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Ion chromatographic separation and quantitative analysis of fluoroacetic acid and formic acid in soil

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Abstract

An analytical method has been developed for the determination of fluoroacetic acid (FC2A) and formic acid (FA) which previously co-eluted in ion chromatographic analysis. The separation is based upon a solvent compatible, ion-exchange column. The analytes are retained by ion exchange, but selectivity is provided by a mechanism that has reversed-phase characteristics. Low detection limits (0.1 μg FC2A/g soil) are achieved through the use of a preconcentrator column. The method is designed to detect small amounts of FC2A in the presence of high concentrations of FA, a major interference found in some western soils. Sample preparation is minimal. The method has been applied to Rocky Mountain Arsenal (RMA) Standard Soil and to samples collected at RMA.

1. Introduction

Fluoroacetic acid (FC2A) is an extremely potent rodenticide first reported shortly after the end of the Second World War [1]. The 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. LD50s for FC2A are extremely low, ranging from 66 μg/kg (dog, oral) to 714 μg/kg (man, oral) [2]. It is currently used as a rodenticide in New Zealand and Australia [3]. FC2A has been historically used in the western US for the control of coyotes and wolves. The US Environmental Protection Agency (USEPA, Washington, DC, USA) has recently denied Federal Insecticide, Rodenticide, and Fungicide Act (FIFRA) registration of FC2A [4].

The Rocky Mountain Arsenal (RMA) is a military installation located near Denver, CO, USA, contaminated with waste from chemical warfare agent, pesticide, and other chemical manufacturing processes. The site is presently being remediated under the set of statues known collectively as "Superfund". F2CA is a suspected chemical of concern at the site. FC2A has been suggested as a possible byproduct from chemical warfare agent manufacture [5]. Historical information indicates that FC2A was used at RMA for the control of small mammals during the 1960s and 1970s. Application of FC2A for small mammal control was usually accomplished through the hand (or mechanical) broadcast of treated grain baits. Previous investigations have found quantities of suspected FC2A in RMA soils. However, the analytical method used did not separate FC2A from formic acid (FA), a

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naturally occurring compound at RMA [6]. Additionally, the existing detection limit of 2 μg/g for FC2A exceeded the desired, risk-based, detection limit of 0.2 μg/g [7]. Formic acid concentrations may be as high as 40 μg/g in RMA soil.

Most of the existing methods for the analysis of FC2A utilized derivatization followed by quantification by GC [8–19] or HPLC [20–22]. Derivatization methods have, in general, long preparation times and variable recoveries. Ion-pair methods [23] or ion chromatographic methods [24] designed for the analysis of formulations lack sensitivity. The US Army Toxic and Hazardous Materials Agency (USATHAMA) method previously in use at RMA does not discriminate against the formic acid interference. ^{19}F NMR has been used for investigations into FC2A metabolism [25–27]. NMR is highly specific, but suffers from low sensitivity. Fluoride ion-specific electrodes are sensitive, but non-specific to FC2A [28,29].

The method presented in this paper is based upon the use of new solvent compatible anion chromatographic columns that can utilize multiple retention mechanisms for the separation of organic acids that have similar ion-exchange characteristics. We have recently applied the same approach to the separation of five chemical warfare agent related compounds, pinacolyl methylphosphonic acid, isopropyl methylphosphonic acid, ethyl methylphosphonic acid, methyl methylphosphonic acid, and methylphosphonic acid [30]. The method uses high concentrations of organic modifier (acetonitrile) to separate FC2A and FA while the compounds are retained by ion exchange on the solvent compatible column.

2. Experimental

2.1. Materials

Type I deionized water was obtained from a Barnstead (Dubuque, IA, USA) NANOpure reagent water system fed by a Corning still. Optima grade acetonitrile (ACN) was obtained from Fisher Scientific (Pittsburgh, PA, USA). NaOH solutions were prepared using 50% (w/w) Fisher certified reagent. Regenerant solution was prepared from trace metal grade H_2SO_4 (Fisher). Fluoroacetic acid (>96%) was obtained from Aldrich (Milwaukee, WI, USA). Formic acid (>95%) was purchased from Fisher. Ag^+-form strong cation-exchange solid-phase extraction cartridges (Ag^+-SPE) were obtained from Alltech Chromatography. All other chemicals used were ACS grade or reagent grade.

2.2. Apparatus

The basic chromatographic system was a 4500i ion chromatograph with GPM pump, AMMS-II micromembrane suppressor, and a PED (conductivity mode) detector, all from Dionex (Sunnyvale, CA, USA). Samples were injected by a Dionex ASM autosampler, set either in loop or concentrator mode (<1 ml/min). The system was controlled, and data collected, by a Dionex AI-450 interface and software (Version 3.21) from an IBM PS/2 Model 35 PC. Dionex OmniPac PAX-100 column and OmniPac PAX-100G guard column were used as the stationary phase. Either a 250-μl loop or an OmniPac PAX-500G guard column (as a preconcentrator) were used for injection. The preconcentrator column was loaded in reverse flow by the ASM prior to injection, and had a minimum of tubing [<2 cm of 0.010 in. (0.0254 cm) I.D.] on the down-flow (towards the stationary phase) side to minimize carry over.

2.3. Procedure

The following four eluents were used: (1) deionized water, (2) 1 m*M* NaOH, (3) 100% ACN, and (4) 200 m*M* NaOH. Regenerant (50 m*M* H_2SO_4) was stored under helium in 4-l plastic reservoirs, pressurized to provide a flow-rate through the suppressor of 7–8 ml/min. When using the autosampler for extended and untended operations, regenerant is the limiting reagent in the system. Two 4-l reservoirs were

linked in series to provide in excess of 16 h operating time.

Soil (2 g) was extracted with 20 ml deionized water in 50-ml glass centrifuge tubes by shaking for 1 h on a reciprocal shaker (100 rpm). Equilibrated suspensions were centrifuged, and the supernatant filtered through a 0.45-μm membrane filter. Free metals in the extract were complexed by the addition of 10 μl of 0.1 *M* EDTA to prevent precipitation inside the chromatograph. Excess chloride, a major interferant which can cause unacceptable peak broadening, was removed by solid-phase extraction with Ag^+ strong cation-exchange resin (Ag^+-SPE).

Eluent flow-rate was 1 ml/min. The gradient program used 0.2 m*M* NaOH–70% (v/v) ACN from 0–15 min (after a 20 min equilibration) with a ramp to 60 m*M* NaOH–70% ACN from 15–20 min and held for 5 min. The ramp is required to elute strongly retained analytes prior to the next run. Detection was by suppressed conductivity.

3. Results and discussion

3.1. Aqueous method development

The initial experiments were performed using a 200 μg/l combined standard (CS) of FC2A and FA. A 250-μl loop was used. FA elutes just prior to FC2A using ion exchange as the sole retention mechanism (Fig. 1). The elution order of FC2A and FA reverses with increasing concentration of organic modifier. However, an analysis of the capacity factors indicates that reversed-phase behavior occurs only at organic modifier concentrations exceeding 40% (Fig. 2). This is in contrast to the alkyl methylphosphonates which exhibited the classical reversed-phase response at all concentrations of organic modifier. We speculate that the effect may be due to column swelling effects [31] exceeding the reversed-phase effect at low organic modifier concentrations because of the small size of FC2A and FA.

An optimization experiment was completed using a two-factor, four-by-six level, fractional

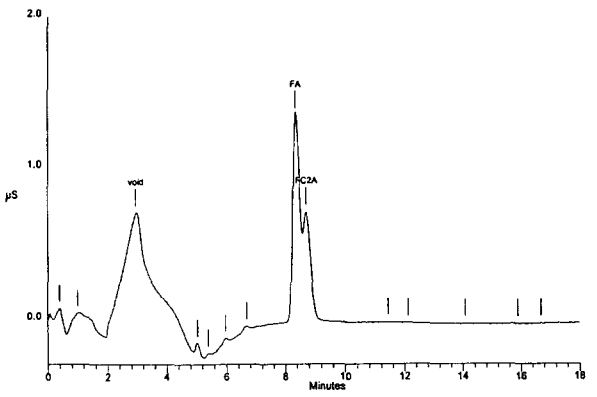

Fig. 1. Separation of FC2A and FA under conventional ion-exchange conditions. Experimental: 0.8 m*M* NaOH–10% (v/v) ACN; 1 ml/min; 250-μl loop; 250 μg/l each analyte.

factorial design [32]. NaOH was varied at 1.2, 0.8, 0.4, and 0.2 m*M*. ACN was varied at 10, 25, 40, 55, 70 and 85% (v/v). All samples used a isocratic mobile phase from 0–15 min, ramping to 60 m*M* NaOH from 15–25 min with the same concentration of organic modifier, and flow-rate of 1 ml/min.

Response was measured as the resolution between FC2A and FA. The resolution response was fitted to a quadratic function with a linear interaction term as the simplest function that would significantly fit ($p = 0.05$) the results (Fig. 3).

Acceptable resolution between FC2A and FA was chosen to be 1.5, but due to the expected

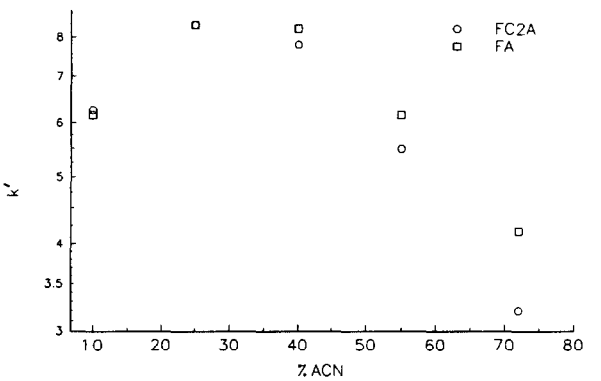

Fig. 2. Effect of organic modifier on the capacity factors of (○) FC2A and (□) FA. Experimental: 0.2 m*M* NaOH; 1 ml/min; 250-μl loop; 200 μg/l each analyte.

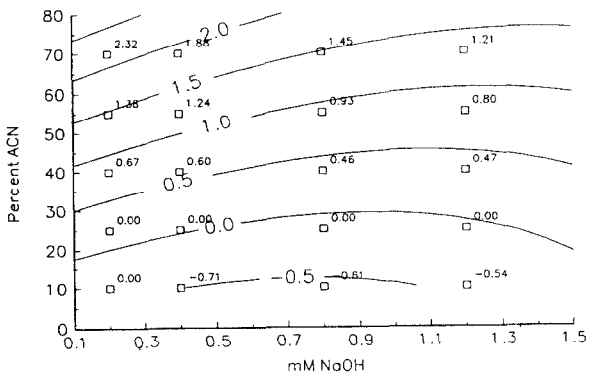

Fig. 3. Resolution between FC2A and FA as a function of mobile phase composition.

high levels of FA in the samples, an eluent composition was chosen [0.2 m*M* NaOH–70% (v/v) ACN] that produced the highest resolution compatible with our experience with soil matrices. Self-elution of soil extracts at the head of the column can be a problem when using eluent concentrations less than 0.2 m*M* NaOH.

The gradient program was designed to provide a long enough initial elution to separate the compounds, particularly when using the preconcentrator column, and to insure that late eluting compounds would be removed from the column. When using the preconcentrator column, retention times increase as the column is overloaded with FA and other interferences because of self-elution.

Initial calibration of the aqueous method using the preconcentrator column was accomplished using a concentration range from 0.5–20 μg/l FC2A. The results were linear, but with a non-zero intercept due to a minor interference.

3.2. Soils method development

The aqueous method was extended to soils using the techniques we have developed for the analysis of alkyl methylphosphonates. Lakewood Sand, a standard, well characterized, New Jersey soil was used as a test soil. Spiked soil samples were shaken on a reciprocal shaker for 24 h at 125 rpm to insure equilibration. Calibration experiments using Lakewood Sand demonstrated that the method produced a linear response from 0.05 to 2.5 μg/g FC2A, and with a zero intercept. Calculation of the mass balance indicated that sorption by the soil is not significant in the concentration range tested.

The calibration was repeated with the addition of 5 μg/g of FA. The response factors were compared by Student's *t*-test and found to be statistically similar ($p < 0.05$) [32]. A test using 2 μg/g FC2A and 50 μg/g FA on Lakewood Sand showed good resolution ($R_s = 1.88$) between the compounds (Fig. 4).

3.3. RMA Standard Soil

RMA Standard Soil was obtained during a site visit to RMA. The soil is a reddish-brown, sandy, well-mixed material with a very small percentage of particles exceeding 2 mm (0.6%). The soil had been previously air dried in storage.

A fractional matrix calibration was performed using RMA Standard Soil spiked with 0.02–2.00 μg/g of FC2A with a cross calibration of 0–10 μg/g of FA. The results were linear ($r = 0.994$), had a zero intercept, and showed insignificant differences between the samples spiked with FC2A only, and those spiked with added FA (Fig. 5).

Retention time of FC2A did vary from sample to sample because of variances in the ionic strength of the sample. Fluoride was used as a

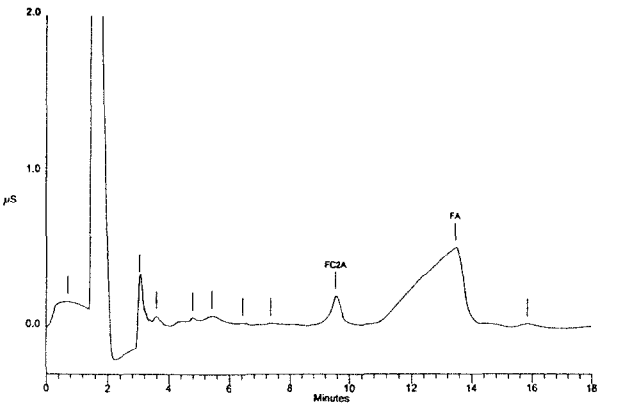

Fig. 4. Lakewood Sand soil spiked with FC2A and FA. 2 g soil/20 ml deionized water; 250-μl loop; 2 μg/g FC2A and 50 μg/g FA.

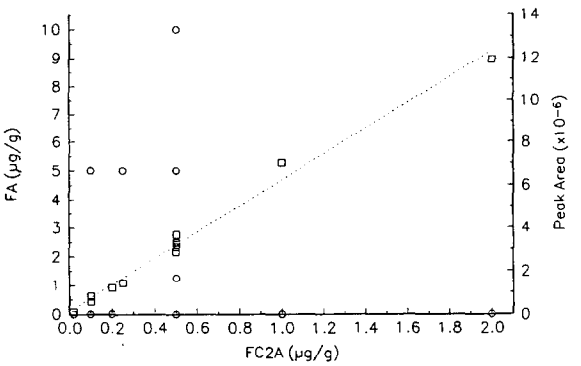

Fig. 5. Experimental design (○) and results (□) of RMA Standard Soil calibration.

reference peak. Retention time variance is much less of a problem when using a loop injector. The sample size is smaller, and sample movement in the preconcentrator column is wholly controlled by the elution strength of the sample.

RMA Standard Soil did sorb significant amounts of FC2A, in contrast to the Lakewood Sand soil. However, recovery was constant (60 ± 4%, $n = 12$) across the range tested. A Langmuir sorption isotherm was insignificantly different from a linear sorption isotherm.

The amount of FA present was estimated by the method of standard additions. The range of this method, using the preconcentrator column, is 0.1–2 µg/g of FC2A. The chromatographic peaks representing FA had generally poor peak shape due to column overloading, with a resultant increase in the variability of the integrated peak areas.

3.4. RMA field samples

Fifteen field samples suspected of containing FC2A were collected by Woodward-Clyde Federal Services (Denver, CO, USA) from three borings on RMA. The core samples were field-packed in plexiglass cylinders and immediately refrigerated. The samples were express shipped to the University of Delaware in coolers packed with "blue ice". Upon receipt, the samples were transferred to a refrigerator and maintained at 4°C. Samples were not removed from the original sample containers until just prior to analysis.

Each sample was transferred to new plastic bags and homogenized by hand. A subsample (about 20 g) was removed, weighed, and placed in a vacuum desiccator for drying. Another subsample (2.00 g) was processed and chromatographed according to the soils method described above.

No fluoroacetic acid was detected in any of the samples (Fig. 6). Formic acid was detected in every sample. Estimated FA concentrations ranged from 1–45 µg/g (Table 1). The FA concentration data was verified by replacing the preconcentrator with a 250-µl loop, and repeating the analysis with a new calibration. All of the three samples checked resulted in sightly lower concentrations, with deviations of −7 to −23%.

The absence of FC2A in the RMA samples

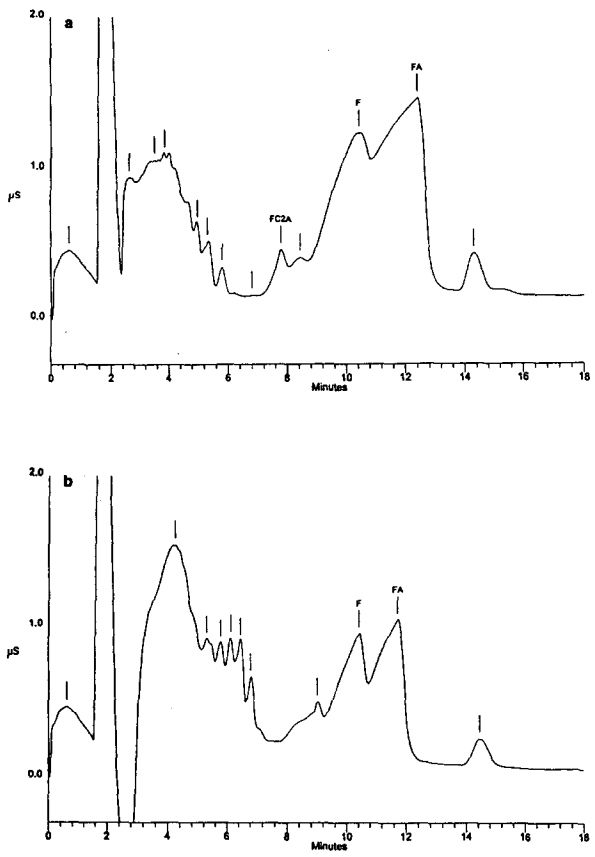

Fig. 6. (a) RMA Standard Soil spiked with 0.5 µg/g FC2A and 10 µg/g FA. (b) RMA sample 3003S011.

Table 1
RMA field sample results

Boring and sample ID	Sample depth (m)	Moisture (%)	Est. FA (μg/g)
Boring 3003			
3003S011	0–0.3	8.90	6.4
3003S031	0.61–0.91	18.51	9.1
3003S051	1.22–1.52	30.63	44.6
3003S101	2.74–3.05	29.97	11.9
3003S151	4.27–4.57	30.41	10.3
Boring 2635			
2635S011	0–0.3	5.26	8.2
2635S031	0.61–0.91	7.00	1.9
2635S051	1.22–1.52	10.94	1.5
2635S101	2.74–3.05	15.71	2.8
2635S151	4.27–4.57	17.51	1.6
Boring 2636			
2636S011	0–0.3	5.89	1.7
2636S031	0.61–0.91	11.78	1.2
2636S051	1.22–1.52	11.68	3.8
2636S101	2.74–3.05	11.74	1.5
2636S151	4.27–4.57	2.72	1.3

was not surprising. Ample evidence exists for the biodegradation of FC2A in soil matrices [33–39]. The degradation products have been shown to be glycolate and fluoride [40–42]. Half-times for FC2A degradation are on the order of days for acclimated soils [38] or weeks for freshly exposed soils [34]. The time since application of FC2A to RMA soils is at least 20 years.

4. Conclusions

The method presented here can quantitatively analyze water and soil samples suspected of containing FC2A in the presence of several major interferences, including relatively high concentrations of formic acid. The method is sensitive, quantitative, requires minimal sample preparation, and is suitable for the routine analysis of environmental samples in site investigations and fate studies. A confirmatory detector, such as a mass spectrometer, would improve the method. The method is also suitable for application studies and could be easily modified to accept other sample matrices, such as food and animal tissue.

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