Analysis and quantification of organic acids in simulated Hanford tank waste and Hanford tank waste

A.K. Sharma*, S.A. Clauss, G.M. Mong, K.L. Wahl, J.A. Campbell*

Pacific Northwest National Laboratory, Richland, WA 99352, USA

Abstract

Simulated Hanford tank waste samples were analyzed for organic acids before and after γ-irradiation. Ion chromatography (IC) was used for the analysis for low-molecular-mass (LMM) organic acids and proved to be an improvement over the previously used non-suppressed IC with ultraviolet (UV) detection method. Known quantities of sodium salts of ethylenediaminetetraacetic acid, N-(2-hydroxyethyl)ethylenediaminetriacetic acid, citric acid and glycolic acid were added to the tank waste simulants before exposure. The breakdown products of γ-irradiated simulated tank waste samples included formic, succinic and oxalic acids. These acids were identified and quantified using IC without any interference from nitrates, nitrites, or any other inorganic anions in the simulated waste. However, when non-suppressed IC with UV detection was used, nitrates and nitrites were found to interfere with the quantification of LMM organic acids. Ion chromatography techniques were also used on actual Hanford tank waste to quantify and analyze LMM organic acids. These efforts will assist in understanding Hanford tank waste chemistry and improving the carbon balance of tank waste samples. © 1998 Elsevier Science B.V.

Keywords: Hanford tank waste; Simulant waste material; Radioactive waste; Organic acids

1. Introduction

The US Department of Energy has 177 single and double shelled tanks at the Hanford site in south-central Washington state that contain mixed hazardous waste. A mixed hazardous waste is defined as a waste containing both hazardous chemicals and radionuclides. In addition, these tanks contain large quantities (150 000–250 000 kg) of chelators, including ethylenediaminetetraacetic acid (EDTA) and N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) [1]. The chelators form water-soluble complexes with cations, including radionuclides and

heavy metals, thus enhancing their migration in soils [2,3]. Furthermore, after over 40 years of storage under radiolytic conditions, chelator degradation fragments may have been produced that may also form cation complexes. Therefore, knowledge of chelator degradation mechanisms and their breakdown products is essential for the safe handling and storage of tank waste. Efforts are under way to study the effects of radiolysis on these chelators and their breakdown products by exposing simulated waste to radiolytic conditions for varying lengths of time. Simulant waste material (SWM) is a preparation used to study Hanford tank waste chemistry. The SWM contains most of the constituents found in Hanford tanks with the exception of the radionu-

*Corresponding author.

clides. This material can be studied without the hindrance associated with highly radioactive samples. Previous experiments with SWM have indicated that low-molecular-mass (LMM) organic acids, including formic and oxalic acids, are formed when HEDTA and EDTA, in an inorganic matrix, are exposed to radiolysis. However, organic quantification is difficult in the complex tank waste matrices, due to interference from inorganic components.

The usual method for LMM organic acid analysis involves capillary gas chromatography (GC), with or without mass spectrometry, after solvent extraction and derivatization [4,5]. The derivatization techniques used are: (a) the formation of methyl esters using BF_3–methanol or diazomethane, (b) the formation of trimethylsilyl esters using trimethylsilyl reagents and (c) the formation of butyl esters using HCl–butanol. Another routine method for analyzing LMM organic acids is high-performance liquid chromatography (HPLC). Organic acids have been analyzed using normal-phase silica separation, but, more frequently, they have been separated underivatized [6,7] or as their phenacyl derivatives [8]. Ion-exclusion chromatography with UV detection at 210 nm has also been applied for LMM organic acid analysis [9]. However, UV detection is not specific, as several organic and inorganic species absorb at 210 nm. Other methods of organic acid analysis include plasmaspray liquid chromatography [10,11] and ion-exclusion partition chromatography [12].

Historically, LMM organic acids, such as oxalic and glycolic acid, in tank waste samples were analyzed using non-suppressed IC with UV detection [13]. However, high concentrations of nitrate and nitrite often interfered with quantitation, and UV detection exhibited poor sensitivity for LMM organic acids. Thermospray liquid chromatography–mass spectrometry (LC–MS) has also been used for the qualitative determination of LMM organic acids and chelator fragments with moderate success [4]. One advantage of using LC–MS over GC–MS is that derivatization is not required in LC–MS, and non-volatile inorganic species do not have to be removed, as long as they are soluble in the mobile phase [4]. However, oxalic acid could not be detected by LC–MS. Therefore, a simple but robust IC technique was developed for the analysis of LMM organic acids. This method required minimum sample preparation

and was found to be effective for the identification and quantification of these acids [14].

The IC method developed by our research group was used to detect and analyze LMM organic acids in simulated tank waste and actual tank waste. The components identified and quantified in actual Hanford tank waste include formic, oxalic and citric acid. The results of these analyses are reported here. This method can potentially be applied in the analysis of effluents containing nitrates and nitrites, such as those collected from biotech, pesticides and explosives processing plants. The results from our investigation show that IC can be effectively used to identify and quantify LMM organic acids in the presence of the high nitrate and nitrite concentrations found in Hanford tank waste samples.

2. Experimental

2.1. Standard organic acid preparation

Organic acid stock solutions were prepared fresh daily by dissolving 25–50 mg of free acids or sodium salts of the free acids in 25 ml of deionized water. All standard solutions were made from commercially obtained reagent-grade chemicals without further purification.

Initially, standard solutions of glyoxalic acid, glycolic acid, oxalic acid, sodium citrate, sodium acetate, succinic acid, butyric acid and formic acid were prepared. These acids were expected since previous experiments with SWM have indicated that LMM organic acids are formed when HEDTA and EDTA, in an inorganic matrix, are exposed to radiolysis. The chelator breakdown mechanism is believed to be free-radical based under radiolytic conditions. The proposed mechanism predicted the presence of these acids. However, glyoxalic acid and butyric acid were not detected in the samples and these two acid standards were not used.

2.2. Analysis by ion-exchange chromatography

Analyses of LMM organic acid anions, including formic, glycolic, citric and oxalic acids were carried out using a Dionex Model 500 DX IC unit (Dionex, Sunnyvale, CA, USA) equipped with a Dionex

Model CD20 conductivity detector. Most analyses were carried out using a Dionex IonPac AS-11 column. We used a Dionex IonPAc ICE AS-6 column for glycolic acid quantification, since glycolic acid co-eluted with acetic acid on the AS-11 column. The standard concentrations bracketed the estimated concentrations of the samples.

The mobile phase contained a gradient of deionized water and a weak solution of sodium hydroxide for the AS-11 column. Two solutions, 5 and 100 mM NaOH, were prepared from an 18.5 M NaOH stock solution [15]. The water used to prepare the mobile phase and run the gradient was stirred under vacuum for over 12 h, and then sparged with helium to avoid interference from dissolved carbon dioxide. The column was allowed to equilibrate under the initial conditions for at least 7 min before each run.

The mobile phase for the AS-6 column was made up of 0.4 mM heptafluorobutyric acid in deionized water [16]. We used 5 mM tetrabutylammonium hydroxide as a suppression eluent.

2.3. Chromatography conditions for Hanford tank waste samples

Radioactive samples were analyzed within a laboratory-fabricated chromatography enclosure, which was located in a radiation fume hood. The enclosure was equipped with an AS-11 column, an ASRS-I Suppresser and a conductivity cell. Samples were injected through a Rheodyne 9126 (Cotati, CA, USA) manual injection valve. The HPLC pump, the suppressor and the detector's electronics were located outside the radiation hood. This arrangement

allowed for simple and rapid switching between radioactive and non-radioactive analyses without concern for radioactive contamination of the key system components. The chromatographic conditions used for the analysis of radioactive and non-radioactive samples were identical.

2.4. Simulated tank waste preparation

About 130 ml of simulant slurry were prepared by mixing a variety of inorganic salts with sodium hydroxide and deionized water. The specific chemical composition of the simulant is summarized in Table 1 [17].

The simulant samples were exposed to various doses of γ-irradiation for one–two weeks in a sealed stainless steel bomb reactor. The bomb reactor was recovered after irradiation. Four aging tests were run; one each at 0.3, 0.5, 1.0 and 1.5 MGy at 70°C. The average temperature within the tanks was estimated to be above 65°C, therefore, these experiments were conducted at 70°C. After irradiation, the contents of the vessel were quantitatively transferred to a 500-ml volumetric flask and diluted to volume with water. The resulting solution was further diluted 250-fold and analyzed using IC for organic acids. In addition, a non-irradiated control simulant was mixed and then analyzed.

2.5. Preparation of Hanford tank waste samples

Samples collected from Hanford tank AN-107 are typical examples of highly aged, relatively organic-rich, Hanford tank waste matrices. The clean-up

Table 1
Composition of simulated tank waste

Species	Concentration (mg/g)	Species	Concentration (mg/g)	Species	Concentration (mg/g)
HEDTA^{3-}	16.9	Al^{3+}	1.493	Ca^{2+}	0.080
EDTA^{4-}	3.1	F$^-$	1.281	Mn^{2+}	0.068
Citrate^{3-}	17.3	Pb^{2+}	1.066	Cr^{3+}	0.044
Glycolate$^-$	11.3	PO$_4^{3-}$	0.507	Cl$^-$	0.004
NO$_3^-$	109	SO$_4^{2-}$	0.506	Pd^{2+}	0.003
Na$^+$	107	Bi^{2+}	0.419	Rh^{3+}	0.003
OH$^-$	39.3	Ce^{3+}	0.377	Ru^{4+}	0.003
NO$_2^-$	37.9	Ni^{2+}	0.099	Water	640
Fe^{3+}	2.61				

procedure, performed within hot cell facilities at Hanford, reduced the amount of fission products present in the sample [18]. A hot cell is a room built with thick walls (~1.3 m), equipped with a sample entry port, viewing windows made from leaded glass and filled with oil, and remote manipulators [5]. A hot cell must be used for the safe handling of highly radioactive wastes (~3–11 R/h). All sample preparation is carried out in the hot cell using remotely controlled mechanical arms. The clean-up procedure used Poly-prep, 40×8 mm, disposable fritted columns packed with AG 50W-X8 cation-exchange resin, sodium form (Bio-Rad, Hercules, CA, USA). The treatment within the hot cell also results in a tenfold dilution (w/w) of the sample into a dilute caustic matrix that is not significantly different from the matrix of the original sample. An additional 500-fold dilution was performed to dilute the major inorganic ions (nitrite and nitrate) to levels that would not overload the capacity of the analytical column. Previous experience has demonstrated that ion-exchange sites within the IC column apparently do not recover quickly from an overload of these inorganic species, which results in a non-uniform elution of the weakly retained analytes (e.g. acetate, formate). This phenomenon is evident to the analyst by virtue of poorly resolved peaks, and decreased column efficiency for the monovalent carboxylates. We have found that diluting nitrate to a concentration that delivers a 10–20 μS response eliminates this problem.

3. Results and discussion

Analysis of organic acids in a complex matrix (slurries and sludge) containing excess amounts of nitrates, nitrites and other transition metal salts is difficult by conventional techniques. Separation using HPLC followed by UV–Vis detection is not practical because the target analytes do not contain a chromophore.

Analytes including citric, succinic, glycolic and formic acid could be separated and quantitated by non-suppressed IC with UV detection. However, in the presence of nitrate and nitrite, these LMM organic acids could not be quantitated by non-suppressed IC. Diluting the simulated waste sample was

not an effective solution for reducing the interference from nitrate and nitrite, because dilution further reduced the already low response of LMM acids. Alternatively, we found that IC using a gradient elution profile and suppressed conductivity detection was an effective method of analysis for quantifying organic acids in the presence of nitrates, nitrites and other impurities. All target acids, except glycolic, succinic and acetic acid, were analyzed using the AS-11 column. Glycolic acid was found to co-elute with acetic acid on the AS-11 column, therefore, ion-exclusion chromatography with the AS-6 column was used to quantify glycolic and acetic acid. An IC chromatogram of a simulated waste solution obtained using an AS-11 column is shown in Fig. 1. A continuing calibration standard of 4 μg/g was run prior to each series of samples.

As shown in Fig. 1, no interference from any inorganic anion was observed. Furthermore, the response of the LMM organic acid was significantly improved under IC conditions compared to HPLC conditions for identical concentrations. It is unlikely that glycolic and acetic acid can be quantified by other means, such as GC–MS analysis, in this matrix. The samples contain such minor amounts of
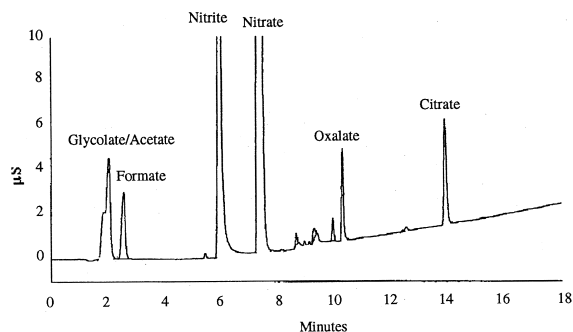

Fig. 1. IC chromatogram of LMM acids in simulated waste (after 1 MGy exposure) with conductivity detection using a Dionex AS-11 analytical column (250×4 mm) and an AG-11 (50×4 mm) guard column, at ambient temperature with a 25-μl sample loop. A 4-mm Dionex anion suppressor unit (ASRS-I) was used. The flow-rate of the mobile phase (dilute NaOH) was 2.0 ml/min. The gradient conditions were: (a) 0.0 min 0% 100 m*M* NaOH, 90% deionized water and 10% 5 m*M* NaOH; (b) 2.9 min 0% 100 m*M* NaOH, 90% deionized water and 10% 5 m*M* NaOH; (c) 6.4 min 0% 100 m*M* NaOH, 0% deionized water and 100% 5 m*M* NaOH; (d) 18.4 min 35% 100 m*M* NaOH, 0% deionized water and 65% 5 m*M* NaOH [15].

these materials that the preparation/handling steps associated with derivatization to make them amenable to GC analysis will give the samples ample opportunity to lose the extremely volatile methyl esters of these acids. Succinate anion was also quantified using the AS-6 column. Although succinate could be effectively analyzed by the AS-11 column, the AS-6 column was used for procedural convenience. Concentrations were determined using a linear calibration curve. Quantification based on high dilution is not ideal, but appears to be permissible, as the plots of standard concentration versus response exhibit linear behavior down to 100 ng/g for the key analytes. These analytes include acetate/ glycolate, formate, oxalate and citrate in our samples. The retention time for acetate and succinate anions, separated and analyzed by the AS-6 column, were 15.37 ± 0.20 and 16.35 ± 0.20 min, respectively. The IonPac ICE-AS6 column uses an ion-exclusion mechanism that allows retention and separation of weakly ionized acids based on the differences in pK_a values. Therefore, strong inorganic acids, including nitric and nitrous acids, are not retained by the stationary phase and elute in the void volume of the column.

An ion-exclusion chromatogram of a simulated waste sample by the AS-6 column is shown in Fig. 2. A continuing calibration standard of 4 μg/g was run prior to each series of samples.

As shown in Table 1, citric acid and glycolic acid were added to the slurry before irradiation. Therefore, the concentration of these acids in the control sample should be non-zero. Table 2 lists results from the analysis of irradiated and unirradiated simulant using IC. As shown in Table 2, all target analytes were successfully analyzed using IC, without any inorganic interference. Significant quantities of formic, oxalic, glycolic and citric acid were determined along with small amounts of acetic and succinic acid. For example, the detected levels of oxalic acid were as high as 8.5 mg/g (1.5 MGy dose rate). The highest concentration observed for acetic acid was 0.55 mg/g and for succinic acid, it was 1.78 mg/g (1.5 MGy dose rate).

3.1. Analysis of Hanford tank waste

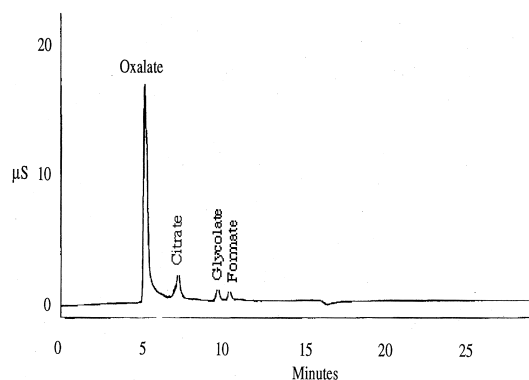Several actual waste samples were successfully

Fig. 2. Ion-exclusion chromatogram of LMM acids in simulated waste (after 1 MGy exposure) with conductivity detection using a Dionex ICE-IonPac AS-6 column (250×9 mm) at ambient temperature and a 25-μl sample loop. The flow-rate of the mobile phase (0.4 mM heptafluorobutyric acid) was 1 ml/min. A Dionex AMMS-ICE suppressor was used with 5 mM tetrabutylammonium hydroxide as the suppression eluent, at a flow-rate of 3 ml/min. The analysis was carried out under isocratic conditions [16].

analyzed for LMM organic acids using IC and an AS-11 column. Fig. 3 illustrates the elution scheme for LMM organic acids in a sample from Hanford tank AN-107. The concentrations of these acids were determined by an external standard calculation and are listed in Table 3.

The only questionable separation at this point is the discrimination of acetate from glycolate, both of which are apparently feasible components in actual tank waste materials. To address this question, we will use an AS-6 column that employs a separate chromatographic mechanism based on ion exclusion to distinguish these relatively similar acids.

4. Conclusion

Analysis and quantitation of LMM organic acid anions, in the presence of nitrate, nitrites and transition metal elements, at high pH values ($>$13) can be carried out effectively by using ion-exchange chromatography techniques. Thus, extensive sample preparation, such as that needed for analysis by GC–MS (e.g., BF$_3$–methanol derivatization) can be avoided. Additionally, the IC technique exhibited a significant improvement in analysis, separation and quantification over non-suppressed IC with UV detection and GC–MS techniques. The information

Table 2
Concentrations of reactants and products in γ-irradiated tank waste simulant

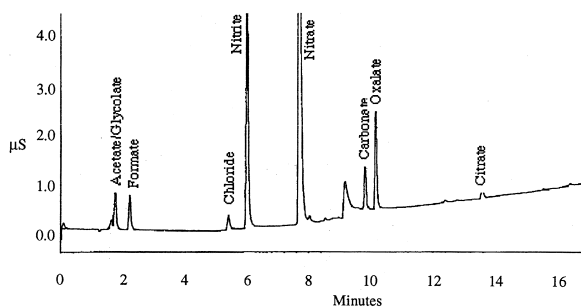| Dose (MGy)	Concentration (mg/g)					
	Formic acid	Oxalic acid	Glycolic acid	Citric acid	Acetic acid	Succinic acid
0 (control)	0.00	0.00	8.34±0.03	15.4±0.1	0.19±0.2	0.00
0.30	0.8±0.1	1.7±0.1	7.54±0.11	14.9±0.1	0.35±0.1	0.10
0.50	1.7±0.2	2.8±0.2	6.77±0.02	13.8±0.1	0.42±0.1	0.29
1.00	2.5±0.1	3.5±0.2	5.91±0.01	12.6	0.48±0.1	1.09
1.50	4.5±0.2	8.5±0.2	5.30±0.01	11.4±0.1	0.55±0.01	1.78

Fig. 3. IC chromatogram of LMM acids in Hanford tank waste (tank identity, AN-107). The chromatography conditions, gradient, column and the detection system were identical to that used for the analysis of simulated waste shown in Fig. 1.

gathered using IC will help in determining the mechanism of chemical transformation of organic acids in the presence of γ-radiation. Furthermore, accurate determination of organic species will assist in predicting the energetics in Hanford tanks. This study shows that the IC technique can be used for the analysis of LMM organic acid anions at high pH values ($>$13), in the presence of nitrate, nitrite and other impurities, such as those found in effluent from explosive and pesticide processing.

Acknowledgements

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Table 3
Concentrations of low-molecular-mass organic acids in Hanford tank waste

Tank identity	Concentration (mg/g)			
	Acetic/glycolic acid	Formic acid	Oxalic acid	Citric acid
S-102	1.2	1.7	4.4	0.0
U-107	2.3±0.1	2.5±0.3	0.6±0.1	0.5±0.1
AN-107	7.6±0.5	4.5±0.5	14.2±3.3	4.4±0.2

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