a]
[a] Institut für Spektrochemie und Angewandte Spektroskopie, Dortmund, Germany [b] Department of Analytical Chemistry, Universitat de les Illes Balears, Spain

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GENERATION OF TEST ATMOSPHERES OF 2,4-DINITROPHENOL AND EVALUATION OF SAMPLING METHODS FOR ITS DETERMINATION IN AIR

M. T. OMS-MOLLA* and D. KLOCKOW

*Institut für Spektrochemie und Angewandte Spektroskopie. Bunsen-Kirchhoff Straße 11,
44139 Dortmund, Germany*

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A dynamic system for producing test atmospheres of 2,4-dinitrophenol through evaporation of solid matter is described. A stream of nitrogen is passed through a thermostated U-tube filled with glass beads coated with 2,4-dinitrophenol, in order to generate a saturated atmosphere of the compound. Performance of the described system at different temperatures, gas flow rates and humidities is shown. The use of impingers and denuder tubes for the collection of gaseous 2,4-dinitrophenol is also investigated.

KEY WORDS: Test atmospheres, denuder tubes, impingers, 2,4-dinitrophenol.

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INTRODUCTION

2,4-Dinitrophenol is listed as one of the priority pollutants by the US Environmental Protection Agency (EPA)[1]. It has been described that dinitrophenol isomers uncouple oxidative phosphorylation and photosynthetic phosphorylation and affect cell metabolism at levels lower than 10 μM[2,3]. Because of these phytotoxic effects, their possible contribution to forest decline has been postulated[4]. They are also suspected to be responsible for some symptoms observed on victims of photochemical smog in Japan[5].

2,4-Dinitrophenol has been found in rain[6] in concentrations up to 4.6 μg L^{-1}. One of the major sources of 2,4-dinitrophenol in air and precipitation is photochemically induced conversion of aromatic hydrocarbons, such as benzene, through OH radicals in the presence of nitrogen oxides[5]. 2,4-Dinitrophenol is also a metabolite of many currently used pesticides such as bromofenoxim, which undergoes photodecomposition with 2,4-dinitrophenol being one of the products[7]. Therefore, the degradation of pesticides containing dinitrated phenol as a building block (e.g. dinoseb, DNOC, bromofenoxim) can also be an important source for this compound in the atmosphere.

The determination of 2,4-dinitrophenol in ambient air requires the development of standard methods for sampling, preconcentration and analysis. In order to assess the performance and efficiency of the sampling devices it is necessary to have available a system capable of producing controlled test atmospheres of the compound of interest.

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*To whom correspondence should be addressed at: Department of Analytical Chemistry. Universitat de les Illes Balears. 07071—Palma de Mallorca. Spain.

Many methods for the generation of test atmospheres have been described which are usually divided into static and dynamic ones. Static methods are based on the introduction of an exactly known amount of a standard substance, either in the form of a gas or a liquid, into a closed vessel. Although they have been successfully applied in certain cases, problems such as adsorption and condensation onto the container walls and difficulties in the preparation of gas mixtures have limited their application. Dynamic methods provide a continuous flow of carrier gas containing a definite amount of the standard substance. They include gas stream mixing, permeation and diffusion systems, injection, evaporation, chemical reaction methods, etc. This great variety makes dynamic methods suitable for the generation of test atmospheres of a wide range of compounds. Other additional advantages over static methods are the possibility to prepare gas mixtures and to use unstable compounds which are impossible to store in static systems.

Dynamic systems based on evaporation of compounds previously deposited on solid supports have been described. Vejrosta *et al.*[8] designed a generator in which saturation was achieved by passing a gas stream through a chromatographic support (Chromosorb P) impregnated with the substance under study. Benzene was employed as a model compound to prepare test atmospheres at ppmv to ppbv concentration levels, with a reproducibility of about 4%. Determination was made by direct injection into a gas chromatograph. A similar system has been described by Meddle *et al.*[9] who used sand impregnated with aromatic amines for the generation of test atmospheres. In this case the volatilized amines were collected using a bubbler, and analysis was carried out by GLC after derivatization.

On the basis of the physical properties of 2,4-dinitrophenol, which is in solid form under normal conditions, a dynamic system to produce test atmospheres through evaporation has been developed. Small glass beads coated with 2,4-dinitrophenol are packed in a U-tube and a gas stream is passed through it. Thus, the contact surface between the compound to be volatilized and the carrier gas is sufficiently large to approach saturation conditions.

The most common methods for collection and preconcentration of gaseous organic pollutants are absorption in a solution and adsorption on solids at ambient temperatures. In this paper, the described generator is used to test the efficiency of impingers and denuder tubes as sampling devices for 2,4-dinitrophenol in the gas phase.

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EXPERIMENTAL

Generation of test atmospheres of 2,4-dinitrophenol

The generator is based on the vapour saturation technique and its scheme is shown in Figure 1.

A stream of nitrogen is passed through a U-shaped glass tube (25 cm length, 0.4 cm i.d.) which is filled with glass beads (1 mm diameter) coated with 2,4-dinitrophenol. A Teflon® filter (0.5 μm pore diameter) is placed behind the U-tube in order to retain any particulate matter formed.

In order to coat the glass beads, a solution containing approximately 10 g L^{-1} of 2,4-dinitrophenol in acetone is prepared. Five mL of the solution are mixed with 5 g of the glass beads (approximately 3000 beads), and the solvent is evaporated under magnetic stirring. Then, the U-shaped glass tube is filled with the coated beads and closed at both ends with glasswool plugs. For control of the temperature, it is placed into a

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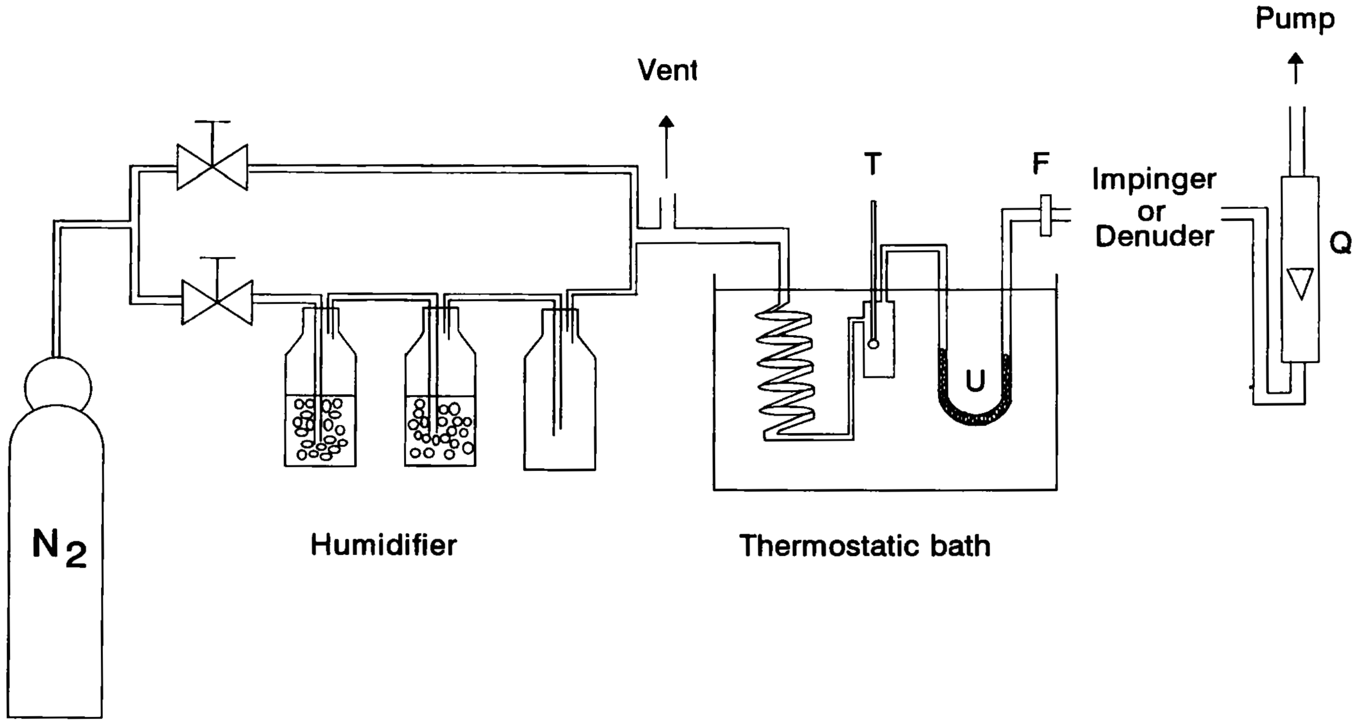

Figure 1 Schematic diagram of the generator used to produce test atmospheres of 2,4-dinitrophenol. F = filter holder, Q = flowmeter, U = U-tube, T = thermometer.

thermostated water bath, and the carrier gas (nitrogen) is allowed to flow through it for 2 hours before any sample is taken. The nitrogen supplied to the U-tube is also thermostated by passing it through a copper coil immersed into the same thermostatic bath. The relative humidity of the carrier gas is controlled and kept constant at values ranging between 2 and 90% by mixing water vapour saturated and dry streams before entering the U-tube.

Collection of 2,4-dinitrophenol vapour

Some experiments were carried out with an impinger containing 5 mL of a 0.01 M NaOH solution and with a nitrogen flow rate of 1 L min^{-1}. After sampling times ranging from 10 to 30 minutes, the solutions were analyzed by HPLC-UV[7] without any further treatment. The generator temperature ranged from 25 to 38°C

For the coating of glass tubes (500 mm length and 6 mm i.d.) to be used as denuders, 1 mL of a solution 0.1 M NaOH and 0.1 M $Ca(OH)_2$ in methanol was placed into each tube which was then slowly rotated horizontally under a dry N_2 stream in order to evaporate the solvent[10,11]. After coating, the denuders were closed at both ends and stored until further use.

For sampling, a piece of uncoated glass tube (150 mm length, 6 mm i.d.) was placed before the coated denuder to ensure that the flow at its entrance was laminar. The carrier gas flow rates ranged from 0.5 L min^{-1} to 1.75 L min^{-1}, and the sampling times were between 5 and 30 minutes.

In order to test the collection efficiency of the denuder tubes, 10 µL of a solution containing 24.74 nmoles of 2,4-dinitrophenol in acetone were pipetted onto the bottom of a U-tube immersed into a water bath at temperatures varying between 20 and 38°C. The tube was immediately connected to a vertically mounted sampling train consisting of a filter holder with a prefilter, the uncoated tube and a denuder in series. Then, a stream of nitrogen with 70% relative humidity was passed at 1 L min^{-1} over the solution in the U-tube for 45 minutes, and the volatilized 2,4-dinitrophenol was collected in the denuder tube.

At the end of each run the U-tube, the prefilter and the uncoated glass tube were rinsed each with 0.5 mL of methanol and the solutions analyzed by HPLC-UV. The material in the denuder tube was analyzed as described in the following section.

Analysis of collected matter

Impinger solutions were injected directly into the HPLC system without any further treatment.

Denuder tubes were extracted with 2 × 1.5 mL of distilled water and the extracts centrifuged for 3 minutes prior to analysis.

The analytical instrumentation consisted of a SYCAM HPLC system equipped with a Rheodyne injector (20 µL sample volume) and coupled to a Waters 440 UV detector operated at 254 nm. For separation, a Nucleosil 300-5 C18 analytical column, 250 × 4.6 mm, 5 µm particle size, was used. A 2 cm long precolumn with the same characteristics was placed before the analytical column.

The mobile phase was acetonitrile/water (50:50, v/v) containing 0.02 M sodium acetate with the pH adjusted to 3.5 by adding acetic acid. The flow rate was 0.9 mL min^{-1} and the temperature 25°C. All solvents were distilled and degassed with helium before they were used.

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RESULTS AND DISCUSSION

Employing the described HPLC conditions, the retention time for 2,4-dinitrophenol is 3.9 minutes, the calibration function is linear up to 80 μM and the determination limit is 0.1 μM.

Retention of 2,4-dinitrophenol vapours in the prefilter and uncoated tube

Four different types of filters were investigated to be used as prefilters: Teflon® (Millipore 0.45 μm), cellulose (Whatman 41), glass fiber (Schleicher & Schuell) and Nylon (Millipore AH 0.45 μm). 2,4-Dinitrophenol vapours were observed to be retained in cellulose (> 90%), glass fiber (> 30%) and nylon filters (> 50%), while no 2,4-dinitrophenol could be detected in the teflon filter in the temperature range from 20 to 38°C, 70% relative humidity and carrier gas flow rates from 0.5 to 1.75 L min^{-1}. In all subsequent experiments Teflon® filters were used to eliminate any possible particulate matter coming from the test atmosphere generator.

Deposition on the walls of the uncoated tube placed before the denuder was observed to be dependent on the temperature of the U-tube generator and the carrier gas flow rate. No deposition was observed in the temperature range of 20–25°C and at flow rates of 0.5–1.75 L min^{-1}. At higher temperatures deposition increased when carrier gas flow rates decreased. For instance, at 30°C wall losses were up to 15% with a carrier gas flow of 0.5 L min^{-1} while they where only 4% at carrier gas flows higher than 1 L min^{-1}. The same tendency was observed a 38°C with wall losses of 25% at 0.5 L min^{-1} of carrier gas and only 5% when the flow was equal to or higher than 1 L min^{-1}. The reason for these losses most probably is the difference in temperature between the saturated gas at the exit of the generator and the sampling device placed at ambient temperature (22°C) such causing condensation of 2,4-dinitrophenol vapour on the colder surface.

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Denuder sampling and analysis

Denuder tubes coated with NaOH-$Ca(OH)_2$ have been successfully applied to the collection of vapours of carboxylic acids, namely formic, acetic and propionic acids[10,11]. According to the authors, the efficiency of carboxylic acid deposition in NaOH coated tubes is higher than 98%. However, the stability of the coating is poor under high humidity conditions due to the hygroscopic behaviour of NaOH. The addition of $Ca(OH)_2$ increases the stability of the coating, thus allowing one to work under high relative humidity conditions even at long sampling times (24 hours). Because of the pK_a of 2,4-dinitrophenol (3.94) it was expected that the same coating might also be used for the collection of its vapours.

Collection efficiency of the denuder tubes coated with NaOH-$Ca(OH)_2$ was determined by comparing the absolute amount of 2,4-dinitrophenol found in a denuder with the absolute amount left in the U-tube (Table 1). An average collection efficiency of 97.5% ± 4.2 was achieved.

Test atmosphere generator

Although in solid form under normal conditions, the vapour pressure of the solid (5.39×10^{-3} Pa at 25°C and 1 atm) suggests that this compound will be found also in the gaseous phase of the atmosphere.

Table 1 Collection efficiency for 2,4-dinitrophenol vapour in denuder tubes coated with $Na(OH)$-$Ca(OH)_2$. Tubes: 50 cm length, 0.6 cm i.d., absolute amount placed into the U-tube: 24.74 nmoles, flow rate 1 L min^{-1}, relative humidity 70%.

Run time (min)	*Amount added—amount left in U-tube (nmol)*	*Amount found in the denuder (nmol)*	*Recovery %*
45	17.51	17.36	99.2
45	17.30	15.94	92.2
45	16.03	15.59	97.9
30	15.64	15.04	96.2
30	15.19	14.22	93.6
30	15.11	14.52	96.1
20	9.20	9.62	105.7
10	4.67	4.65	99.6

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With the purpose of generating a test atmosphere for calibration and comparison of sampling devices, a dynamic system based on the evaporation of the solid was built. The aim was to produce a stream of saturated vapour that could be subsequently diluted by mixing it with another gas stream. The vapor saturation method has the advantages of requiring only simple equipment, minimum maintenance, relatively short time periods of stabilization after changing conditions and, the most important aspect, of calculating the gas phase concentration (C) of 2,4-dinitrophenol from the relationship[8]:

$$C = \frac{p_i M}{RT} \; \frac{P}{P - p_i}$$

where p_i is the vapour pressure of the component, M is its molecular weight, T is the absolute temperature of the saturator (thermostatic bath), R is the universal gas constant and P is the total gas pressure.

On the basis of this equation and vapour pressure values of solid 2,4-dinitrophenol[12], vapor phase concentrations in the saturation equilibrium were calculated and used as a reference.

First attempts based on passing a gas stream over the solid compound directly were unsuccessful, not only because of the low concentrations achieved (only 10% of the theoretical values) but also because of the large amount of particles generated, which deposited in the connecting tubes and led to irreproducible results.

In order to approach the saturation condition, the set-up described in the experimental section, with coated glass beads, was built. The use of small glass beads as an inert support for solid 2,4-dinitrophenol substantially increased the contact surface between the carrier gas and the compound, thus facilitating the establishment of equilibrium.

Table 2 shows the concentrations of 2,4-dinitrophenol at different temperatures calculated on the basis of saturation equilibrium, and the measured concentrations when an impinger and a denuder tube were used as devices for its collection from the test atmospheres. The results show that the saturation condition was reached with the described device and that test atmospheres of 2,4-dinitrophenol in the concentration range of 1 to 10 µmol m^{-3} could be generated at temperatures between 20 and 38°C.

The stability of the generation system was checked up daily during two weeks. Three samples were taken every day at 25°C using denuder tubes for the collection of 2,4-

Table 2 Comparison of calculated and measured test atmosphere concentrations of 2,4-dinitrophenol collected with impinger (5 mL NaOH, 0.1 M) and denuder tubes (50 cm length, 0.6 cm i.d.) coated with NaOH-Ca(OH)$_2$. The generation system is that shown in Figure 1. Carrier gas: dry nitrogen at 1 L min^{-1}.

		Impinger				*Denuder*			
T (°C)	*Calc.conc. (equation 1) (μmol m^{-3})*	*N*	*Conc.found (μmol m^{-3})*	*RSD %*	*Recovery %*	*N*	*Conc.found (μmol m^{-3})*	*RSD %*	*Recovery %*
20	1.08	4	0.57	7.1	53.1	–	–	–	–
22	1.43	–	–	–	–	4	1.40	16.9	97.7
25	2.18	5	1.30	3.9	59.7	6	2.03	5.3	94.0
30	4.31	4	2.43	8.2	56.3	4	4.10	6.1	95.1
33	6.41	4	3.48	9.3	54.3	4	6.24	4.4	97.4
38	12.22	5	4.23	11.1	34.6	5	11.16	7.7	91.3

dinitrophenol at a sampling flow rate of 1 L min^{-1}. The mean value of 21 determinations was 2.06 ± 0.28 μmol m^{-3}.

The influence of humidity on the generation and collection of gaseous 2,4-dinitrophenol was tested using a nitrogen flow rate of 1 L min^{-1} with relative humidities varying between 0 and 90%. The water bath temperature was 25°C. In Table 3 results of analyses of generated atmospheres show that there is no influence due to relative humidity of the carrier gas.

Comparison of impinger and denuder sampling

Comparison of collection efficiencies of impinger and denuders (Table 2) shows that 2,4-dinitrophenol vapours are quantitatively adsorbed in denuder tubes (in agreement with the results above), whereas the recovery in case of impinger is only around 50% due to adsorption of 2,4-dinitrophenol along the walls of the inlet tube. The relatively large volume of absorber solution leads to low analyte concentrations which are sometimes

Table 3 Concentration of 2,4-dinitrophenol in test atmospheres at several relative humidities. Carrier gas: 1 L min^{-1} of nitrogen, temperature 25°C. Collection with NaOH-Ca(OH)$_2$ coated denuder tubes, sampling time 5 minutes. Calculated concentration (saturation equilibrium): 2.18 μmol m^{-3}.

RH (%)	*N*	*Concentration μmol m^{-3}*	*rsd %*
0	3	2.15	1.2
15	3	2.12	8.2
22	2	2.16	8.4
30	3	2.12	5.1
45	2	2.01	2.5
60	3	2.10	0.5
70	2	2.24	2.5
80	2	2.00	8.5
90	2	2.14	1.2

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near the detection limit thus causing large errors in the quantitative determination. As mentioned above, denuder tubes showed a high efficiency for collection of 2,4-dinitrophenol and they allow also separation of gaseous and particulate fractions. Other advantages such as little effect of relative humidity of the carrier gas on collection efficiency, reasonably high sampling flow rates and the possibility of being exposed for long sampling periods in ambient measurements make denuders a more suitable device for the collection of 2,4-dinitrophenol vapours. Because of these reasons they were used as collectors in experiments of optimization of the generation system.

CONCLUSIONS

The described system based on evaporation of solid 2,4-dinitrophenol has been found to be a reliable method to generate test atmospheres of this compound. The use of glass beads which act as an inert support for solid 2,4-dinitrophenol, allows the saturation equilibrium to be reached within 1–2 hours. The concentrations of 2,4-dinitrophenol in the generated test atmospheres are in good agreement with the calculated ones. No influence of the relative humidity of the carrier gas on the generator output and the denuder collection efficiancy was observed.

In case impingers are used for collection of 2,4-dinitrophenol, prefilters made of Teflon® have to be employed to remove particulate matter. This is not necessary when denuder tubes with a $NaOH$-$Ca(OH)_2$ coating are used for sampling. In addition, the collection efficiency of denuders (97% in average) is much higher than that of impingers ($\leq 55\%$).

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