Simultaneous Determination of C_1-C_2 Aldehydes and Organic Acids in Aqueous Atmospheric Samples by High-Performance Liquid Chromatography

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SIMULTANEOUS DETERMINATION OF C_1-C_2 ALDEHYDES AND ORGANIC ACIDS IN AQUEOUS ATMOSPHERIC SAMPLES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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A high-performance liquid chromatographic method for the simultaneous determination of C_1-C_2 aldehydes and organic acids in aqueous samples has been developed. Aldehydes and organic acids are separated after derivatization of the aldehydes by 2,4,-dinitrophenylhydrazine and by gradient elution on reversed-phase material. Measurement is by UV and conductivity, respectively. The detection limits, using an injection volume of $100 \mu l$, for formaldehyde, acetaldehyde, formic acid and acetic acid are $5 \mu g l^{-1}$, $10 \mu g l^{-1}$, $15 \mu g l^{-1}$ and $30 \mu g l^{-1}$, respectively. Aldehydes are stabilized by the derivatization reagent for a period of maximal five days in the field. Results of measurements of rain, mist and dew samples, collected in Petten (The Netherlands) indicate the presence of C_1-C_2 aldehydes and organic acids in the range from 0.01 to $3 mg l^{-1}$.

KEY WORDS: Precipitation samples, liquid chromatography, aldehydes, organic acids.

INTRODUCTION

Interest in the possible role of aldehydes and organic acids in atmospheric processes related to acid deposition is mounting rapidly.[1-8]

The most abundant aldehydes in the atmosphere are formaldehyde and acetaldehyde which are present in air and rain in concentrations ranging from 1–$50 \mu g m^{-3}$ and from 10–$500 \mu g l^{-1}$, respectively.[9-11] Sources of aldehydes are direct emissions from industrialized areas and photochemical oxidation of hydrocarbons. Aldehydes play an important role in the formation of photochemical smog. They are a major source of free radicals in the atmosphere. The aqueous phase reaction of formaldehyde with dissolved SO_2 leads to the formation of hydroxymethanesulfonic acid (HMSA).[12] This reaction increases uptake of SO_2 in cloud and rain droplets which has consequences for the long-range transport of SO_2 and the acidity of wet deposition.[13] Carboxylic acids ranging from C_1 to C_{34} have been identified in precipitation samples.[14] Formic and acetic acid are predominant acids with concentrations of 50–$1200 \mu g l^{-1}$.[15,16] Their most impor-

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tant sources in precipitation are volatile vegetative emissions and a minor source is the aqueous phase oxidation of their corresponding aldehydes.[17] In areas, remote from anthropogenic emissions, formic and acetic acid can account for 40–60% of the free acidity in rain water samples while in industrialized regions a contribution of 20% has been measured.[18]

Several methods are available for the analysis of aldehydes and organic acids in precipitation samples. Aldehydes are generally determined by derivatization with 2,4-dinitrophenylhydrazine followed by high-performance liquid chromatography (HPLC) with either UV[19–23] or electrochemical detection.[24] This selective and sensitive technique has replaced gas chromatography[25,26] and spectrophotometric methods based on reaction with chromotropic acid,[27] Schiff's reagent[28] or Hantzsch reaction.[29] For the determination of organic acids, gas chromatography and HPLC are applied using laborious and time consuming derivatization with p-bromophenacyl ester.[30–32] Recently organic acids are determined directly by liquid chromatographic methods based on anion-exchange or ion-exclusion.[33–37] Gillet et al.[38] reported the determination of formic and acetic acid by separation on reversed-phase material (Spherisorb RP-18) and UV detection. Retention times are in the order of 3 minutes. N-octylamine as ion-pairing reagent is used to prevent co-elution of nitrite and nitrate with organic acids. The sensitivity of the system is improved by the use of a cation-exchange concentrator column (Vydac 302SC) and a large injection volume (1 ml).

In our laboratory these components are analyzed in aqueous atmospheric samples to evaluate the importance of C_1-C_2 aldehydes and organic acids in relation to acid deposition. This type of research has special analytical problems as only small sample volumes are available, especially for samples of fog, cloud and dew. Large series of samples are analyzed and the concentrations are rather low. Furthermore, these samples are sensitive to biological degradation resulting in artifacts.

This paper describes a method developed for the simultaneous determination of C_1-C_2 aldehydes and organic acids. The analysis is based on ion-pairing reversed-phase HPLC with conductivity detection of the organic acids and UV detection of the derivatized aldehydes. Advantages of the method are: the samples are stabilized directly by the derivatization reagent, the method is fast and only small sample volumes are required as just one sample injection is necessary.

EXPERIMENTAL SECTION

Reagents

Derivatization reagent. In 10 ml concentrated sulfuric acid (Suprapur, Merck) 3 g 2,4-dinitrophenylhydrazine—Merck (DNPH) is dissolved. At 4 °C the solution can be stored over a month. The solution is stored in a closed glass bottle to prevent contamination from the laboratory atmosphere.

Eluent. A 0.001 M N-octylamine (Merck) solution is adjusted to pH = 3 with HCl.

Standards. Formaldehyde standards are diluted by weight from a stock 37% CH_2O solution of which the concentration was determined according to ISO 2227.[39] Working standards are prepared daily be weighing from stock solutions of 1000 mg l^{-1} formaldehyde, acetaldehyde, formic acid and acetic acid. All solutions are prepared from analytical grade reagents. Water is purified by deionization and removal of organics (Millipore-Q system, Waters).

Instrumentation

Chromatography is performed on a Merck–Hitachi HPLC system. The analytical set-up is shown in Figure 1. The system consists of a pump model 6554-11, a low-pressure gradient module model L-5000, a variable-wavelength UV detector model 6554-22, adjusted to 356 nm and set at a sensitivity of 0.16 absorption units full scale. The conductivity detector used is ECN design with gold-plated electrodes. The data are recorded and integrated by a double channel printer/integrator Merck–Hitachi D2000. Columns are thermostatted at 30 °C by a Spark-Holland Sp H99 thermostat (Chrompack—The Netherlands). The sample volume is 100 μl, automatically injected by a Spark Holland sample-changer model SPH-125 in combination with a Rheodyne model 7125 Syringe Loading Injector. The eluate is directed either to the conductivity detector or to the UV detector by an electropneumatical Valco 3-way valve which is controlled by the gradient module. The eluent solutions are degassed with helium.

Silver-loaded Suppressor Column

A strong cation-exchange resin (2.3 meq ml^{-1}) Biorad AGW-X12 (200–400 mesh) in the silver form is used to suppress the background conductivity of the eluent. The resin is prepared as follows: Approximately 35 ml resin is transferred to a wide-glass column (3 cm diameter) and treated with 200 ml 1 M $AgNO_3$ solution. The resin is then washed with water until the eluate is free of silver as visually detected by the addition of chloride solution. A stainless steel column (Upchurch Scientific, No.: C-140-3-2) is packed with the silver loaded resin at a pressure of 0.5 MPa. The low pressure end of the column has a 2 μm filter to prevent loss of resin material.

Derivatization Procedure

Samples as well as standard mixtures of aldehydes and organic acids are derivatized as follows: To an aliquot of 10 ml sample solution 1 μl 2,4-dinitro-phenylhydrazine solution is added and the reaction is allowed to proceed for at least 4 hours at ambient temperature.
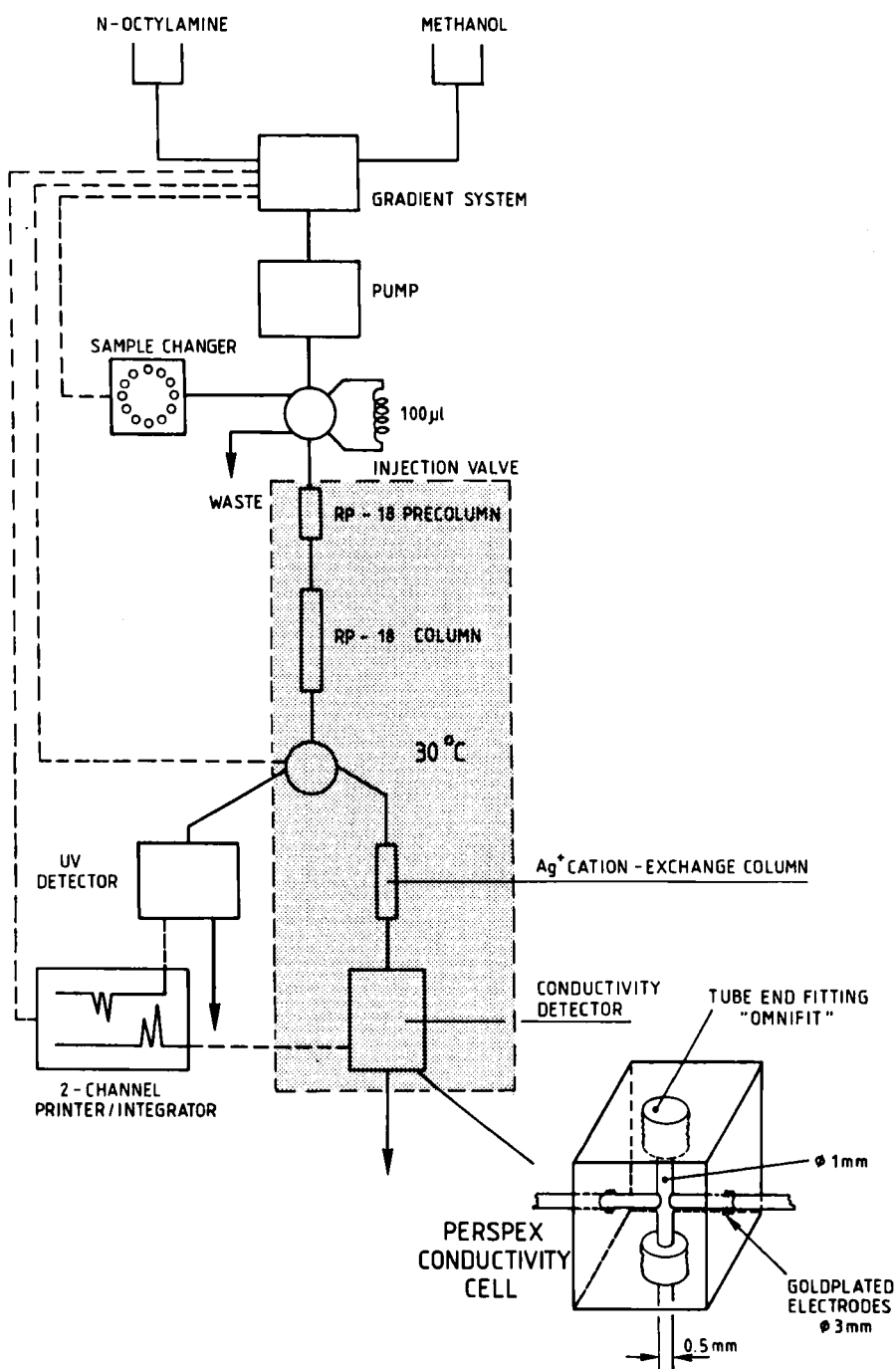
Figure 1   The HPLC set-up and the conductivity cell.

Table 1 The gradient programme

Time min.	A (N-octylamine) %	B (methanol) %	Detection		Flow ml min⁻¹
			UV	Conductivity	
0 –2.8	95	5	no	yes	1.2
2.9–4.6	15	85	no	yes	1.2
4.7–8.4	15	85	yes	no	1.2
8.5–13	95	5	yes	no	2.0
13.1–15	95	5	no	yes	1.2

Analytical Procedure

Separation is performed by a reversed-phase column (Spherisorb, RP-18, 5 micron, 4.6 × 200 mm—Pierce Chemical Company). In the case of conductivity detection a silver loaded suppressor column is used to increase the sensitivity of the detection. The eluent consists of a gradient mixture of 0.001 M N-octylamine at pH = 3 (A) and methanol (B). The gradient programme is shown in Table 1. The sample is injected in an eluent composed of 95% solution A and 5% solution B. After elution of the organic acids as indicated by the conductivity detector, the eluent composition is changed to a 15:85% mixture of solution A and B, respectively. By switching the 3-way valve the eluate is directed to the UV detector for detection of the aldehydes. A flow rate from 1.2–2.0 ml min⁻¹ is maintained throughout analysis. This procedure results in baseline resolution of C_1-C_2 aldehydes and organic acids within a time of analysis of 15 minutes.

RESULTS AND DISCUSSION

Determination of Aldehydes

The determination of aldehydes in precipitation samples by derivatization with DNPH, separation on reversed-phase material and UV detection was tested in our set-up. Two silica based reversed-phase columns (Spherisorb, RP-18, 5 micron, 4.6 × 100 mm) of Waters–Millipore Company and Pierce Chemical Company gave similar results as formaldehyde and acetaldehyde standards were analyzed. The methanol concentration of the water/methanol eluent was optimized in the range 50–90% methanol by analyzing standards containing 1 mg formaldehyde and acetaldehyde per liter. Optimal conditions in terms of speed and resolution were attained at a concentration of 85% methanol in the eluent. The resolution is independent of temperature in the range from ambient to 70 °C. At a setting of 0.16 AUFS of the UV detector and an injection volume of 100 μL, a detection limit of 5 and 10 μg l⁻¹ was obtained for formaldehyde and acetaldehyde, respectively, which is sufficient for the analysis of aqueous atmospheric samples. The interference of hydroxymethanesulfonic acid on the determination of formaldehyde was tested. After derivatization times of 2 and 18 h no response was observed of a 4 mg l⁻¹ HMSA standard solution which is equivalent with 1 mg l⁻¹
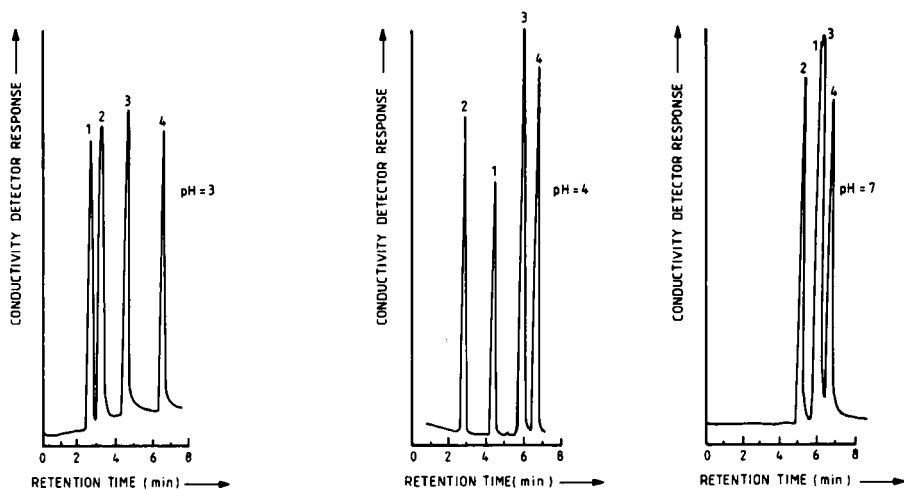
Figure 2 Chromatograms of a $5\,mgl^{-1}$ standard solution of formic acid (1), acetic acid (2), nitrite (3) and nitrate (4) as function of the pH.

formaldehyde concentration. This indicates that HMSA is stable at the derivatization conditions. If the pH of the HMSA standard solution is first adjusted to $pH = 10$, HMSA decomposes into sulfite and formaldehyde. Addition of the derivatization reagent and subsequent analysis yields 70% response of the equivalent formaldehyde concentration. Hence, HMSA can be analyzed by this procedure. However as an alternative method is available in our laboratory,[40] this approach was not further investigated.

Determination of Organic Acids

Reversed-phase chromatography seems the most promising separation technique for the simultaneous determination of aldehydes and organic acids. The application of a concentrator column and a large injection volume to improve the sensitivity of the UV detection of organic acids[38] is not possible in our case as it was observed that derivatized aldehydes are strongly retained by a cation-exchange concentrator column. Therefore, it was decided to test a reversed-phase column in combination with a small injection volume and sensitive, suppressed conductivity detection.

The pH of the eluent is an important parameter for the retention of organic acids. Chromatograms of standards containing $5\,mgl^{-1}$ of each formic acid, acetic acid, nitrite and nitrate are given in Figure 2 for different pH's of the eluent. The analysis was performed by using a reversed-phase column of 200 mm, 0.001 M N-octylamine solution as eluent, an injection volume of $100\,\mu l$ and an eluent-flow of $1.2\,ml\,min^{-1}$. The pK_a of formic and acetic acid are 3.7 and 4.7, respectively. At $pH = 3$ of the eluent the organic acids are protonated and retention is based on ion-exclusion. Ion-paired nitrite and nitrate are more retained by the reversed-

phase material than the protonated organic acids, due to the more apolar character of the ion-pair.

At pH = 4 which is in between the pK_a's of the organic acids the retention of formic acid is based on ion-pairing and that of acetic acid on ion-exclusion chromatography. The eluting order of formic and acetic acid is reversed at pH = 4 compared to that at pH = 3, due to ion-pair formation of formic acid. At pH = 7 of the eluent both formic and acetic acid are subject to ion-pairing chromatography, which results in poor resolution compared to the results obtained at pH = 3 and pH = 4. It was observed that the retention of organic acids at pH = 4 of the eluent is strongly depending on the pH of injected samples.

It is concluded that pH = 3 of the eluent is the optimal pH for the determination of organic acid. A lower pH drastically decreases the life time of the suppressor column. A 200 mm column (Spherisorb, RP-18, 5 micron) is necessary to obtain base-line separation of the acids.

The background conductivity of the eluent can be suppressed by a cation-exchange column in the Ag^+-form.[35,36] Hydrogen and N-octylammonium cations are removed by exchange with Ag^+-cations. The Cl^--anions present in the eluate are precipitated as AgCl by the liberated Ag^+-cations. Consequently, the background conductivity is reduced and the ionization of the weak organic acids is enhanced which results in an increased signal. The sensitivity of the detection increases with decreasing pK_a of the acids. The main disadvantage of this suppressor system is the need to regenerate or replace the Ag^+-column. An alternative is the use of a continuously regenerating membrane-suppressor which exchanges hydrogen and N-octylammonium cations with less conductive tetra-butylammonium cations. An anion micromembrane suppressor (Dionex—AMMS-ICE) was tested with 10 mM tetrabutylammonium hydroxide regenerant at a flow of 5 ml min^{-1}. At pH = 3 of the eluent a background conductivity of 275 uS cm^{-1}, 150 uS cm^{-1} and 2 uS cm^{-1} was measured by using non-suppressed, membrane-suppressed and silver-suppressed conductivity detection, respectively. As a consequence detection limits for formic and acetic acid are in the order of 100 μg l^{-1} and 300 μg l^{-1} using membrane suppression. These detection limits are too high for the analysis of precipitation samples. Therefore the Ag^+-suppressor system is applied in our set-up. The volume of the suppressor column is in the order of 0.3 ml which is equivalent to 0.7 meq. cation-exchange capacity. An eluent-composition of 0.001 M N-octylamine at pH = 3 is equivalent with 3 μmol cations per ml eluent. At an eluent-flow of 1.2 ml min^{-1} this results in complete Ag^+-exchange of the suppressor column after 192 minutes. The eluent flows only during 6 minutes per analysis cycle through the suppressor column, so 32 analyses can be performed at 8 hours of continuous use. Pressure build up or shifting of retention times caused by AgCl precipitation is not significant in our system

Simultaneous Determination of Aldehydes and Organic Acids

Both the analysis of aldehydes and organic acids are performed on a reversed-phase column but in combination with different eluent solutions and detectors.
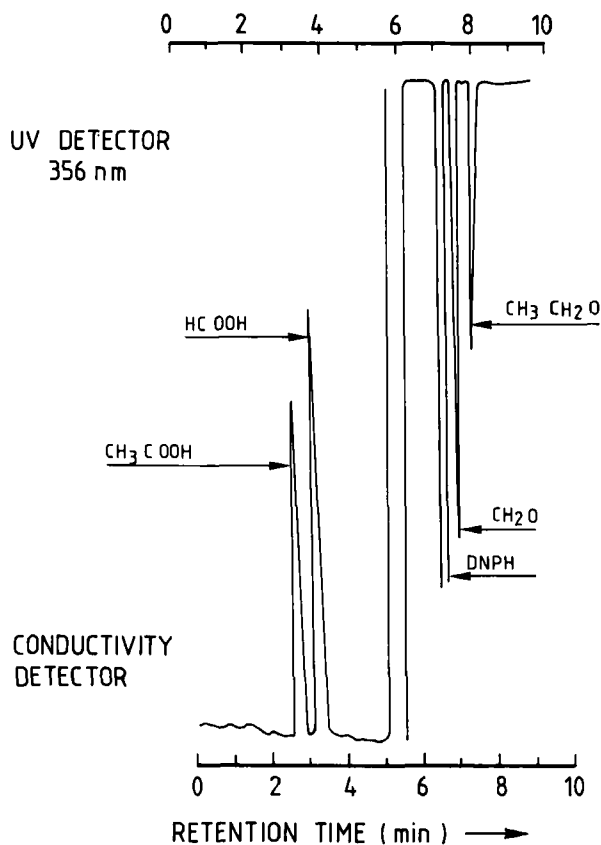
Figure 3 Chromatogram of a $1 \, mg \, l^{-1}$ standard derivatized solution of formic acid, acetic acid, formaldehyde and acetaldehyde, containing $5 \, mg \, l^{-1}$ chloride, nitrate and sulphate.

For the simultaneous determination a gradient elution is used. The life-time of the suppressor column is increased by switching the eluate to the UV detector after detection of the acids by the conductivity detector. The analytical system as shown in Figure 1 is used with the gradient programme presented in Table 1. Resulting retention times of formic acid, acetic acid, formaldehyde and acetaldehyde are 2.6 min, 3.2 min, 7.8 min and 8.2 min, respectively. The retention of the organic acids is not influenced by the presence of the derivatization reagent. Anions with long retention times, such as sulphate (always present in precipitation samples) are retained on the column under conditions chosen for the analysis of acids. They are eluted in the aldehyde analysis. In the UV detection mode sulphate is not detected. A typical chromatogram of a derivatized standard containing HCOOH, CH_3COOH, CH_2O, CH_3CH_2O, Cl^-, NO_3^- and SO_4^{2-} is shown in Figure 3. At the conditions given in Table 1 nitrate is not detected by the conductivity detector, as the eluate is directed to the UV detector at 4.7 minutes after the injection of the sample and the retention time of NO_3^- is 6.5 minutes. In the UV detection mode nitrate either elutes before or in the peak of the derivatization reagent. Calibration curves were obtained by analyzing standards of derivatized aldehydes and organic
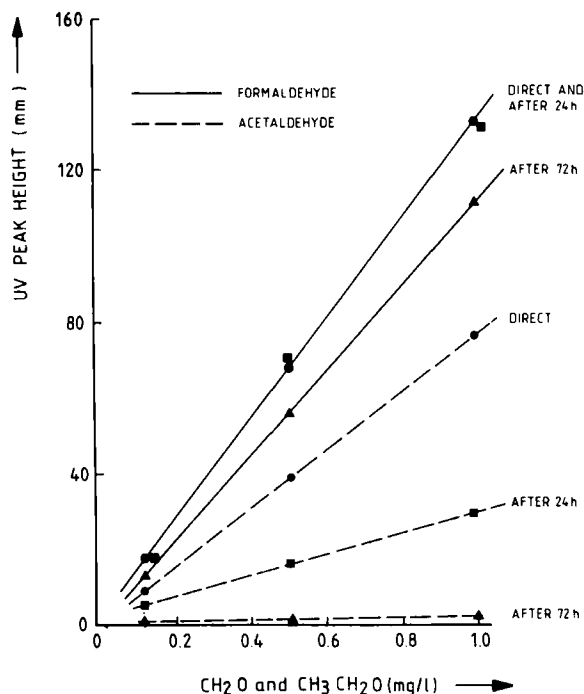
Figure 4 Stability of formaldehyde and acetaldehyde standards in relation with the time of derivatization by DNPH; direct, after 24 h and after 72 h, respectively.

acids. The various peak areas are measured and plotted against the concentrations. The response is linear over the range 50–100 μg l^{-1} for all measured compounds. From replicate analysis of standard mixtures it was observed that the reproducibility in this range is 10% (level of significance 95%). By using the conditions given in Table 1 the detection limits of formic acid, acetic acid, formaldehyde and acetaldehyde are 15 μg l^{-1}, 30 μg l^{-1}, 5 μg l^{-1}, and 10 μg l^{-1} respectively. The detection limit is defined as three times the standard deviation of blank measurements.

Stability of Aqueous Atmospheric Samples

The composition of aqueous samples may change during the time delay between sampling and analysis. This is caused by physico-chemical processes like volatilization and adsorption to the sampling vessel or biological processes. As shown in Figure 4 the concentration of acetaldehyde decreases up to 50% probably in 24 hours by volatilization. Formaldehyde is stabilized in aqueous solutions as it is mainly present in the hydrated form (methylene glycole). Its solutions can be stored under field conditions up to 72 hours with losses of only about 10%. Microbiological activity in precipitation samples may decrease significantly the concentration of organic acids within hours.[41] Usually chloroform or a mercury(II) salt is added to samples to prevent microbial decomposition of

Table 2 Analysis of rain, mist and dew samples in $\mu g l^{-1}$ sampled in Petten, The Netherlands on the North Sea coast

Date yymmdd	Type	CH_2O	CH_3CH_2O	HCOOH	CH_3COOH
870907	rain	90	185	120	40
870929	rain	75	135	65	30
880310	rain	80	80	295	95
880323	rain	85	5	120	110
880327	rain	45	10	125	205
880330	rain	25	5	55	60
880416	rain	100	25	380	645
880418	rain	95	30	550	840
871001	dew	105	200	15	25
880421	dew	95	15	1310	2970
880418	mist	45	30	1750	3300

components. By adding the DNPH derivatization reagent to the tubes in the precipitation sampler, the samples are stabilized up to five days under field conditions. This was tested by standard addition up to a concentration of $500\,\mu g l^{-1}$ C_1-C_2 organic acids and aldehydes in rain water samples. Losses under 10% of the original concentrations were observed in derivatized samples during a 5 days period between sampling and analysis. The concentration of the derivatization reagent in the sample varies with the amount of the sampled water. This has consequences for the peak height of DNPH and the efficiency of the derivatization reaction. Sample volumes in the range of 5–10 ml containing concentrations up to $1000\,\mu g l^{-1}$ of aldehydes are completely derivatized by $1\,\mu l$ DNPH reagent after 4 hours.
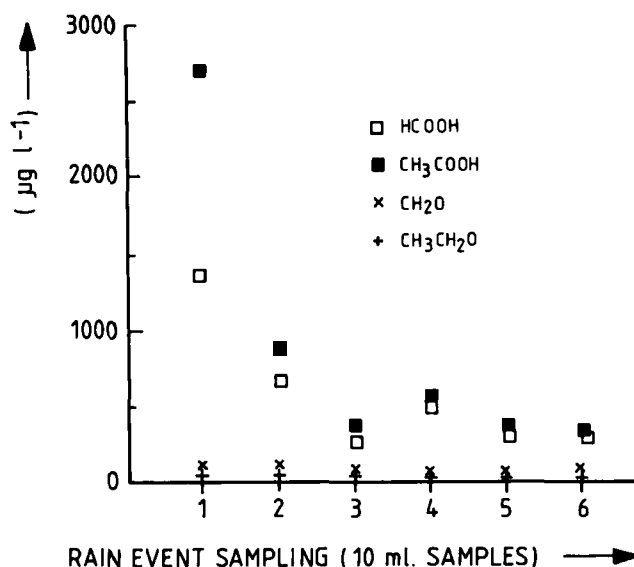
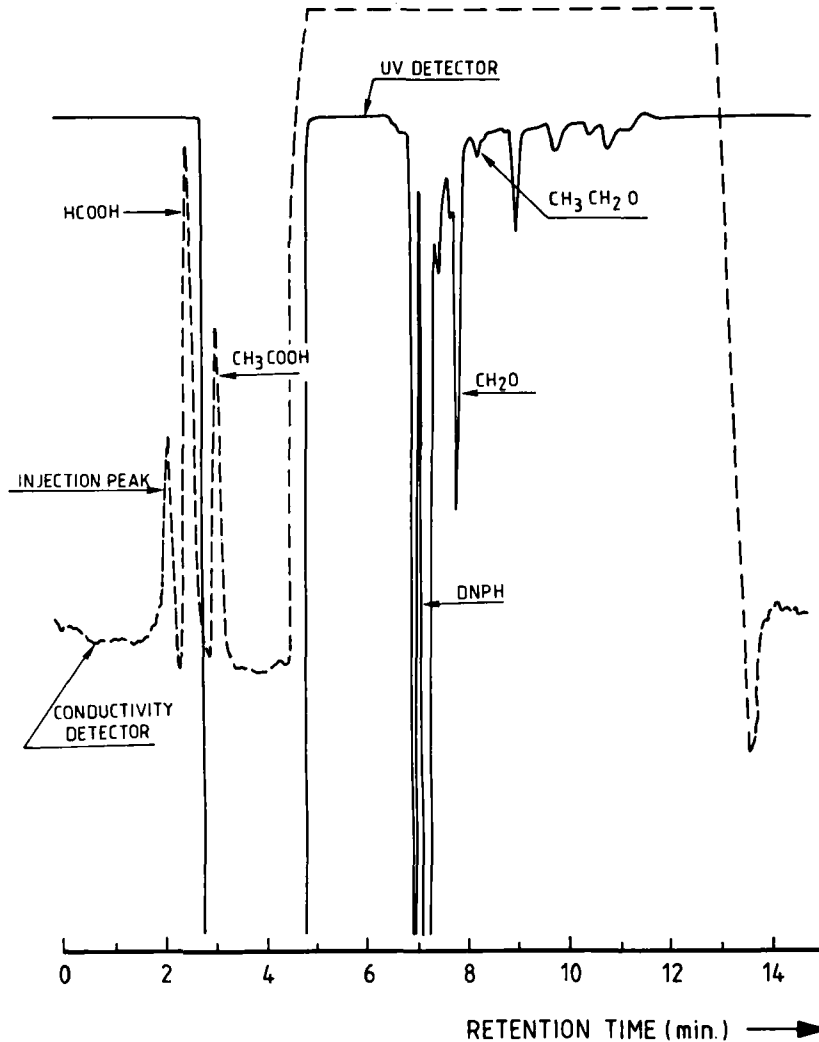**Figure 5** Results of sequentially rain sampling on 18 April 1988 in Petten, The Netherlands by a wet-only sampler.

Figure 6 Chromatogram of rain water sampled by a wet-only sampler on 19 April 1988 in Petten containing $770 \mu g l^{-1}$ formic acid, $800 \mu g l^{-1}$ acetic acid, $120 \mu g l^{-1}$ formaldehyde and 15 $\mu g l^{-1}$ acetaldehyde.

Application to the Analysis of Rain, Mist and Dew Samples

The described procedure is used to analyze precipitation samples. These included samples of rain, mist and dew collected by wet-only and dew- and mist-samplers in Petten (The Netherlands).[42] Results given in Table 2 indicate that organic acids can contribute substantially to the acidity of rain, mist and dew. These preliminary results seem to confirm the fact that biogenic emissions are important sources for organic acids in the atmosphere as their concentrations in rain water drastically increase during the growing season. Formaldehyde concentrations in the order of $4 \mu mol l^{-1}$ indicate that the formation of hydroxymethanesulfonic acid can be significant. In Figure 5 results are shown of event sampling during a shower on 18

April 1988 in Petten. Rain was sampled in batches of 10 ml. The high concentrations of the acids in the first samples suggest effective (below cloud) scavenging of gaseous atmospheric organic acids. Additional measurements of air concentrations before, during and after rain events could be of help. Figure 6 gives a chromatogram of a rainwater sample which shows that other unknown species are present apart from the C_1-C_2 organic acids and aldehydes.

Acknowledgements

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