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Gas chromatographic determination of nitrophenols in atmospheric liquid water and airborne particulates

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ABSTRACT

A method for the determination of nitrophenols in fogwater and atmospheric particles is presented. The gas chromatographic (GC) performances of the underivatized pure compounds and their corresponding acetate esters were compared using four fused-silica columns with three alternative detection modes, *viz.* mass-selective detection, nitrogen-specific detection and electron-capture detection (ECD). Splitless injection of pure nitrophenols suffered from adsorption in the GC system causing unacceptable imprecision in the quantification of semi-volatile nitrophenols. The separation of nitrophenols as their corresponding acetates and ECD improved the GC performance and the analytical results. Acetylation with acetic anhydride in alkaline aqueous solution was found to be a very specific, uncomplicated and rapid method of derivatization. Its high sensitivity and accuracy and excellent suitability for analysing complex aqueous samples such as fogwater is demonstrated in detail as part of a multi-residue procedure.

INTRODUCTION

In 1976, Noijma *et al.* [1] reported the identification of nitrated phenols as secondary pollutants in the urban atmosphere. In their study, and subsequently more intensively [2,3], smog chamber experiments provided evidence for the photochemical generation of nitrated phenols from primary emissions such as aromatic hydrocarbons and nitrogen oxides. However, these is also sufficient evidence for direct emissions from cars [4,5]. In view of the toxic potential of nitrophenol (some dinitrophenols have been used as pesticides with a broad application), it is surprising that the potential for formation of nitrophenols in the atmosphere has not yet been thoroughly investigated. Also, monitoring data have only sporadically been published [5–10]. In connection with research on forest decline, attention has recently been focused on high concentrations of nitrated phenols in atmospheric liquid water [5–8]. Concentrations in cloud- and fogwater exceeding 1 μmol l^{-1} for 4-nitrophenol and 0.5 μmol l^{-1} for highly phytotoxic dinitrophenols[4] raise the questions of the sources, the fate and also the possible toxic effects of these compounds in the corresponding forest ecosystems. Expecting more research activity in this field, we see a need for sophisticated and time-effective analytical schemes by which nitrophenols can be determined reliably in complex matrices such as fogwater, air samples, humic soils or foliage. Many analytical procedures published in recent years [11–14] (see Böhm *et al.* [14] for more

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literature) did not solve this analytical problem satisfactorily with respect to extraction efficiency, sensitivity and selectivity of detection.

Unlike polycyclic aromatics and semivolatile organochlorine pollutants, which can be efficiently extracted from water and separated from the more polar fraction of airborne organics with the help of silica or Florisil columns, similar procedures seem more complicated for polar nitrophenols. Among the great number of organic acids, phenols and carbonyls present in atmospheric samples, nitrophenols can only be separated by means of highly selective detection and/or a distinctive sample preparation taking into account their moderate vapour pressures [15]. With nitrophenols, high-performance liquid chromatography coupled with UV detection, preferably applied for the analysis of phenolic compounds, does not achieve the resolution capacity and selectivity of detection [14] that is achieved in modern gas chromatography (GC). Moreover all isomeric nitrophenols in the atmosphere must be properly identified first, partly without authentic standards. Therefore, it seemed most useful to develop a procedure with the option of GC coupled with mass selective (MS) detection.

In the past, the conversion of phenols to methyl, silyl and pentafluorobenzyl ethers or acetyl derivatives has widely been used to improve their GC performance [13,16,17]. Owing to progress in column manufacture, good chromatographic behaviour is now also claimed for acidic and highly polar underivatized nitrophenols [6] (see also technical notes of column manufacturers). In the first part of this paper pure nitrophenols and their corresponding acetates are compared with respect to their GC performance. Subsequently a modified procedure is presented for the derivatization of nitrophenols with acetic anhydride.

EXPERIMENTAL

Reagents and apparatus

Nitrophenol standards were purchased from Fluka and Aldrich internal standards 2,3,4,5-Tetrachlorophenol (TClP) and aldrin from Promochem. Technical-grade solvents were distilled twice before use. Stock standard solutions of individual nitrophenols of 2 g l^{-1} were prepared in acetone. Standard mixtures for the determination of recoveries and demonstration runs were prepared in pentane–acetone (5:1) (organic standard solution, Table I) and in 0.1 *M* potassium carbonate, referred to as an aqueous standard solution. Calibration samples consisted of an appropriate dilution of this aqueous standard solution in 1.95 ml of 0.1 *M* potassium carbonate. Internal standard solutions containing 10 μmol l^{-1} of TClP in 0.1 *M* potassium carbonate denoted quantification standard (IS_{TClP}), and 0.41 μmol l^{-1} of aldrin in hexane (injection standard, IS_{ALD}) were used. Nitrophenols and internal standards and their concentrations used in demonstration runs are given in Table I.

Bistabil continuous liquid–liquid extraction apparatus and centrifuge tubes were purchased from Brand (Wertheim, Germany). Modified frits of porosity 1 with a cylindrical reservoir 50 mm × 20 mm I.D.) were manufactured by Brand according to our design. GC-analysis was performed on a Varian 3700 instrument with electron-capture (ECD) and nitrogen thermionic-specific detection (TSD). GC–MS runs were made on a Hewlett-Packard HP 5890 gas chromatograph directly coupled to a Model 5790 mass-selective detector. New GC columns from Durabond (DB 5, and DB 17, both 30 m × 0.25 mm I.D., 0.25 μm) J & W (SE-54, 30 m × 0.25 mm I.D. 0.25 μm)

TABLE I

IDENTIFICATION NUMBERS OF NITROPHENOLS AND INTERNAL STANDARDS (IS)

Concentration of pure nitrophenols in the organic standard solution used in demonstration runs in Figs. 1a, 1b and 2a.

Identification number	Compound	Abbreviation	Concentration (μmol l^{-1})
1	2-Nitrophenol	2-NP	3.63
2	3-Methyl-2-nitrophenol	3M-2NP	1.91
3	4-Methyl-2-nitrophenol	4M-2NP	3.32
4	5-Methyl-2-nitrophenol	5M-2NP	1.90
5	2,6-Dinitrophenol	2,6-DNP	0.85
6	3-Nitrophenol	3-NP	6.27
7	2,4-Dinitrophenol	2,4-DNP	11.2
8	4-Nitrophenol	4-NP	5.27
9	4-Methyl-2,6-dinitrophenol	4M-2,6DNP	1.81
10	3-Methyl-4-nitrophenol	3M-4NP	4.44
11	6-Methyl-2,4-dinitrophenol	6M-2,4DNP	4.57
12	2,6-Dimethyl-4-nitrophenol	2,6dM-4NP	4.36
13	2,3,4,5-Tetrachlorophenol	IS_{TCIP}	0.50
14	Aldrin	IS_{ALD}	0.41

and Hewlett-Packard (Ultra 2, 25 m × 0.2 mm I.D., 0.33 μm) were tested. Injection sleeves were freshly silanized prior to the injection of pure nitrophenols.

Procedure

The analytical scheme is organized in six steps as follows: (1) sample extraction; (2) concentration; (3) dissolution in hexane; (4) acid–base partitioning; (5) derivatization with acetic anhydride; and (6) extraction of the acetylated nitrophenols into 1 ml of hexane.

Sample extraction. Atmospheric liquid water is continuously liquid–liquid extracted as follows: pour 80 ml of CH_2Cl_2 into a 250-ml Bistabil liquid–liquid extractor, carefully overlay the solvent with 250 ml of the sample containing 20 g of dissolved NaCl and allow most of the solvent to rinse down into the boiling reservoir. Wash the sample vessel with 30 ml of purified water and add the washings to the sample. Pour more water into the extraction apparatus until the solvent layer is about 20 mm high. Acidify with 0.4 ml of concentrated H_2SO_4, insert the frit, wash the empty sample vessel with 20 ml of CH_2Cl_2, and add the washings to the extractor. In some instances it may be necessary to improve the operation of the frits with the help of a small layer of sea sand in the solvent reservoir of the frits. Run the extraction for 5 h with moderate heat, keeping a flow of about 4 drops s^{-1} from the reflux condenser. After extraction, the solvent underlying the aqueous sample is combined with the solvent in the boiling reservoir. Atmospheric particles filtered from 50–500 m^3 of air on a glass-fibre filter are extracted ultrasonically with 80 ml of CH_2Cl_2. The extract is cleaned from the filter material by centrifugation or filtration over anhydrous Na_2SO_4.

Concentration. Extracts of CH_2Cl_2 are concentrated to about 3 ml by means of a rotary evaporator. The extract is transferred to a 10-ml narrow-bottomed cen-

trifuge tube. At this point storage is recommended until the number of samples has reached 20 or more, allowing the following steps to be done more efficiently.

Solvent exchange. Reduce the volume of CH_2Cl_2 extracts obtained after the previous step to 0.3 ml under a gentle stream of nitrogen with the tubes maintained at room temperature by means of a water bath. Fill to 4 ml with hexane and blow down to 3 ml.

Acid–base partitioning. Add 2.0 ml of 0.1 *M* K_2CO_3 buffer solution of the sample using a transfer pipette, shake vigorously, centrifuge to improve phase separation and transfer 1.95 ml of the buffer extract into a 10-ml round-bottomed centrifuge tube with the help of a transfer pipette and disposable plastic tips.

Derivatization. After atmospheric samples and calibration samples have been spiked with 50 μl of IS_{TCIP}, add exactly 75 μl of acetic anhydride using a transfer pipette, quickly seal the tube and shake it immediately, then open the tube.

Extraction of acetylated phenols. After completion of derivatization of all samples and standards, add 1 ml of IS_{ALD} (reaction time is not critical and hydrolysis of esters has not been observed). In order to drive out CO_2 and suppress coextraction of underivatized acids and phenols, add *ca.* 0.5 g of a mixture of K_2HPO_4 and KCl (2:1), raising the pH to *ca.* 6–7. Shake vigorously for about 10 s. Store the sample at −20°C until analysis within 1 week or remove the hexane extract from the frozen aqueous layer when further concentration or storage over several months is required.

RESULTS AND DISCUSSION

GC performance and detection of nitrophenols

Underivatized nitrophenols. Some pure nitrophenols have been reported to be successfully separated and quantified on suitable fused-silica capillary columns [6].

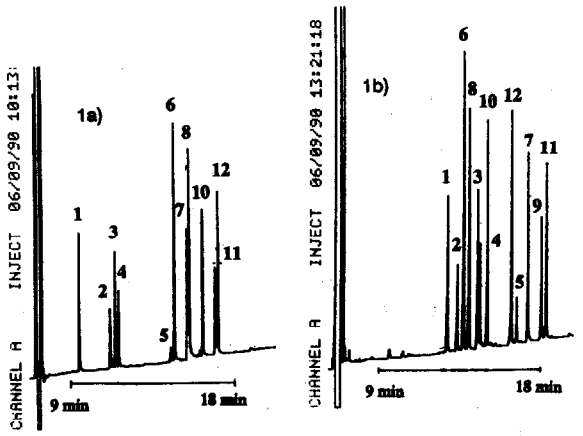

Fig. 1. GC performance of (a) pure nitrophenols and (b) corresponding nitrophenyl acetates on a new Ultra 2 column as specified with nitrogen-specific detection (TSD). Temperature programme: 50°C, held for 1 min, increased at 8°C min^{-1} to 270°C, held for 3 min. (a) Splitless injection of 2 μl of organic standard solution. Peak identification and concentrations as given in Table I. (b) The analytical procedure was started in step 4 (see *Procedure*), after 1 ml of organic standard solution had been redistributed in 3 ml of pentane. If complete derivatization and extraction are assumed, the concentrations of nitrophenyl acetates correspond to those listed in Table I.

Our efforts to determine pure, semi-volatile nitrophenols without the help of labelled standards, however, were not very encouraging, as shown in Fig. 1 and Table II. Comparing the chromatographic performances of underivatized nitrophenols on an HP Ultra 2 column (the most suitable for pure nitrophenols) with that of the corresponding acetates reveals better separation and better peak shapes of lower volatile 4-nitrophenols after acetylation. The precision of quantification (s_w) for underivatized 4-nitrophenols, 4-nitrocresols and dinitrophenols, referred to as semi-volatile nitrophenols (SVNP), turned out to be unsatisfactory, whereas more volatile 2-nitrophenols and 2-nitrocresols (VNP) exhibited excellent reproducibilities.

It must be noted that for demonstration purposes the concentrations of dinitrophenols were set disproportionately high in comparison with mononitrophenols (Table I). In real atmospheric samples 4-nitrophenol loadings normally exceed those of dinitrophenols considerably [5,8]. The low sensitivity for dinitrophenols (response factor, RF_{TSD} = 2.55) and high imprecision of quantification for all SVNPs indicate uncontrolled adsorption in the GC system. This is most valid for 2,4-DNP with the most acidic hydroxyl group (pK_A = 3.91) [15]. Theoretically the response factor of dinitrophenols on a nitrogen-specific detector should be RF_{TSD} = 0.5 if related of 2-NP. These great deviations between expected and measured TSD response factors suggest severe losses in the chromatographic system. Adsorption to active OH sites, existing in the GC inlet and on the column, is well known for semi-volatile polar compounds and for some nitrophenols in particular. This becomes obvious by a low specific response of dinitrophenols, their decreasing abundance with impurities in the inlet, column age and by parabolic calibration graphs (disproportionate response with increasing concentrations). Taking less volatile 3-NP as a reference compound for SVNPs hardly reduced the imprecision. Hence, shortcomings of injecting pure nitrophenols as described above can only be solved with the help of labelled standards. As critical SVNPs behave very differently in the chromatographic system one standard for each nitrophenol is necessary.

Nitrophenyl acetates. As is shown in Table II, acetylation improved the precision of quantification of SVNPs whereas it remained the same for VNPs. A similar quality of data was obtained for MS detection of acetylated mononitrophenols (not shown). Surprisingly, severe losses in sensitivity have been observed in MS detection of acetylated dinitrophenols. As we conclude from runs with TSD, this low sensitivity is not caused by incomplete derivatization of dinitrophenols alone (see below). Obviously dinitrophenyl acetates produce much less stable ions (*e.g.*, for 2,4-dinitrophenyl acetate the most abundant ions are m/z = 226, 184, 168 and 154) than acetylated mononitrophenols. Owing this disadvantage GC–MS quantification of nitrophenols as their acetates is of limited application.

Unacceptably high standard deviations for dinitrophenyl acetates measured with TSD (Table II) may be caused by uncontrolled discrimination in the injection port. Splitless injection and TSD of acetylated nitrophenols also showed severe deviations from linearity in calibration runs covering one order of magnitude. These sources of error, often lying in the injection port, can be substantially suppressed with on-column injection or injection in the split mode and quantitative analysis within a narrow range of concentration, *e.g.*, one order of magnitude. Split injection does not impair the sensitivity for acetylated nitrophenols if highly sensitive ECD is employed. However, in order to use ECD, prior effective sample clean-up is necessary.

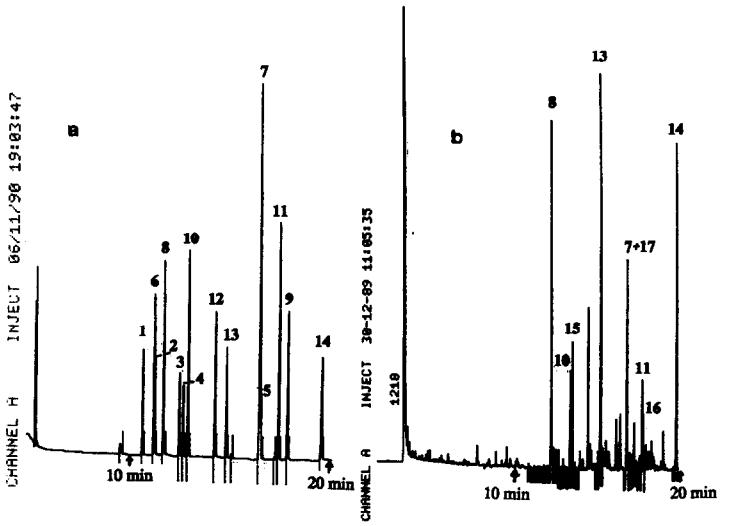

Fig. 2. GC–ECD of nitrophenyl acetates on a DB-17 column as specified. Chromatographic conditions and sensitivity as used in routine analysis: column temperature increased from 110 to 270°C at 6°C min^{-1}, splitting ratio 1:20, injection volume 2 µl. (a) Standard mixture obtained as decribed for Fig. 1b, diluted 1:2 prior to injection, giving *ca.* 0.4 pmol of 4-NP acetate on the column. (b) Moderately polluted cloudwater sample. Peaks: 15 = 2-M-4-NP; 16 = nitrated phenol (not further identified); and 17 = most probably 3-M-2,4DNP.

TABLE II

RESPONSE FACTORS (*RF*) IN RELATION TO 2-NP AND IMPRECISION (s_w, n = 4) OF VARIOUS PURE NITROPHENOLS AND THEIR CORRESPONDING ACETATES WITH NITROGEN TSD, MS AND ECD

s_w = (Standard deviation/mean value) · 100%.

Compound	Pure phenols[a]				Nitrophenyl acetates[b]			
	RF_{MS}	s_w (%)	RF_{TSD}	s_w (%)	RF_{TSD}	s_w (%)	RF_{ECD}	s_w (%)
2-NP	1.00	–	1.00	–	1.00	–	1.00	–
3M-2NP	2.59	6	1.09	1	1.09	2	[c]	
4M-2NP	0.84	4	1.02	1	0.97	2	0.94	1
5M-2NP	0.87	4	0.98	1	0.93	2	0.70	1
2,6-DNP	[d]		[d]		0.87	13	[c]	
3-NP	1.46	13	1.05	14	0.95	2	[c]	
2,4-DNP	4.45	29	2.55	38	2.83	17	0.75	4
4-NP	1.73	17	0.96	18	1.04	2	0.74	2
4M-2,6DNP	[d]		[d]		0.69	6	0.31	2
3M-4NP	2.74	14	1.03	16	1.02	2	0.58	1
6M-2,4DNP	1.44	25	1.64	29	1.23	6	0.46	2
2,6dM-4NP	0.65	19	0.94	6	0.96	7	0.78	3

[a] Concentration of organic standard solution as shown in Table I and used for Fig. 1a.
[b] For concentrations see Table I and legend of Fig. 1b.
[c] Coelution with another compound.
[d] Peak area to small.

Fortunately in alkaline solution acetic anhydride reacts preferably with phenolate anions to form corresponding acetates. This offers the opportunity of combining an acid–base extraction with a specific derivatization procedure in order to discriminate neutral compounds and organic acids. Fig. 2 may demonstrate that this easy and rapid fractionating leads to smooth chromatograms where all relevant aqueous phase nitrophenols can properly be quantified in a short run of 20 min. In samples of fogwater and atmospheric particles the peak of 2,4-DNP exactly combines with that of another nitrated phenolic compound, either 3-M-2,4-DNP or 5-M-2,4-DNP. These dinitrophenols (2,4-DNP, 2,6-DNP and *n*-M-2,4-DNP) are sufficiently separated on an SE-54 or an Ultra 2 column as specified. Despite a similar coating, the DB 5 column exhibited unacceptable peak tailing for nitrophenyl acetates.

Analysis of nitrophenols as nitrophenyl acetates

Derivatization and calibration graphs. The absolute recovery of the analytical procedure, starting in step 4 with 5 nmol of 4-nitrophenol in 3 ml of hexane, was measured to be 81%. This value is related to an equally concentrated standard solution of 4-nitrophenyl acetate in hexane. Incomplete extraction of the esters into 1 ml of hexane accounts for most of these losses. In contrast, extraction of nitrophenols from hexane into the K_2CO_3 solution (volume corrected as 1.95 ml out of 2 ml of buffer solution are recovered) and the yield of derivatization were determined for 4-nitrophenol to be close to 100%. Almost equal response factors of other mononitrophenols on a nitrogen-specific detector (RF_{TSD}) indicate a similar behaviour of all mononitrophenols in the acetylation procedure and the CG system. On the other hand considerably lower RF_{TSD} values for 6-M-2,4-DNP and most striking for 2,4-DNP (Table II) suggest incomplete acetylation. In addition, incomplete derivatization of dinitrophenols is also proved by coextraction of pure dinitrophenols and the remaining yellow colour of highly loaded buffer extracts after acetic anhydride has been added. It is also worth mentioning that the derivatization yields were higher for 4-M-2,6-DNP and 2,6-DNP than for 2,4-dinitrophenols.

In alkaline solution acetylation proceeds via a nucleophilic attack of the phenolate species on an acetyl C atom, producting acetic acid. Acetylation of phenols in alkaline media has to compete with the consumption of acetic anhydride by OH^- first, and with the final depression of pH to about 4 (using 75 μl of acetic anhydride for 2 ml of 0.1 *M* K_2CO_3). The derivatization yield should, therefore, depend greatly on the individual reaction velocity of the deprotonated species. Acetylation of phenolate anions with strong nucleophilic properties (indicated by high pK_A values of the corresponding acid) keeps pace with the pH depression and removal of acetic anhydride. This explanation fits well with increasing yields of acetylation in the order 4-NP (pK = 7.08) > 6-M-2,4-DNP (pK = 4.31) > 2,4-DNP (pK = 3.94).

Efforts to increase the derivatization yield included the use of different molarities of the K_2CO_3 buffer solution, replacement of K_2CO_3 with $KHCO_3$, variable amounts of acetic anhydride, elevated reaction temperatures and reaction times lasting from 1 min to several hours, but with no significant success. Parameters governing reproducibility of the derivatization reaction were found to be a constant volume of buffer solution and acetic anhydride and rapid mixing of the reactants. These conditions can be easily controlled in this micro-derivatization technique to give a linear and reproducible derivatization within a concentration range spanning at least one order of magnitude (Fig. 3).

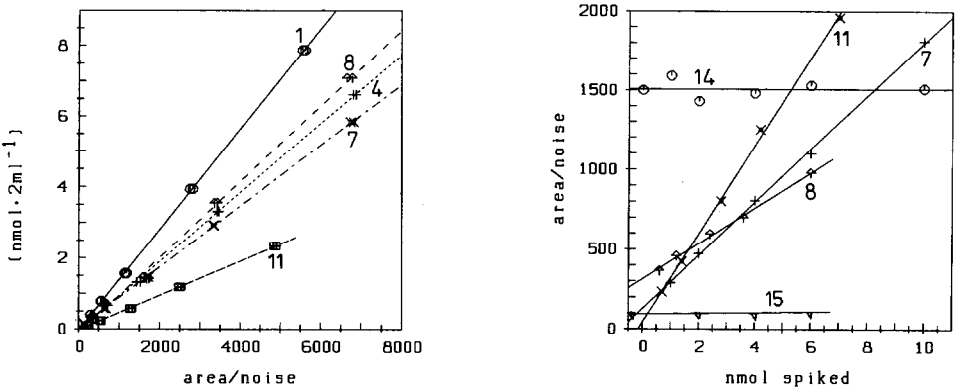

Fig. 3. Calibration lines for selected nitrophenyl acetates. Concentrations given refer to pure nitrophenols in calibration samples (1.95 ml of aqueous standard mixture plus 50 μl of IS_{TCIP}) ready to be derivatized. Noise calculated by the automatic peak threshold function of a Spectra-Physics integrator in front of the 2-NP peak.

Fig. 4. Determination of calibration data for a diluted fogwater sample using the standard addition method. 15 = Relative abundance of 2-M-4P (not spiked) in relation to the quantification standard IS_{TCIP}; 14 = relative abundance of Aldrin in relation to IS_{TCIP}.

Matrix effects. Incomplete derivatization may lead to variable yields of acetylation at different concentrations or from sample to sample. However, despite the incomplete conversion of dinitrophenols, acetylation proceeds rigorously, and is not affected by the addition of 1 ml of hexane, 0.1 g of NaCl, 10 μmol of benzoic acid and 10 μmol of *p*-cresol to 2 ml of buffer solution; note that these amounts are 1000 times higher than the nitrophenol content. Although none has been observed so far, any irregularity with the derivatization step can be readily checked for each individual sample by calculating the relative abundance of a neutral compound and one or more phenolic internal standards. Equal peak-height ratios of the quantification standard IS_{TCIP} (Fig. 4), which is acetylated and coextracted together with nitrophenols and the injection standard IS_{ALD} added after the derivatization step indicate the absence of concentration and matrix effects. Also some smaller peaks, *e.g.*, 2-M-4-NP, retain their initial peak area irrespective of the total amounts of phenols to be derivatized. Consequently, the results of quantitative analysis of a sample using response factors obtained from standard solutions did not deviate significantly from the concentrations measured by internal standard addition (Table III, Fig. 4). This check for matrix effects was applied to difficult samples such as samples of high inversion fogs and of canopy throughfall with no interference.

Recovery experiments and determination limits. Recoveries of analytical standards from spiked drinking water were determined for moderately concentrated samples (Table IV) and at a recommended lower limit of determination of one tenth of the concentration listed. Individual recoveries refer to the concentrations of nitrophenols in 1.95 ml of buffer solution obtained after step 4 (see *Procedure*), and do not include the losses in the derivatization reaction and the final extraction step. These losses are the same of calibration samples which are also prepared in 1.95 ml of buffer solution.

TABLE III

CONCENTRATION OF NITROPHENOLS IN THE BUFFER EXTRACT OF A DILUTED FOG-WATER SAMPLE OBTAINED AFTER STEP 4

Determined using calibration graphs for pure standards (= external calibration) and by means of the standard addition method. Two parellels were combined before injection. See also Fig. 4. H = sensitivity = dx/dc, where x = peak area/baseline noise in calibration runs of pure standards and c = concentration.

Compound	External calibration		Standard addition	
	μmol l^{-1}	H	μmol l^{-1}	H
4-NP	2.6	123	2.8	111
3M-4NP	0.81	174	0.75	167
2,4-DNP	0.63	152	0.67	149
6M-2,4DNP	0.15	271	0.15	276

As is shown, the total recovery, including buffer extraction, concentration and extraction from water, is excellent, Slightly higher standards deviations for dinitrophenols extracted from artificial aqueous samples are due to the derivatization reaction and the GC performance of these compounds. As the defined lower limit of determination in spiked drinking water the recovery was almost the same, with an imprecision still lower then 12% for SVNPs. At this level peak-to-noise ratios greater then 50:1 indicate that the overall sensitivity of this method is not fully exhausted.

Considerable losses occur in the extraction of VNPs from aqueous samples because of their coevaporation during the extraction and concentration step. However, this is not a problem as atmospheric liquid water usually shows VNP concentrations lower than 5 nmol l^{-1} and mostly less than 1% of 4-nitrophenol loadings [5,8,19]. Moreover, using this method the higher baseline noise in real rain- and fogwater samples impairs the proper determination of VNPs at their naturally occurring concentrations in rural areas. Apart from this, standard-derived imprecision

TABLE IV

RECOVERY FROM 250 ml OF SPIKED DRINKING WATER AND IMPRECISION (s_w, n = 5) OF THE OVERALL ANALYTICAL PROCEDURE

Compound	Level (nmol l^{-1})	Recovery (%)	s_w (%)
2-NP	20	61	23.0
4M-2NP	24	69	21.0
3M-2NP	10	80	15.0
5M-2NP	10	75	23.0
4-NP	22	98	3.4
3M-4NP	6	99	3.1
2,6dM-4NP	10	99	4.4
2,4-DNP	8	94	6.5
6M-2,4DNP	4	102	5.5

data and consequently lower limits of determination rarely apply for real samples. We also note that accurately defined limits of detection and determination imply reliable verification of the compounds measured. This rule, however, is often violated in highly sensitive but rather unspecific ECD and UV detection, if detection limits are calculated as a multiple of peak-to-noise ratios in calibration runs and peaks are identified from their retention times only. In view of this limitation, attention should be directed to the replicate analysis of real samples (Table V). At these low amounts compounds still can be verified in the individual sample using MS or TSD.

Quantitative analysis of a routine basis. Owing to the characteristics of ECD (high sensitivity but a narrow linear range), high-quality results necessitate multiple point calibration and a narrow span of concentrations. Dissociated nitrophenols exhibit an intense yellow colour, which offers the possiblity of dilution of unexpected highly loaded samples at this stage of the analytical scheme. As the individual composition of one kind of sample does not vary much from that of another, the concentration of the most abundant nitrophenols can be visually estimated within one order of magnitude. Hence one can adjust the concentration of the buffer extract to fit into the range of calibration samples. Addition of the quantification standard IS_{TCIP} after step 4 (see *Procedure*) also produces an equal abundance of the standard compound in calibration runs and samples to be measured. For many quantification problems in highly sensitive GC analysis, equal peak areas of the quantification standard should always be aimed at because a dependence of response factors on total amounts of the injected compound is a common observation. For this reason, addition of a quantification standard prior to the extraction and an optional dilution step is not generally recommended. However, such a compound with a known concentration in the sample, *e.g.*, 3-NP or *n*-M-3-NP, should be added to reveal accidental errors during sample preparation.

Whereas the sensitivity for mononitrophenyl acetates remained constant over several months and hundreds of runs, a substantial deterioration was observed for 2,4-dinitrophenyl derivatives owing to impurities in the injector and column ageing. Although linearity is not seriously hampered, replacement of sleeves and column

TABLE V

REPLICATE ANALYSIS OF SAMPLES OF CLOUDWATER AND ATMOSPHERIC PARTICLES AT DIFFERENT CONCENTRATION LEVELS

A1–4 = particulate matter collected with a single high-volume sampler. Filter cut up as indicated by given air volumes. CWa–d = cloudwater. CH_2Cl_2 extract of one sample divided into aliquots of corresponding water volumes.

Sample	Volume	2-NP	4M-2NP	4-NP	3M-4NP	2,4-DNP	6M-2,4DNP	Units (data)
A1	160 m^3	<0.5	<0.5	28	4.0	1.8	1.3	pmol m^{-3}
A2	80 m^3	<0.5	<0.5	30	4.2	2.0	1.2	(03/12/90)
A4	40 m^3	<0.5	<0.5	31	4.6	1.7	1.2	
CWa	125 ml	<2	<2	89	11.1	45	7.6	nmol l^{-1}
CWb	125 ml	<2	<2	88	10.6	41	7.6	(12/11/89)
CWc	25 ml	<2	<2	93	12.1	44	7.8	
CWd	15 ml	<2	<2	82	11.2	39	7.5	

shortening after about 100 injections proved useful. It is also good analytical practice to determine the calibration graph using standard mixtures that have been derivatized together with the samples.

Some applications with limited sample material, *e.g.*, dew, or difficult matrices, such as humic soil or plant material, demand an even lower measuring range than proposed. As the limits of determination mostly depend on the precision of extraction from water and the final GC quantification, enhanced sensitivity can be achieved by concentrating the final hexane extract prior to injection. Vapour pressures of the 2-nitrophenol acetates are significantly lower than for pure 2-nitrophenols, allowing a further concentration of the final hexane extract.

CONCLUSIONS

Quantitative extraction of water-soluble phenols from water using batch liquid–liquid extraction has always been unsatisfatory. Therefore, continuous liquid–liquid distribution and solid-phase adsorption techniques such as the use of anion-exchange resins, XAD columns [18] and more recently reversed-phase resins [11,19] have been employed. Reversed-phase extraction of nitrophenols from water seems to be the method of choice as is promises high recoveries also for volatile 2-nitrophenols and the omission of the time-consuming evaporation of the organic solvent. However, if large volumes of water ($V > 100$ ml) must be extracted, the effort required for complete and constant recoveries increases disproportionately. In addition, if a multi-residue procedure is employed, continuous liquid–liquid extraction proved to be more time effective.

The efficiency of extraction was found to be considerably dependent on the size and number of solvent droplets produced in the extraction apparatus. The original frits operated inefficiently and had to be modified. With this improvement the described procedure showed remarkably good results for the simultaneous extraction of nitrophenols ($4 < pK_A < 7.5$) and atrazine ($pK_A = 1.68$) [20]. To measure atrazine, the organic phase remaining after step 4 represents a purified extract which can be concentrated and injected into a GC-TSD of GC–MS system.

Adsorption of pure, semi-volatile nitrophenols in the inlet and active sites of the column was confirmed as giving serious problems in their GC determination. High-quality results might be obtained only by using labelled standards, which unfortunately are not yet commercially available. Even if this proves to be the case in the future, it must be emphasized that different physico-chemical properties of pure semi-volatile nitrophenols and excessive concentration and the injection of unpurified extracts, as practised in GC–MS analysis, will require one labelled standard for each compound of be measured.

Alternatively, nitrophenols can be determined as their nitrophenyl acetates with nitrogen-specific detection or highly sensitively with ECD without extra time-consuming clean-up steps. Good separation and determination of the seven most abundant nitrophenols, *i.e.*, 4-NP, 2-M-4-NP, 3-M-4-NP, 2,4-DNP, 6-M-2,4-DNP and two other N-methyl-2,4-dinitrophenols, in atmospheric liquid water and suspended particulate matter of the polluted and unpolluted atmosphere have been accomplished. With an additional purfication step this procedure also proved suitable for determining nitrophenols in humic soils and foliage. Vapour-phase measurements

using solid absorbents, however, require detailed investigations of possible artefact formation during sampling [5,21].

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