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AN IMPROVED ION CHROMATOGRAPHY METHOD FOR ANALYSIS OF ACETIC AND FORMIC ACID VAPOURS

Robyn E. Hodgkins[1]*, Cecily M. Grzywacz[2], Robin L. Garrell[1]

1. Department of Chemistry and Biochemistry & California NanoSystems Institute (CNSI), University of California, Los Angeles, Box 951569, Los Angeles, CA 90095-1569, USA
2. National Gallery of Art, 6th Street & Constitution Ave NW, Washington DC 20565, USA, formerly at The Getty Conservation Institute

corresponding author:
Robyn.Hodgkins@gmail.com

Air quality monitoring for acetic and formic acid vapours in museum galleries and storage environments is commonly conducted using passive sampling and ion chromatography (IC). We report development of a rapid IC method with 2 to 60-fold improvement in detection limits for acetate and formate. Baseline resolution is achieved in 4.5 min using an AS11-HC anion exchange column with 4 mM NaOH eluent at 1.5 mL/min flow rate. The detection limits are 12 µg/mL (0.24 ng) for acetate and 11 µg/mL (0.21 ng) for formate. The method was successfully used for air quality monitoring in a Los Angeles museum warehouse.

1   Introduction

Monitoring indoor and outdoor air quality requires accurate collection and quantification of volatile organic compounds. Acetic and formic acids are the most abundant carboxylic acids in the troposphere, having both anthropogenic and biogenic origins.[1-4] Anthropogenic sources include vehicle emissions resulting from incomplete combustion of ethanol-based fuel,[3,5-7] biomass burning,[3,4,6,8] industrial heat generation[7] and synthetic materials.[9,10] Biogenic sources include emissions from vegetation, forests, and oceans,[3,4,6,7,11-13] photochemical synthesis involving ozone and olefins,[2,3,6,14-16] and secretions from microorganisms.[13] Acetic and formic acids have been linked to increased cloud and fog formation,[4,17,18] increased acidity of rain water,[5,19-22] and to the corrosion of cultural heritage objects,[23-32] historical buildings and monuments.[33-36] Museum collections are at risk when acetic and/or formic acid are present at low µg/m³ concentrations.[9,37,38] At these concentrations, the corrosion of metals and calcareous objects such as limestone, ceramics, and fossils has been documented.[23,25-32,39-43] Over time, this corrosion can lead to complete deterioration of the object.

Acetic and formic acid vapours are collected by active sampling or passive sampling.[2,5,7,37,44-56] Quantitative analysis can be performed directly on gas phase samples obtained by active sampling using gas chromatography mass spectrometery.[11,12,16,55] Alternatively, the acid vapours can be collected and trapped passively as solid salts. Some passive samplers can be read directly, while others must be analyzed in a laboratory.[9] The trapped salts in laboratory-analyzed passive samplers are usually extracted in water and quantified by ion chromatography (IC).[3,17,48,50-54,57] Passive sampling is often preferred in museums because it requires neit-

	Retention time (min)	Limit of detection (ng/mL)	Calibration standards (µg/mL)	Upper limit of dynamic range (µg/mL)	Correlation coefficient (r²)
Dionex IonPac AS4A[51,52] 5 mM Na₂B₄O₇ at 1.0 mL/min					
Acetate			1-10		
Formate			1-10		
Dionex IonPac AS11[45] 0-50 mM NaOH gradient at 1.0 mL/min					
Acetate	5.0ᵃ		0.1-1		≥0.99
Formate	6.5ᵃ		0.1-1		≥0.99
Dionex IonPac AS14[46] 2.0 mM Na₂B₄O₇ at 0.8 mL/min					
Acetate	8.8	600		200	
Formate	9.4	370		100	
Alltech Allsep A-2[46] 1.5 mM NaHCO₃/1.2 mM Na₂CO₃ at 1.6 mL/min					
Acetate	4.1	560		300	
Formate	5.1	460		100	
Shodex IC SI-50 4E[46] 1.0 mM NaHCO₃/3.2 mM Na₂CO₃ at 1.0 mL/min					
Acetate	3.8	200		500	
Formate	4.3	160		200	
Alltech Allsep A-2 Custom[47] 0.9 mM NaHCO₃/1.2 mM Na₂CO₃ at 1.0 mL/min					
Acetate	5.6		1.05-210ᵇ		≥0.99
Formate	6.9		1.22-244ᵇ		≥0.99
Dionex IonPac AS11-HC[53] 1-32 mM NaOH gradient at 1.5 mL/min					
Acetate	5.5	28	0.1-2		≥0.99
Formate	6.1	26	0.1-2		0.98
Dionex IonPac AS11-HC (this work) 4 mM NaOH at 1.5 mL/min					
Acetate	3.6	12	0-40	45	≥0.99
Formate	4.4	11	0-40	45	≥0.99

a) Retention times were taken from chromatogram, b) Values were determined using densities of acetic and formic acids.

Table 1: Analytical figures of merit of IC methods using conductivity detection for analyzing formic and acetic acid vapours collected with passive samplers.

her high-level skills nor special equipment, it is less expensive than active sampling, and the samplers can be placed discreetly in exhibitions for extended periods of time.[9]

Currently, commercial passive samplers are available for detecting acetic acid in the parts per million by volume (ppmv) or mg/m³ range.[9] Formic acid can be quantified with the same direct-read sampler, but only in the absence of acetic acid. In 1997, Gibson and co-workers developed passive samplers based on Palmes diffusion tubes, to detect acetic and formic acids simultaneously in the parts per billion by volume (ppbv) or µg/m³ range.[51] These passive samplers, referred to as museum diffusion tubes (MDTs), use potassium hydroxide (KOH) to trap the organic acid vapours by forming deprotonated acid salts.[9] The salts are dissolved in water and analyzed by IC. The time-weighted average acid vapour concentration, C,

is calculated based on Fick's law of diffusion, using equation 1: $C = Lm/DAt$ (1)

where L is the length of the tube, m is the mass of acid collected, D is the vapour phase diffusion coefficient, A is the cross-sectional area of the diffusion path, and t is the collection time.

Since Gibson's work, further improvements in organic acid vapour analysis have been obtained by modifying the passive sampler and the IC method, as summarized in Table 1. The fastest elution times with baseline resolution reported to-date are 5.0 min for acetate[45] and 6.1 min for formate.[53] The lowest detection limits obtained without the use of organic solvents are 28 ng/mL for acetate and 26 ng/mL for formate.[53]

To detect low concentrations, baseline resolution, short elution times and detection limits less than 100 ng/mL are desirable. The method in Table 1 that provides low detection limits requires longer elution times, while the methods that provide shorter elution times do not give baseline resolution. The IC method reported in this paper combines low detection limits and baseline resolution with fast elution times to quantify acetic and formic acid vapours collected by MDTs exposed to museum storage environments.

2 Materials and methods

2.1 Chemicals

All chemicals were ACS reagent grade unless otherwise stated and were used as received. Sodium acetate, sodium formate, and potassium hydroxide pellets were from JT Baker (Phillipsburg, NJ, USA). Sodium hydroxide 50 wt% was from Fisher Scientific (Pittsburg, PA, USA). Ethylene glycol dimethyl ether (99.9% HPLC grade) was from Sigma-Aldrich (St. Louis, MO, USA). Glacial acetic acid (HPLC grade) was from VWR International, LLC (West Chester, PA, USA). Formic acid (88% in water) was from EM Science (Gibbstown, NJ, USA). All solutions were made using deionized reverse osmosis water filtered with a MilliQ system (Millipore, Billerica, MA, USA), referred to as MilliQ water.

2.2 Preparation of Museum Diffusion Tubes

MDTs were assembled using clear poly(methyl methacrylate) tubes (7.1 x 1.1 cm), acrylic caps, and stainless steel mesh disks (Gradko International Ltd., Hampshire, United Kingdom). The trapping solution, 40 µL of 5 M KOH with 10% ethylene glycol dimethyl ether in MilliQ water, was pipetted into coloured caps containing two stainless steel mesh disks and allowed to air dry for 3 h. The MDTs were assembled by pushing a clear tube onto the coloured cap and sealing with a clear cap. The MDTs were divided into three categories for analysis: laboratory blank MDTs, monitoring blank MDTs, and exposure MDTs. The laboratory blank MDTs were unexposed tubes used to evaluate potential contamination of the MDTs during preparation. Monitoring blank MDTs were unexposed tubes that remained sealed inside the

microclimate during exposure and were used to determine if there was contamination during transportation to the site or during exposure.

2.3 Museum Warehouse Environment

Acetate and formate-induced efflorescence was identified on fossils in the Invertebrate Paleontology (IP) warehouse at the Natural History Museum (NHM) of Los Angeles County. The IP collection is stored in metal cabinets with wooden drawers. Air quality monitoring (AQM) was conducted in multiple locations within the warehouse to determine whether acetic acid and/or formic acid vapours were present and whether they present an ongoing risk to the collection. Two storage cabinets containing fossils with efflorescence were chosen and the ambient warehouse environment was monitored as a control.

2.4 Air Sampling Using Museum Diffusion Tubes

MDTs were exposed by removing the clear caps and placing the tubes in the microclimate to be monitored for an appropriate length of time, based on the expected acid vapour concentrations. Each environment was sampled with three exposure MDTs and two monitoring blank MDTs. Monitoring blank MDTs were left sealed inside the sampled environment during exposure. Exposure MDTs were capped at the end of exposure by replacing the clear caps, and all MDTs were stored in a refrigerator at 5 °C until analysis. The results from replicate MDTs were averaged and used in the final calculations.

Exposure times for the samplers are planned based on the most likely concentration ranges. Ambient concentrations are usually in the low μg/m^3 range, while microclimates can range from 1 to 2500 μg/m^3.[1-5,9,17-22,37,38,58] To obtain more representative air quality monitoring results, microclimates should be closed for at least one month prior to exposing MDTs.[9] Opening the microclimate dilutes any analytes present with external air. Once MDTs have been placed in the microclimate, they should remain for a period long enough to allow for re-equilibration of the environment and to ensure enough analyte is collected for analysis. With this in mind, MDTs are usually exposed for at least 28 d.[9] The MDTs exposed in the warehouse and storage cabinets at the Natural History Museum of Los Angeles County were collected after 33 days.

2.5 MDT IC Sample Preparation

Ion chromatography samples were prepared in disposable 15 mL BD Falcon polypropylene centrifuge tubes (VWR International, LLC, West Chester, PA, USA). The coloured MDT cap containing the trapping agent was removed and the steel mesh disks were tapped into a disposable centrifuge tube. The MDT cap was rinsed five times with 1 mL aliquots of MilliQ water, the centrifuge tube was sealed, and the solution was sonicated for 1 min using a Bransonic® 1510 ultrasonic cleaner (Branson, Danbury, CT, USA). The

IC autosampler vials were 1 mL polypropylene with PTFE clear snap caps (Agilent, Foster City, CA, USA). Before adding sample for analysis, the vials were rinsed twice with the sample extract to remove inherent unidentified contaminates, described in Section 2.8.

2.6 Instrumentation and Analysis

A Dionex DX-500 ion chromatograph (Dionex Corp., Sunnyvale, CA, USA) was used for all analyses. It consisted of an AS3500 autosampler, EO1 mobile phase station, GP40 pump, ED40 conductivity detector, and LC20 column compartment. An ASRS-300 anion self-regenerating suppressor was used at a current of 50 mA. Separation of acetate and formate was achieved using an IonPac® AS11-HC (4 x 250 mm) anion exchange column with an IonPac® AG11-HC (4 x 50 mm) guard column. The eluent was 4 mM NaOH at a flow rate of 1.5 mL/min. After each run, the column was cleaned with 50 mM NaOH eluent and re-equilibrated, producing a combined run time of 19 min (Table 2). Details of the method optimization are provided in Section 2.8. Chromeleon® software version 6.8 (Dionex Corp.) was used for data acquisition, peak analysis and calibration. Acetate and formate standards were made from their sodium salts. For instrument calibration, standards (5, 10, 20, 30, and 40 μg/mL) were prepared daily. Standard concentrations were known to three significant figures. A sample of the MilliQ water used for dilutions was saved to be used as a blank (0 μg/mL) standard.

Time (min)	Eluent concentration (mM NaOH)	Flow rate (mL/min)	Suppressor Current (mA)
0	4.0	1.5	50
6.5	4.0	1.5	100
7.0	50.0	2.0	100
12.0	50.0	2.0	100
12.5	4.0	2.0	50
17.0	4.0	2.0	50
17.2	4.0	1.5	50
19.0	4.0	1.5	50

Table 2: AS11-HC mobile phase gradient used for analysis with subsequent flushing and re-equilibration.

2.7 Calculation of Acetic and Formic Acids in Air

Anion peak areas were converted to concentrations using a calibration curve in post-run data processing. The concentrations were subsequently corrected by subtracting the anion concentrations found in monitoring blank MDTs specific to the experiment. These corrected concentrations (μg/mL) were converted into time-weighted averages of acid in air (μg/m^3) based on the exposure time, using equation (1) and constants given by Gibson.[51,59]
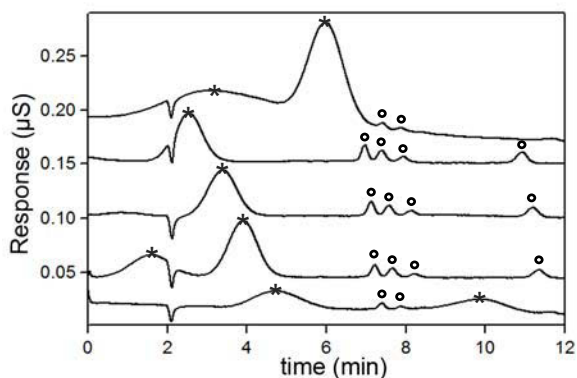
Figure 1: Ion chromatograms of water blank run multiple times with 1 mM NaOH eluent at 1.5 mL/min showing the contamination peaks from a vial or filter (∘) and non-reproducible peaks (·). The chromatograms have been offset for clarity.

2.8 Troubleshooting contamination sources and retention time drifting

During method development and validation, several problems were identified and resolved. In running standards with 1 mM NaOH eluent, several peaks not attributed to acetate or formate consistently appeared in the chromatograms and interfered with acetate and formate analysis (Figure 1). Three origins of the unwanted peaks were identified. The first was the 0.2 μm Acrodisc® filters (Pall Corporation, Port Washington, NY, USA) that were used to remove any undissolved particles that might be present in standards or samples. Some of the unidentified peaks appeared only in chromatograms of filtered standards. Additionally, 0.2 and 0.45 μm Phenex-RC filters (Phenomenex, Torrance, CA, USA) were tested, and they too yielded samples with contamination peaks. We therefore discontinued all use of filters. The unrinsed Agilent IC sample vials were determined to be the second source of unwanted peaks. To remove contaminates from the vials, they were rinsed twice with 1 mL aliquots of sample.

The third source of contamination peaks was the water used to make the standards and eluent, and to extract salts from MDTs. Initially, we thought the MilliQ system was not working properly. Deionized reverse osmosis water and high performance liquid chromatography-grade water were evaluated as replacements, but they proved inadequate. We finally determined that the in-house deionized water supply to the MilliQ system was frequently failing, generating inferior water. Therefore, all water was tested prior to sample preparation. If contamination peaks were present in the water, extraction samples from the MDTs were not prepared. The final protocol eliminated contamination peaks by testing water prior to sample preparation, avoiding filters, and rinsing vials twice with sample before filling for analysis.

While running reproducibility studies with 4 mM NaOH eluent and 1.5 mL/min flow rate, we observed the retention times of both acetate and formate were inconsistent between runs. In a 12 h period, the retention times deviated by 2 min. The IC system we used did not have column temperature control. Although small retention time drifting was expected with changes in the ambient temperature, these fluctuations should not have resulted in such large devia-

tions in retention time. Additionally, inconsistent unidentified peaks eluted at various retention times during a single run, as seen in Figure 1. These problems could have resulted from two factors: 1) carbonate was present in the eluent and/or samples, and 2) there was column carryover. The AS11-HC column is considered a high capacity column that allows more concentrated samples up to 290 μeq to be analyzed without overloading the column or creating peak broadening. According to the IC literature, the column must be flushed with a higher concentration of eluent than used for separation to remove retained analytes.[60] Therefore, the column was flushed with 50 mM NaOH eluent at the beginning of each day and after each analysis with subsequent equilibration (Table 2). Incorporating the 50 mM NaOH flush eliminated both retention time and non-reproducible peak problems.

3 Results and Discussion

3.1 Analytical Figures of Merit

The analytical performance of the method was determined using multiple 20 μL injections of 0-40 μg/mL calibration standards and 4 mM NaOH eluent at 1.5 mL/min, summarized in Table 3. The retention times for acetate and formate were 3.6 and 4.4 min, respectively (Figure 2). The resolution was 4.03 with 40 μg/mL standards and 4.50 with 5.0 μg/mL standards. The precision in the peak areas ranged from 1.2 – 5.2 % relative standard deviation (n = 4). The signal detection limit of three times the average height of the noise was determined to be 1.2 nS (nanoSiemens). The corresponding detection limit of the method was 12 ng/mL (0.24 ng) for acetate and 11 ng/mL (0.21 ng) for formate. These are among the lowest detection limits achieved to date (Table 1). With 20 μL injections, the dynamic range of this method is 0.20 - 45 μg/mL. This range can be modified by adjusting the injection volumes to between 5 and 50 μL without adverse peak broadening effects for this system. For instance, using a 5 μL injection corresponds to a range of 0.80 – 180 μg/mL, while a 50 μL injection corresponds to 0.08 - 18 μg/mL. The upper limit of the dynamic range is not as high as that obtained with AS14, A-2, and IC SI-50 4E columns (Table 1); however, our AS11-HC column and method provides complete baseline separation of acetate and formate, an important merit the other methods did not achieve.
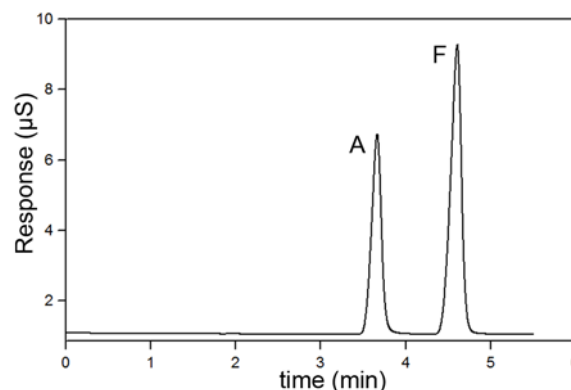

Figure 2: Ion chromatogram of 42 μg/mL acetate (A) and 39 μg/mLformate (F) using the AS11-HC column with 4 mM NaOH eluent at 1.5 mL/min.

Although a custom A-2 column used by Stranger[47] did provide baseline resolution, it is not clear that the column could be used for concentrations below 1 µg/mL. A further advantage of our method is that it accomplishes separation of acetate and formate in less than 5 min, comparable to the fastest elution times reported (Table 1). The 19 min total run time (analysis, flushing, and equilibration) is equivalent to, or shorter than, that reported for AS14, A-2, and IC SI-50 4E columns. [Stranger's reported analysis time with the custom A-2 of 10 min is shorter than our total run time, but it is not clear whether 10 min is the total run time or only the analysis time.] In summary, our method combines very low detection limits (~12 ng/mL) with rapid and efficient separation of acetate and formate.

Parameter	Acetate	Formate
Retention time (min)	3.57 ± 0.05	4.41 ± 0.03
Retention factor (k')	0.93 ± 0.02	1.38 ± 0.02
Relative retention time to H_2O (min)	1.72 ± 0.05	2.56 ± 0.03
Upper confidence of calibration[b] (µg/mL)	42.9 ± 0.2	40.1 ± 0.3
Lower confidence of calibration[c] (µg/mL)	1.2 ± 0.4	1.2 ± 0.6
Detection limit[d] (ng)	0.24	0.21

a) Calculated by Chromeleon using 20 µL injections, a water blank, and 5-40 µg/mL standards
b) Determined using Chromeleon software at 95% confidence
c) Determined using Hubaux-Vos detection limit[61]
d) Determined by analysis of diluted standard solutions

Table 3: Analytical performance of the method with the AS11-HC column.[a] The intervals represent one standard deviation.

3.2 Air Quality Monitoring of Museum Warehouse Environment

AQM was conducted in the IP warehouse at the NHM. The interior of two metal cabinets and the ambient warehouse environment were sampled to determine whether acetic acid and/or formic acid were present, and whether they were at a concentration that could pose as an ongoing risk to the collections. The MDTs were exposed to the stagnant air in the warehouse for 33 days. Recommended concentrations of acetic and formic acids for sensitive collections, such as those containing fossils and other calcareous materials, are less than 10 µg/m^3.[9] The two IP cabinets contained 150 and 630 µg/m^3 acetic acid and 42 and 90 µg/m^3 formic acid. The complete results are reported in Table 4. In the ambient warehouse environment, acetic acid was detected at 26 µg/m^3, while formic acid was not detected. The fact that the acid concentrations within the cabinets were higher than in the sur-

Sampling	Acetic acid		Formic acid	
Site	µg/m^3	ppbv[a]	µg/m^3	ppbv[a]
Cabinet 1	633 ± 16	253 ± 6	89 ± 6	46 ± 3
Cabinet 2	149 ± 12	60 ± 5	42 ± 3	22 ± 2
Warehouse	26 ± 4	11 ± 1	ND	ND

ND = not detected
[a] ppbv calculated at T = 293 K and P = 1 atm.[9]

Table 4: Air quality monitoring results in the IP warehouse at the NHM. The intervals represent one standard deviation for triplicate injection.

rounding warehouse indicates that the wood trays within the cabinets were a source of acetic and formic acid contamination.[9,11,12,38,52]

4 Conclusions

A rapid and sensitive ion chromatographic method was developed to quantify acetic and formic acid vapours from samples collected by MDTs. During analysis, anion separation was achieved with an AS11-HC anion exchange column equipped with an AG11-HC guard column, using 4 mM NaOH as the eluent at 1.5 mL/min. The detection limits were 0.24 ng for acetate and 0.21 ng for formate, among the lowest reported to-date. For the analysis of the MDTs, we used calibration standards with concentrations between 5 and 40 µg/mL, and MilliQ water as a zero standard. The presented method achieves baseline separation of both acetate and formate in 4.5 min. This IC method provides elution times up to 5.2 min faster and 2 to 60-fold lower detection limits than methods reported previously. While the method was developed to analyze acid vapours, it can also be applied to the analysis of aqueous and water-soluble samples containing acetate and formate.

This method was successfully used to quantify acetic and formic acid vapours in the µg/m^3 range collected by MDT passive samplers in museum environments. We determined that the acid levels within the storage cabinets in the Natural History Museum of Los Angeles County are higher than recommended, contributing to the efflorescence that has been observed on calcareous objects stored in the cabinets. As a result of this study, steps will be taken to mitigate these acid levels, which may include replacing the wooden trays with a less reactive material.

5 Acknowledgements

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