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Simultaneous determination of monofluoroacetate, difluoroacetate and trifluoroacetate in environmental samples by ion chromatography

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Abstract

A method is reported for the sensitive, simultaneous determination of mono- (MFA), di- (DFA), and trifluoroacetates (TFA) by ion chromatography (IC). These species were separated using a Dionex AS17 anion-exchange column employed with a potassium hydroxide gradient (via a Dionex EG40 eluent generator) and suppressed conductivity detection. The fluoroacetates were successfully separated from a range of inorganic and organic species likely to be present in environmental samples, in a total analysis time of 35 min (including re-equilibration of the column). Detection limits for mono-, di- and trifluoroacetate were 21, 38 and 36 μg/l, respectively, determined using a signal-to-noise ratio of 3, and were obtained using a sample injection volume of 50 μl. Precision was less than 0.83% relative standard deviation (RSD) for replicate injections performed over a period of 30 days. The method was applied to the determination of monofluoroacetate in river water samples and also in carrot baits.

Keywords: Gradient elution; Environmental analysis; Fluoroacetates

1. Introduction

The polyfluoroacetates comprise mono- (MFA), di- (DFA), and trifluoroacetate (TFA) and these species are present in many environmental samples due to their use in various industrial applications. Trace amounts are found in drinking water, chemical waste, animal products and plants. MFA is used as the active chemical in some rodenticides and was first reported for this application shortly after the end of the Second World War [1]. This compound is still commonly referred to under the laboratory serial number, "1080" (sodium fluoroacetate), assigned by the Economic Investigations Laboratory, US Fish and Wildlife Service, at Patuxet, MD, USA. LD_{50} values for MFA are extremely low, ranging from 66 μg/kg (dog, oral) to 714 μg/kg (human male, oral) [2] and it has been used as a vertebrate pesticide for more than 50 years, particularly throughout North America, Australia and New Zealand with peak usage occurring in the 1960s [3]. Every year, about 80 t of carrot laced with MFA is laid as baits in Australia. DFA is reported as being acutely toxic [4], but no value for its LD_{50} could be found in a current literature review. The LD_{50} for TFA is reported to be 200 mg/kg. Few reports on the biodegradation of DFA and TFA are available, although Visscher et al. [5] reported instances of reductive defluorination of TFA under methanogenic and sulfate-reducing conditions. It was found that TFA was sequentially defluorinated to DFA, MFA, and acetic acid, the latter component ultimately yielding methane. TFA is also produced as a by-product of the metabolism of the anaesthetic, halothane. As all fluoroacetates are toxic, the availability of a reliable method for their determination is considered important.

The standard method for determining fluoroacetates is liquid-liquid extraction followed by gas chromatography (GC) using electron-capture detection. This method is described in US Environmental Protection Agency (EPA) method 552 [6] and is applicable to the determination of six halogenated acetic acids in drinking, ground and raw water. Even though the detection limits for the acids are in the low μg/l range, this method is complicated and time-consuming, with two significant problems being evident. First, the high polarity of fluoroacetates makes these substances unsuitable for direct GC analysis and derivatization to their alkyl esters is necessary prior to analysis. Second, the fluoroacetates have high water solubility, which makes their separation from water difficult and is often the cause of low recoveries [7,8]. HPLC has also been used for the determination of

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Table 1
Physical properties of fluoroacetates

Name	Abbreviation	Formula	pK_a	ε (l/mol cm)
Monofluoroacetate	MFA	CH_2FCO_2H	2.59	1.74×10^3 (187 nm)
Difluoroacetate	DFA	CHF_2CO_2H	1.33	1.57×10^3 (187 nm)
Trifluoroacetate	TFA	CF_3CO_2H	0.50	4.47×10^3 (190 nm)

MFA and TFA in baits [9–11], but due to their low UV absorptivities (Table 1) appropriate derivatization is necessary to enhance their sensitivity to UV or fluorescence detection. These derivatizations reactions are often difficult to drive to completion, so that reaction times of up to 10 h are normally needed [12]. Although the derivatization time was reduced to less than 30 min by Collins et al [9] and Collins [10], extraction and drying procedures prior to derivatization were still needed since the derivatization reaction occurred only in non-aqueous solution, making this method unsuitable for the analysis of large numbers of samples. Determination of fluoroacetates can be achieved using ion-interaction or anion-exchange chromatography with detection by UV absorbance at 210 nm or refractive index [13]. Currently, these methods cannot be used for trace analysis due to sensitivity problems. Ion chromatography (IC) with suppressed conductivity detection is particularly well-suited to the separation of small ions such as fluoroacetates. Several IC methods using both ion-exchange and ion-exclusion as the separation principle (the latter approach being possible due to the differing pK_a values of the analytes, see Table 1) have been described in the literature [14–18]. However, none of these methods is capable of simultaneous determination of all three fluoroacetates at the levels found commonly in environmental samples. We have therefore investigated the use of anion-exchange IC utilising gradient elution with hydroxide eluents, coupled with suppressed conductivity detection. Using this approach, simple sample preparation procedures can be used and appropriate detection limits can be realized. Samples analyzed include river water and carrot baits.

2. Experimental

2.1. Reagents

Stock solutions containing MFA, DFA and TFA were prepared from analytical grade reagents obtained from Aldrich (Milwaukee, WI, USA). Water purified on a Milli-Q water purification system (Millipore, Milford, MA, USA) was used to prepare all solutions, including eluents, stock solutions, and standard solutions. All other chemicals employed were analytical reagent grade unless otherwise specified.

2.2. Apparatus and operating conditions

The ion chromatograph used was a Dionex (Sunnyvale, CA, USA) model DX600 instrument, equipped with a GP50 gradient pump, a CD25 conductivity detector with ASRS suppression, EG40 eluent generator, AS50 Auto sampler and thermal compartment containing a Dionex IonPac AS17 (4 mm × 250 mm) analytical column, and IonPac AG17 (4 mm × 50 mm) guard column. Unless stated otherwise, the sample injection volume was 50 μl. Other conditions were: suppressor current of 50 mA; column temperature of 30 °C; pump flow rate of 1.00 ml/min. Data acquired during the determination were collected and processed using Dionex Peaknet 6.3 software. The optimized gradient profile is detailed in Table 2.

2.3. Preparation of samples

Water samples were filtered through a 0.45 μm nylon syringe filter. The filtrate was analyzed directly and after spiking with one of three standard mixtures of the fluoroacetates containing concentrations of 0.1, 0.2 or 0.4 ppm of each analyte.

Carrot baits were prepared according to a published method [19] in which the sample was homogenized in a blender and soaked in a standard aqueous solution of 1.5% MFA for 20 min. The supernatant liquid was removed and the sample partially dried for 2 h under nitrogen. For analysis, a 1.00 g portion was added to 100 ml of water, the mixture shaken for 1 h on a reciprocating shaker, followed by ultrasonic digestion for 3 h at 20 °C. Finally, the supernatant liquid was filtered through a 0.45 μm nylon syringe filter, prior to MFA analysis. An actual field bait carrot sample, which had dried for 3 months after exposure to 1080, was also analyzed. An accurately weighed portion comprising about 1 g of the sample was divided into small pieces and added to 100 ml of deionized water. Different procedures were applied for the fresh and aged field samples as there was an insufficient quantity of the latter sample. The remaining steps for the extraction were as described above.

Table 2
Optimized gradient profile for separation of trifluoroacetates by anion-exchange IC

Time (min)	Flow (ml/min)	KOH (mmol/l)	Comment
Initial	1.0	0.5	
0	1.0	0.5	Sample injection
10	1.0	2.5	
30	1.0	20	
30	1.0	0.5	End of step gradient
35	1.0	0.5	

3. Results and discussion

3.1. Optimization of gradient elution for the separation of fluoroacetates

Potassium hydroxide gradients were produced using a Dionex EG40 eluent generator. The gradient profile was optimized empirically using isocratic eluents to establish elution behavior of the analytes and common inorganic and organic ions likely to be present in environmental samples. In general, MFA and DFA were retained weakly and were separated poorly from other singly charged anions such as formate, fluoride, acetate and chloride, whilst TFA was retained strongly. For these reasons, it was necessary to use a very weakly eluting eluent composition at the start of the separation and to rapidly increase the eluent strength so that TFA could be eluted in a reasonable time (<35 min). The optimized gradient conditions are given in Table 2, while Table 3 lists retention times of the fluoroacetates and potential interferents under the optimal gradient conditions. Using the optimized gradient profile, the three fluoroacetates were resolved from each other and also from other common inorganic and organic anions. A representative chromatogram obtained for a standard mixture of fluoroacetates using this gradient profile is illustrated in Fig. 1.

Table 3
Retention times of the fluoroacetates and potential interferents under the optimized gradient conditions

Analyte	Retention time (min)	Analyte	Retention time (min)
F^-	6.08	TFA	18.14
Acetate	6.35	Br^-	18.67
Formate	7.63	NO_3^-	19.47
MFA	8.01	PO_4^{3-}	24.95
DFA	12.06	Succinate	25.61
BrO_3^-	12.69	Tartrate	26.97
Cl^-	13.19	SO_4^{2-}	28.52
Phthalate	13.23	ClO_4^-	29.22
NO_2^-	14.70	Oxalate	29.94

3.2. Analytical performance characteristics

The use of an eluent generator coupled with suppressed conductivity detection allowed very low detection limits to be achieved. Linear calibration plots ($R^2 > 0.9986$) were obtained for each of the fluoroacetates over the range 2.5–6400 μg/l. Using a signal-to-noise ratio of 3, the detection limits for MFA, DFA, and TFA were 21 μg/l, 38 μg/l, and 36 μg/l, respectively. Replicate injections over a period of 30 days gave relative standard deviation (RSD) values for peak area of 0.83, 0.56, and 0.48% for MFA, DFA and TFA, respectively. Both UV absorbance and conductivity detectors were employed simultaneously. Comparison of these showed that the sensitivity of UV detection was much lower than that for suppressed conductivity detection, but the UV detector was more selective and therefore was of some value in the analysis of real samples.

3.3. Applications

Environmental concerns are high in areas where MFA baits have been laid, particularly with regard to MFA being leached from baits and entering water courses. A series of samples collected from baited regions in Tasmania was

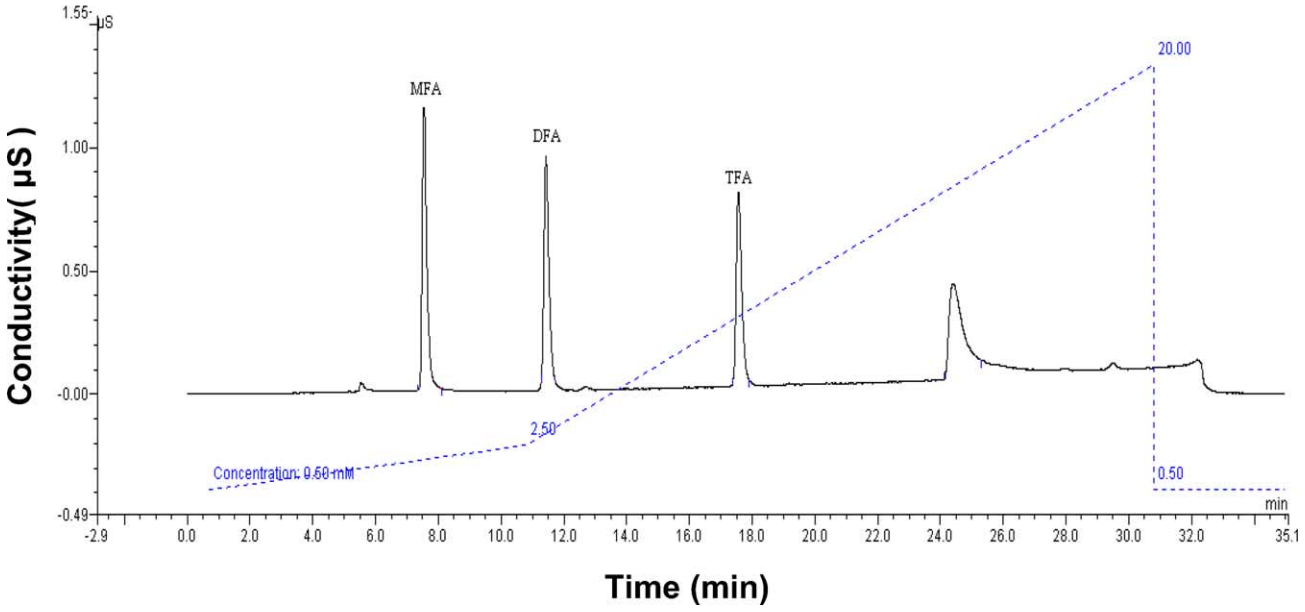

Fig. 1. Chromatogram for the separation of a standard mixture of fluoroacetates. Conditions: column, Dionex IonPac AS17 (4 mm × 250 mm) plus AG17 guard column; eluent, see Table 1; injection volume, 50 μl; detection, suppressed conductivity ASRS®-ULTRA. Analyte concentrations: 800 μg/l.

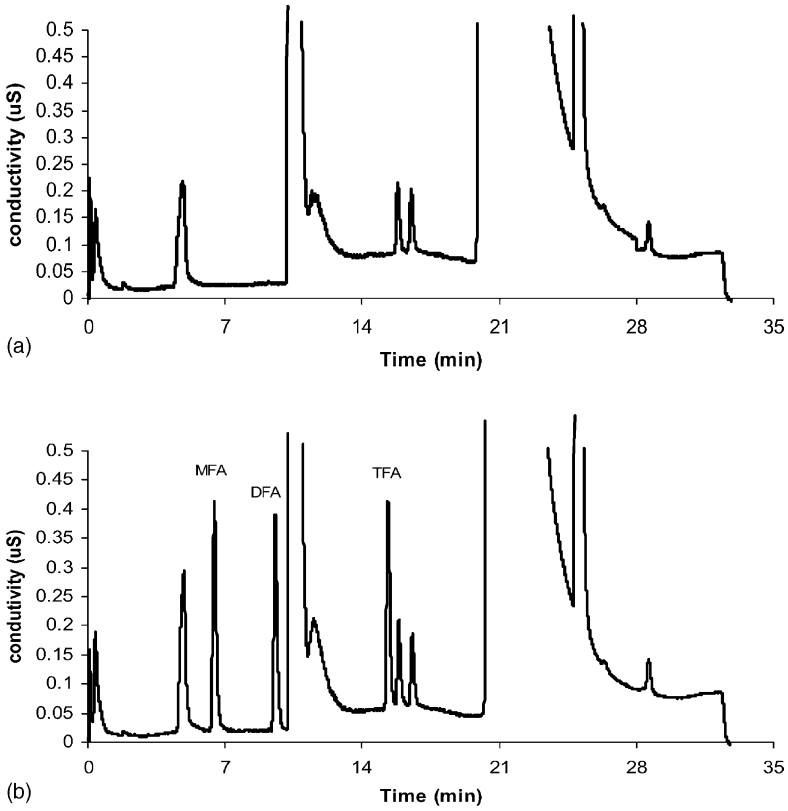

Fig. 2. Chromatogram of (a) river water sample and (b) the same river water sample spiked at 200 μg/l of each fluoroacetate. Other conditions as for Fig. 1.

analyzed, but no MFA could be detected in these samples. In order to establish that the proposed method could be used for such samples, three water samples were spiked with fluoracetates at a concentration of 200 μg/l. A representative chromatogram of a river water sample is shown in Fig. 2a, while Fig. 2b shows the same river water sample after spiking with a standard mixture. Table 4 lists the recoveries for each of the fluoroacetates. Fig. 2b shows that well-defined peaks for MFA, DFA and TFA were obtained and there was good separation from chloride, which was the most probable interferent present in the samples. Two smaller peaks were eluted after TFA, but no attempt was made to identify these analytes. Table 4 shows that the recovery values for the spiked fluoroacetates were in the range of 96–102%.

Table 4
Recovery values for fluoroacetates spiked into river water at 200 μg/l

Sample no.	MFA (%)	DFA (%)	TFA (%)
1	105	98	99
2	96	99	97
3	99	97	99

Analysis of carrot baits is also of interest in order to determine the rate of loss of MFA from the baits and hence their

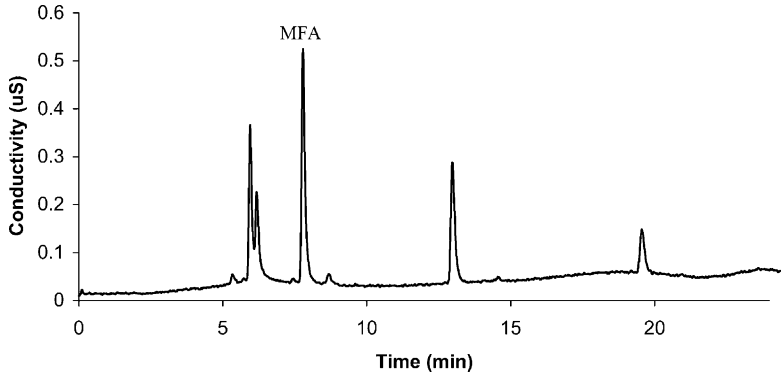

Fig. 3. Chromatogram of a freshly prepared carrot bait. Conditions: column, Dionex IonPac AS17 (4 mm × 250 mm) plus AG17 guard column; eluent, see Table 1; injection volume, 50 μl; detection, suppressed conductivity ASRS®-ULTRA.

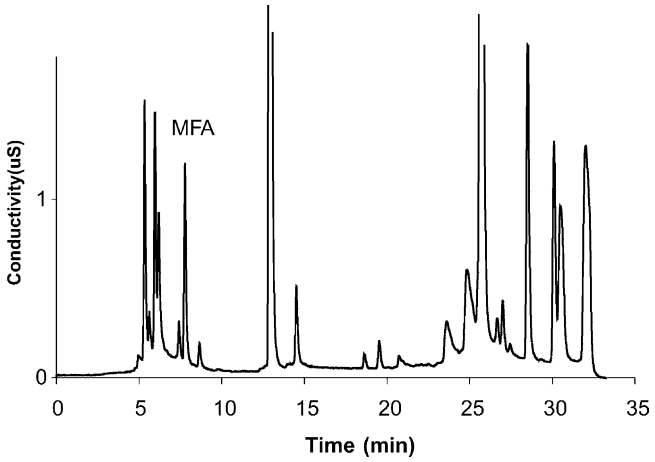

Fig. 4. Chromatogram of an aged field carrot bait. Conditions: column, Dionex IonPac AS17 (4 mm × 250 mm) plus AG17 guard column; eluent, see Table 1; injection volume, 50 μl; detection, suppressed conductivity ASRS®-ULTRA.

practical lifetime. Two kinds of carrot baits were analyzed, the first being a bait prepared freshly from raw carrots according to an established method, and the second being an aged sample taken from the field after exposure for 3 months. The chromatogram for freshly prepared sample is shown in Fig. 3, and gave an MFA level of 37 ppm ± 0.5 ppm, determined from triplicate determinations (RSD: 3.5%). The chromatogram for the aged bait sample is given in Fig. 4 and shows that a more complex chromatogram was obtained than was the case for the freshly prepared sample, presumably due to the presence of contaminants arising from field exposure and also to the dye Monsperse blue which is added as a marker to identify toxic baits. The level of MFA in the aged bait was 88 ± 0.5 ppm (RSD: 3.8%), which while appearing to be an increase over the fresh bait was in fact due to the aged bait having a very much lower water content than the fresh bait. However, this shows that MFA in carrot baits is very persistent. The recovery of a sample spiked with 0.8 ppm MFA was 96%.

4. Conclusions

Simultaneous determination of fluoroacetates was achieved using anion-exchange ion chromatography with suppressed conductivity detection. Under optimized conditions, MFA, DFA and TFA were rapidly and completely separated with high detection sensitivity. The method suffers from no significant interferences from concurrent inorganic and organic ions, and was successfully used to analyze MFA in carrot and water samples. Compared to existing alternative methods for fluoroacetates, IC offers a straightforward and convenient approach to routine analyses of fluoroacetates.

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