ELSEVIER

Journal of Chromatography A, 804 (1998) 265–272

JOURNAL OF CHROMATOGRAPHY A

Improved application of ion chromatographic determination of carboxylic acids in ozonated drinking water

Ching-yuan Kuo

The Metropolitan Water District of Southern California, Water Quality Division, 700 Moreno Avenue, La Verne, CA 91750-3399, USA

Abstract

A direct ion chromatographic method of measuring carboxylic acids was modified and expanded to include measurement of eight components at parts-per-billion levels. These components, listed by eluting order, were acetate, propionate, formate, pyruvate, glyoxalate, dichloroacetate, oxalate and ketomalonate. The calculated method detection limits were 2–6 μg/l. Preliminary data were obtained by using California state project water from the filter influent of the Oxidation Demonstration Plant of the Metropolitan Water District of Southern California. Oxalate was measured at levels above 200 μg/l, formate above 100 μg/l, acetate above 50 μg/l, pyruvate and glyoxalate at approximately 30 μg/l and propionate and ketomalonate at trace levels near the detection limits. This method utilizes a new preservative, benzalkonium chloride, as a substitute for the environmentally unsafe mercuric chloride that had previously been used. Preservation studies indicate that all eight compounds are stable for a testing period of 30 days when benzalkonium chloride is maintained at or above 30 mg/l in the water sample. © 1998 Elsevier Science B.V.

Keywords: Water analysis; Carboxylic acids; Benzalkonium chloride

1. Introduction

Although separation of carboxylic acids has been demonstrated by Révész et al. [1], using an AS4A column and a sodium hydroxide (NaOH) eluent, these authors did not apply their separation procedure to the determination of carboxylic acids in real samples with other anions such as fluoride, chloride and sulfate. [The source waters of the Metropolitan Water District of Southern California (Metropolitan) contain chloride and sulfate at levels as high as 110 and 300 ppm, respectively.] Peldszus et al. [2], using an AS10 column and a ''heart-cut'' column-switching technique for carboxylic acids at ppb levels, successfully developed a separation procedure applicable to drinking water. However, a more direct analytical procedure is needed for simplified testing of large numbers of routine water samples.

Metropolitan, in developing a method of measuring short-chain carboxylic acids in ozonated drinking water by ion chromatography (IC), incorporated three experimental phases into its overall biofiltration project plan at the full-scale Oxidation Demonstration Plant (ODP) in La Verne, CA, USA. Ozone was utilized as the primary disinfectant, followed by conventional treatment and biological filtration [3]. Ozone can break down a source water's natural organic matter into biodegradable organic compounds such as aldehydes and carboxylic acids, which are largely consumed by microorganisms during the water treatment process [4]. Ideally, these compounds are to be held to minimum amounts in the distribution system to prevent regrowth of microorganisms.

In order to study the carboxylic acids' formation and removal efficiency, the first-phase study focused

0021-9673/98/$19.00
PII S0021-9673(98)00089-2

on the development of a direct method of measuring three major carboxylic acids (acetate, formate and oxalate) in the treatment process trains. The analytical method and some preliminary results from the first-phase study were reported at the 210th National Meeting of the American Chemical Society in 1995 [5]. The results of the first-phase study also indicated that carboxylic acids measured by IC would be a good surrogate for the biodegradable organic compounds commonly referred to as assimilable organic carbon; this measurement procedure requires at least nine days to determine the removal efficiency of the biofiltration process [6]. A high biofiltration removal efficiency would minimize the levels of carboxylic acids in the distribution system and, in turn, minimize the regrowth of undesirable microorganisms.

The second-phase study was conducted to expand the method to include (1) measurement of additional carboxylic acids and (2) a new preservative to replace mercuric chloride. The changes made in the analytical method between the first- and second-phase studies are discussed in this paper. In the third-phase study, the method will be tested on different waters.

2. Experimental

2.1. Materials

2.1.1. Reagents

Standards were prepared by using reagent-grade (>99% pure) carboxylic acids in the form of their sodium salts (except for ketomalonic acid). Acetate, formate, propionate, dichloroacetate and ketomalonic acid were obtained from Aldrich (Milwaukee, WI, USA); pyruvate and glyoxalate were obtained from Fluka (Milwaukee, WI, USA); and oxalate was obtained from Spectrum (Gardena, CA, USA). An anti-biodegradation agent was prepared by dissolving 1000 mg of reagent-grade benzalkonium chloride (from Fluka) in 100 ml of ultrapure water.

2.1.2. Stock and working calibration solutions

Individual stock carboxylic acid (acetate, propionate, formate, pyruvate, glyoxalate, dichloroacetate, oxalate and ketomalonate) solutions at 10 000 mg/l were prepared in ultrapure water (double-deionized Super-Q; Millipore, Bedford, MA, USA) and stored in amber glass bottles at 4°C. An intermediate stock standard solution of mixed acids (at concentrations of 10 mg/l each), excluding glyoxalate and ketomalonate, was prepared weekly from the individual stock solutions. Mixed intermediate stock standard of glyoxalate and ketomalonate was kept in a separate container. Working calibration standards were prepared daily at concentration levels of 20, 50, 100, 250 and 500 μg/l from the 10 mg/l intermediate stock solution. Fig. 1 shows a typical chromatogram of a 100 μg/l standard.

2.1.3. Eluent

The procedure to prepare working eluents was simplified as follows: the first NaOH eluent bottle at approximately 1.0 m*M* was prepared by pipetting and mixing 0.1 ml of the 50% NaOH solution into 2000 ml of helium gas-purged ultrapure water. A second NaOH eluent at approximately 100 m*M* was prepared by pipetting and mixing 10 ml of 50% stock NaOH solution into 2000 ml of helium gas-purged ultrapure water.

2.2. Sample preparation

2.2.1. Anti-biodegradation agents

Because (1) pyruvate could not be detected in the mercuric chloride-preserved sample and (2) extra costs and special procedures were required to handle and dispose of mercuric chloride, the search for a new preservative was set as a first priority in the

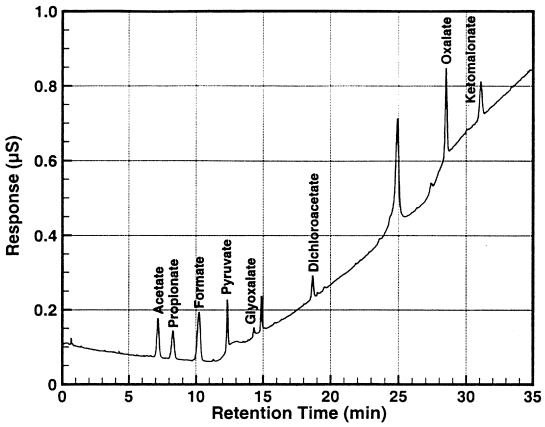

Fig. 1. Chromatogram of a 100 μg/l calibration standard.

second-phase studies. Benzalkonium chloride was the chosen preservative; it has been used as a common disinfectant or preservative in food, pharmaceutical and many other industrial applications, and it has shown no apparent interference in carboxylic acids analysis.

2.2.2. Solid-phase sample pretreatment

A hydrogen cartridge (OnGuard-H^+, P/N 39596; Dionex, Sunnyvale, CA, USA) was attached in-line between the autosampler outlet and the sample injector loop to convert sample to proton form and to remove cations (primarily the mercury that was used as a preservative before switching to benzalkonium chloride) from the sample matrix. However, it was discovered that using the OnGuard-H^+ cartridge on actual samples has an additional advantage: the H^+ cartridge produces sharp, narrow peaks instead of the broad, flat-topped peaks which, without the H^+ cartridge, normally appear during the early detection period (isocratic mode) of the chromatogram [5]. The AS11 column is a medium-capacity column, and the peaks may not be completely resolved with low-concentration eluents (0.1–0.2 m*M* NaOH) [7].

2.3. Analysis and maintenance

2.3.1. Analysis conditions

All samples were filled with a headspace in 40-ml, PTFE septum-sealed, brown glass vials to which the benzalkonium chloride had been added; they were kept in a refrigerator at 4°C before analysis. All samples were handled with extra care to avoid skin contact and minimize contamination [2]. The IC system setup and analytical conditions are summarized in Table 1. The ratio of eluent–water can be gradually adjusted from 20:80 to 10:90, if necessary, to compensate for the forward shift of retention time

Table 1
IC system[a] configurations

Components	Conditions
IC system	Dionex 2000 IC
Autosampler	ASM-2
Analytical column	Ionpac AS11
Guard column	Ionpac AG11
Detector output range	0.01 μS
Anion trap column	Ionpac ATC-1
Gradient pump	GPM-2 at 1 ml/min
Stock eluent	Eluent 1 approx. 1 m*M* NaOH
	Eluent 2 approx. 100 m*M* NaOH
	Eluent 3 ultrapure water
Working eluents	Isocratic mode 5 min, approx. 0.2 m*M* NaOH
	Eluent 1 20%
	Eluent 3 80%
	Gradient mode 30 min, linear increase from approx. 0.2 m*M* to approx. 20 m*M* NaOH
	Initial stage/final stage
	Eluent 1 20/0%
	Eluent 2 0/20%
	Eluent 3 80/80%
	Stabilizing mode 15 min, approx. 0.2 m*M* NaOH
	Eluent 1 20%
	Eluent 3 80%
Suppression	ASRS in external water mode at 7 p.s.i. (1 p.s.i.=6894.76 Pa)
	Controller current at setting no. 1; 50 mA
Detection	Conductivity detector
Sample size	50 μl
Sample pretreatment	On-line H^+ cartridge
Suppressor cleaning	0.25 *M* H_2SO_4 injected through eluent outlet
Anion trap column cleaning	Highest concentration eluent for 15 min

[a] All components from Dionex.

caused by gradual loss of the separation column's active site with usage. Glyoxalate and ketomalonate were run separately, without the H^+ cartridge, because the cartridge could possibly cause acid hydrolysis.

2.3.2. Cleaning of ATC-1

The ATC-1 column was cleaned to acquire a stable and low signal system baseline during analysis. This cleaning step should be done before the starting of the IC system and should not be omitted. The procedures were as follows: (1) disconnect the ATC-1 from the system inlet to prevent this high-concentration NaOH eluent from being introduced into the separation columns and the suppressor; (2) pump the highest concentrations of NaOH through the ATC-1 column for at least 15 min; (3) switch to working eluent for a few minutes to flush out any remaining high-concentration NaOH; and (4) connect the ATC-1 back to the system and pump the working eluent to stabilize the IC system until a constant conductivity reading is obtained.

2.3.3. Stability tests

Sample preservation stability tests were conducted over a period of up to four weeks (testing was stopped when a component showed a significant decrease in concentration) with benzalkonium chloride at final concentrations of 2, 10, 30 and 50 mg/l. The filter influent sample for the stability test was spiked with 250 μg/l of the carboxylic acids to increase the background signals of the carboxylic acids for a better observation of any downward drift in concentrations. Samples were stored in a refrigerator at 4°C when not being analyzed and were brought to room temperature before being prepared for analysis.

2.3.4. ODP studies

At the ODP, two types of biological filters were utilized: granular activated carbon (GAC) and anthracite coal-packed filters. Ozone dosages were 1.3 to 1.7 mg/l during the tests for the benzalkonium chloride studies. The ODP water flows were in the range of 4.5 to 4.8 million gallons per day (MGD) (1 gallon=3.785 l). The pH values for the raw water were approximately 7.9 to 8.3, and the water temperatures ranged approximately from 15 to 24°C. The turbidity varied from 3.8 to 8.6 NTU during the testing period.

3. Results and discussion

3.1. Analytical parameters

3.1.1. Stability tests

The ozonated filter influent samples (no ozone residue) containing benzalkonium chloride at 2 mg/l showed a decrease in the concentrations of most carboxylic acids on the second day of testing (Fig. 2), whereas the samples with benzalkonium chloride at 10 mg/l stayed at fairly level concentrations of carboxylic acids until the seventh day (Fig. 3). The preserved ozonated sample showed excellent stability throughout the 30-day test period when the sample had more than 30 mg/l of benzalkonium chloride (Figs. 4 and 5). For different types of matrix water, adding 30 mg/l (final concentration) of benzalkonium chloride may not be adequate. In this case, low recovery of spiked values on samples could indicate ineffective preservation rather than matrix interference.

3.1.2. Anti-biodegradation agent

Fig. 6 represents the results of the comparisons of acetate, formate and oxalate concentrations between the samples preserved with mercuric chloride at 12.5 mg/l and those with benzalkonium chloride at 30

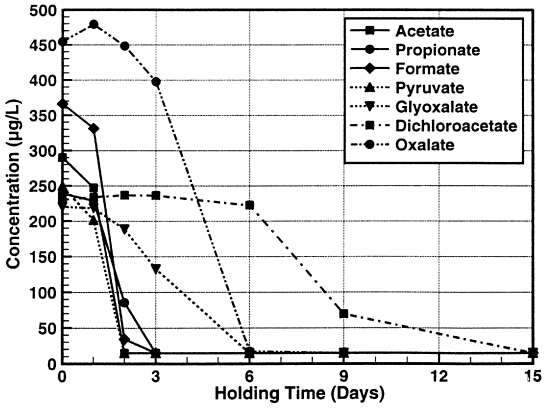

Fig. 2. Stability of carboxylic acids in fortified filter influent preserved with 2 mg/l benzalkonium chloride.

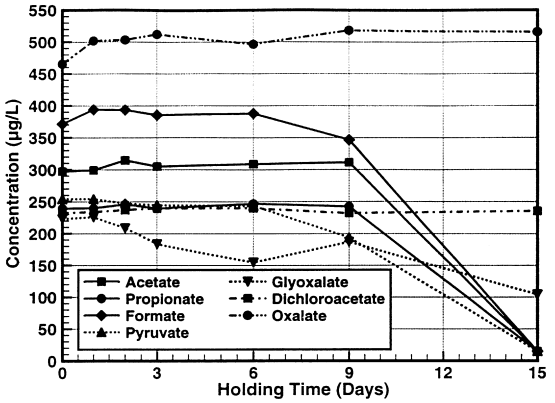

Fig. 3. Stability of carboxylic acids in fortified filter influent preserved with 10 mg/l benzalkonium chloride.

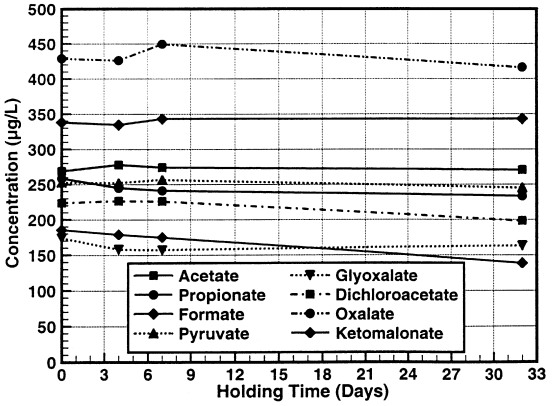

Fig. 4. Stability of carboxylic acids in fortified filter influent preserved with 30 mg/l benzalkonium chloride.

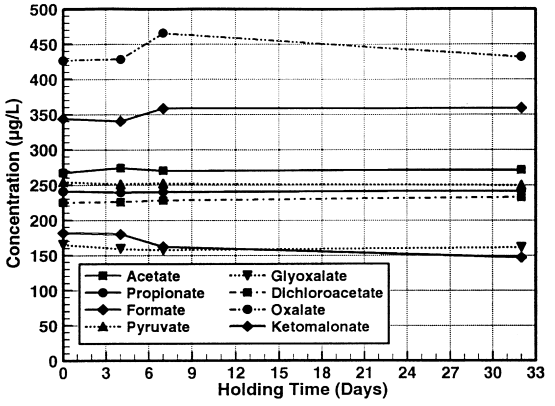

Fig. 5. Stability of carboxylic acids in fortified filter influent preserved with 50 mg/l benzalkonium chloride.

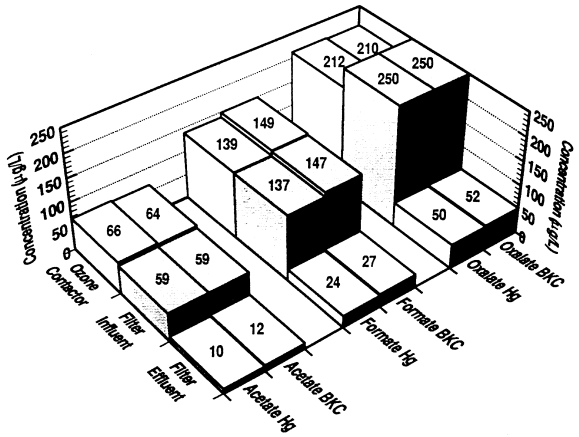

Fig. 6. Comparisons of acetate, formate and oxalate in sample preserved with mercuric chloride and benzalkonium chloride.

mg/l. There were no apparent differences between the data obtained from these two preservatives.

3.2. Quality assurance

3.2.1. Calibration curves

Small amounts of oxalate (about 10 ppb or less) were often observed in the reagent water; therefore, a blank was included in the daily analytical run so that blank-adjusted area values of the standards could be used to construct the calibration curve. The calibration curves of the carboxylic acids were linear over the range studied (20–500 μg/l). The regression coefficient of the calibration curve was usually 0.999 or better for all carboxylic acids.

3.2.2. Method detection limits (MDLs) and minimum reporting limits (MRLs)

MDLs for the carboxylic acids were determined by measuring the 20 μg/l standard seven times under the same analytical conditions and were calculated at a 95% confidence level based on tripling the standard deviation (S.D.) value. The analytical results are presented in Table 2. The calculated MDLs were 2–6 μg/l for the eight carboxylic acids. Currently, the MRL is set to 15 μg/l for all eight acids as a result of detection of the analytes in the blank. The MRL of 15 μg/l for some carboxylic acids is probably over-conservative.

Table 2
Method detection limits (μg/l)

	Mean (n=7)	S.D.	3×S.D.
Acetate	27.62	0.636	1.907
Propionate	21.60	0.910	2.731
Formate	26.27	1.360	4.081
Pyruvate	21.17	0.519	1.567
Glyoxalate	20.57	0.988	2.965
Dichloroacetate	19.86	0.868	2.604
Oxalate	29.00	2.001	6.002
Ketomalonate	18.33	1.029	3.086

3.3. ODP studies

3.3.1. Preliminary carboxylic acid results

Fig. 7 represents a typical chromatogram of an ozone-treated filter influent sample. Fig. 8 represents a chromatogram of a prechlorinated filter effluent sample, which showed an additional peak of dichloroacetate. Preliminary results for the carboxylic acids from the ODP ozone contactor, filter influent and filter effluents are presented in Table 3. Data were obtained from stabilized operating conditions in the ODP and biologically active filter beds.

The carboxylic acid that was produced in the largest amounts from the filter influent was oxalate (at approximately 250 μg/l), followed by formate (at approximately 150 μg/l), acetate (at approximately 60 μg/l), pyruvate (at approximately 30 μg/l), glyoxalate (at approximately 20 μg/l) and both propionate and ketomalonate at trace amounts near the detection limit. The sum of all carboxylic acids

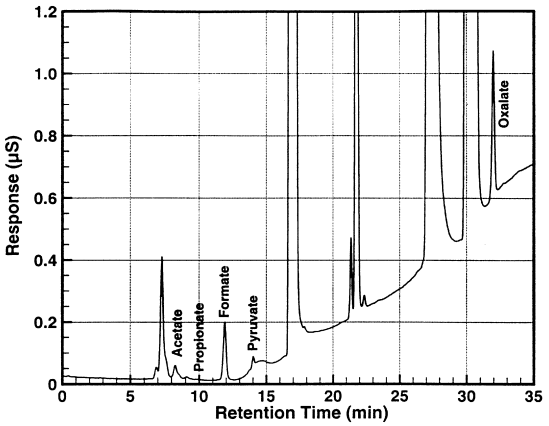

Fig. 7. Chromatogram of filter influent.

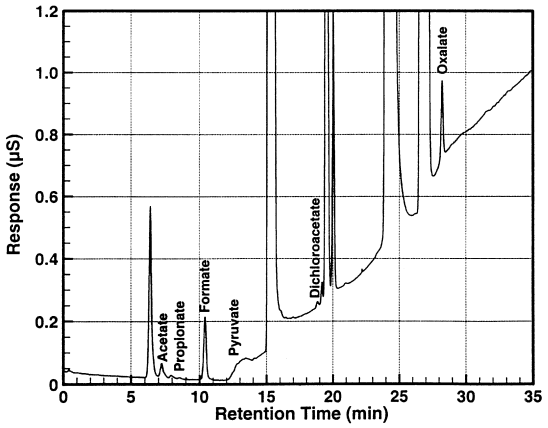

Fig. 8. Chromatogram of prechlorinated filter effluent.

on a carbon basis was approximately 150 μg/l. Fig. 9 represents the distribution of the carboxylic acids in percentages calculated on a carbon basis.

3.3.2. Removal of carboxylic acids through filter media

In general, the average percent removal of the three carboxylic acids (acetate, formate and oxalate) from either type of biologically active filter was approximately 80%, whereas pyruvate removal was nearly 60% (Table 4). These removal percentages are based on comparisons of the filter effluent and influent concentrations. Glyoxalate and ketomalonate were not detected in the filter effluent in most cases, and they appeared in small amounts near the detection limit in the filter influent; therefore, they were not used in the evaluation of media removal efficiency.

4. Summary and conclusions

IC is an excellent tool for the quantitative and qualitative determination of low-molecular-mass carboxylic acids such as acetate, propionate, formate, pyruvate, glyoxalate, dichloroacetate, oxalate and ketomalonate in water treated with ozone. This method uses a straightforward procedure (AS11 analytical and guard columns, isocratic and gradient-stage separation modes, and conductivity detection) with direct injection and in-line H^+ cartridge sample

Table 3
Carboxylic acids (μg/l) from ozonated[a]/biofiltered California state project water[b]

	Ozone contractor	Filter influent	GAC filter effluent	Anthracite filter effluent
Acetate	63.6	58.6	11.8	14.4
Propionate	3.7	4.7		
Formate	149.1	146.7	27.1	35.4
Pyruvate	22.2	29.5	13.1	11.5
Glyoxalate	26.6	21.1		
Oxalate	210.3	250.5	52.0	55.8
Ketomalonate	14.5	6.8		

[a] Ozone dose=1.6 mg/l, pH=8.3.
[b] Sample preserved with benzalkonium chloride.

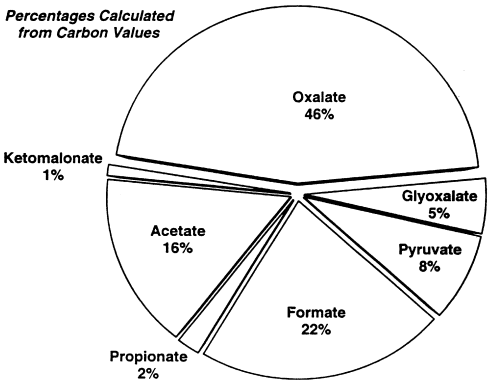

Fig. 9. Distribution of carboxylic acids in filter influent.

pretreatment processes. The samples can be analyzed without the use of a column-switching technique.

The separation and quantitation of acetate, propionate and formate, analyzed at very low-concentration NaOH eluents (0.1–0.2 m*M*), can realistically be accomplished on protonated samples with the help of an H^+ cartridge. For calibration standards prepared with ultrapure water, pretreatment of the H^+ cartridge is not necessary. Metropolitan's source waters have hardness and alkalinity at levels as high as 330 mg/l ($CaCO_3$) and 130 mg/l ($CaCO_3$), respectively; the pH of the source waters is commonly in the range of 8.00–8.60. The drawback of this procedure is that glyoxalate and ketomalonate must be run separately, without using an H^+ cartridge, because of the possibility of acid hydrolysis when the samples pass through the H^+ cartridge.

Table 4
Percent removal of carboxylic acids between filter influent and effluent

Filter media	Percent removal			
	Acetate	Formate	Pyruvate	Oxalate
GAC no. 1	88.3	79.4	61.5	81.1
Anthracite	81.1	71.5	60.9	80.9
GAC no. 2	78.6	80.0	55.6	83.6
Average	82.7	77.0	59.3	81.9

The preservation of samples with benzalkonium chloride (at a minimum amount of 30 mg/l) in water samples eliminated biodegradation and allowed samples to be stored for analysis for at least 30 days. For enhanced protection, 50 mg/l of benzalkonium chloride in the sample is recommended. Another advantage of using benzalkonium chloride as a preservative instead of mercuric chloride is that pyruvate can now be determined, with excellent recovery.

In addition, cleaning of the ATC-1 and the anion self-regenerating suppressor (ASRS) before each analytical run was necessary in order to acquire low baseline conductivity output and high area values during analysis. Frequent cleaning of the deionized water device is highly desirable to cut down contamination in background blank water.

The preliminary ODP data showed interesting results, which were comparable to the earlier reported pilot-plant results [5]. At an ozone dose of 1.6 mg/l, the ozone effluent samples of California state project water produced carboxylic acids at approximately 150 μg C/l. The oxalate was the major product of all carboxylic acids, accounting for approximately 50% of all carboxylic acids, followed by formate at 25%, acetate at 15% and pyruvate at 8%.

There was approximately an 80% reduction of the acetate, formate and oxalate through the biologically active filter, whereas the pyruvate reduction was about 60%.

Acknowledgements

The author thanks the ODP staff for preparing the ozonated samples; H.-C. Wang for reviewing the manuscript; and Peggy Kimball and Robert La Londe for technical editing of the manuscript and preparation of the graphics, respectively.

References

[1] G. Révész, P. Hajós, H. Csiszár, J. Chromatogr. A 753 (1996) 253.

[2] S. Peldszus, P. Huck and S. Andrews, in Proceedings: AWWA Water Quality Technology Conference, Boston, MA, 17–21 November 1996, American Water Works Association, Denver, CO, 1996 (CD-ROM), p. 49.

[3] B.M. Coffey, S.W. Krasner, M.J. Sclimenti, P.A. Hacker and J.T. Gramith, in Proceedings: AWWA Water Quality Technology Conference, New Orleans, LA, 12–16 November 1995, American Water Works Association, Denver, CO, 1996, p. 503.

[4] S.A. Andrews and P.M. Huck, in R.A. Minera and G.L. Amy (Editors), Disinfection By-Products in Water Treatment: The Chemistry of Their Formation and Control, CRC Press, Boca Raton, FL, 1966, p. 411.

[5] C.-y. Kuo, H.-C. Wang, S.W. Krasner and M.K. Davis, in R.A. Minera and G.L. Amy (Editors), Water Disinfection and Natural Organic Matter: Characterization and Control (ACS Symposium Series, No. 649), American Chemical Society, Washington, DC, 1996, p. 350.

[6] P.A. Hacker, C.M. Paszko-Kolva, M.H. Stewart, Ozone Sci. Eng. 16 (1994) 197.

[7] C. Sain, Dionex Corp., Sunnyvale, CA, personal communication, 15 September 1997.