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Determination of fenpyroximate in apples by supercritical fluid extraction and packed capillary liquid chromatography with UV detection

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Abstract

A method using off-line supercritical fluid extraction (SFE) and micro liquid chromatography (μLC) with UV detection at 260 nm, was developed for selective determination of fenpyroximate in apple samples. The packed capillary liquid chromatography method utilises 20 μl injection volumes with on-column focusing. A 350×0.32 mm capillary column packed with Kromasil 100-C_{18} of 5 μm particle size was used with a mobile phase of acetonitrile–10 m*M* ammonium acetate (85:15, v/v) at a flow of 5 μl/min. A two-step SFE procedure was used to extract fenpyroximate selectively in 2 g apple samples, with Hydromatrix (HMX) added as a water absorbent at a 1:1 (w:w) ratio. Fenpyroximate was extracted at 200 bar and 90°C for 15 min using carbon dioxide at a flow of 2 ml/min, and solvent trapping collection in 10 ml acetonitrile. The volume of the acetonitrile extract was reduced by evaporation and water was added to a final composition of acetonitrile–water (40:60, v/v). The resulting 2.0 ml solution was filtered using a 0.45 μm poly(vinylidene difluoride) syringe filter before μLC analysis. Validation of the method was accomplished with apple samples spiked with fenpyroximate, covering the range of 0.1 to 1.0 μg/kg. The within-day and between-day repeatabilities were in the range 4–18% relative standard deviation. Accuracy, measured as recovery, was found to be approximately 60%. Apple samples from a field treated with fenpyroximate were analysed. None of the samples contained fenpyroximate above the quantification level.

Keywords: Apples; Fruits; Food analysis; Extraction methods; Fenpyroximate; Pesticides

1. Introduction

Fenpyroximate (Fig. 1) is an acaricide developed in 1985 [1] belonging to the phenoxypyrazole group and showing selective activity on phytophagous mites [1,2]. A study of the photodegradation of fenpyroximate in aqueous buffer at pH 7 showed that degradation is rapid and that accumulation in an aqueous environment will not occur [3].

A review concerning physical and chemical properties, metabolism and environmental fate including both published and unpublished results from analytical methods and supervised trials of fenpyroximate has been published [4]. Fenpyroximate was first registered and marketed for the control of mites in Japan, China and Switzerland in 1991 and was registered in 27 countries in 1995 [2]. Because it has been applied only for a few years, the analytical methods are few. Determination of fenpyroximate in apples by gas chromatography (GC) with nitrogen–phosphorus detection (NPD) after conversion in $HCl–H_2SO_4$ has been reported [5]. A report from

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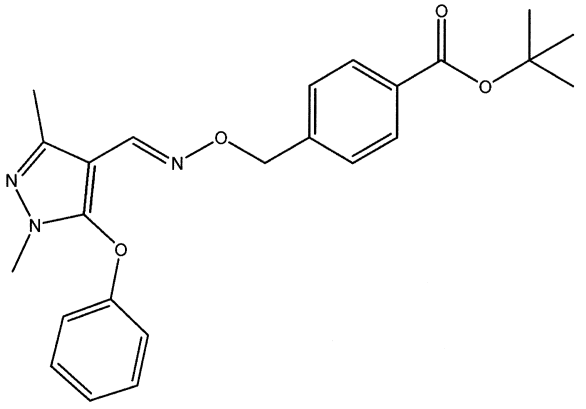

Fig. 1. Structure of fenpyroximate.

FAO and WHO [4] describes several unpublished methods based on liquid chromatography (LC) with ultraviolet (UV) detection and GC–NPD.

Pesticide residues in apples have been determined by use of a wide range of chromatographic procedures after sample preparation with ordinary organic solvents [6–11]. Efforts have been made the recent years to minimize the consumption of organic solvents in pesticide residue analysis and a review on the subject has been published by Wan and Wong [12]. Supercritical fluid extraction (SFE) is an attractive alternative for conventional methods [13–19]. A review on SFE of pesticides in food was published by Lehotay [20] in 1997.

The aim of this work was to develop a SFE procedure for extraction and clean-up of fenpyroximate residues in apple samples. A packed capillary LC (μLC) method, utilising large volume injection and on-column UV detection, has been used for determining the level of fenpyroximate in the samples. The method enables quantification of fenpyroximate at the 0.1 mg/kg level. National maximum residual levels (MRLs) for fenpyroximate in apples between 0.1 mg/kg and 2.0 mg/kg have been reported [4].

2. Experimental

2.1. Instrumentation

2.1.1. SFE

An Isco (Lincoln, NE, USA) Model 260 *M* syringe pump was used for delivery of carbon dioxide. A Varian (Walnut Creek, CA, USA) gas chromatograph was used to control the temperature during extractions. The CO_2 flow and the restrictor temperature were regulated by an Isco Restrictor Temperature Controller. Two high-pressure extraction vessels of volume 4.85 ml and 9.7 ml, both from Keystone Scientific (Bellefonte, PA, USA) were used. The extraction vessel was connected to the pump and the restrictor with steel tubing. Small Whatman GF/B filter papers (Maidstone, UK) were stamped out from bigger ones and placed between the sample and the outlet frit to eliminate plugging. Glass vials of ca 60×26 mm were used for collection of the extracts. Two holes were made in the plastic snap-cap; one to fit exactly around the restrictor and the other (about 1 mm in diameter) to release the CO_2 gas.

2.1.2. μLC–UV with large volume injection

A Waters (Milford, MA, USA) Model 590 piston pump served as the mobile phase delivery system. A Model 7725 (Rheodyne, Cotati, CA, USA) injector with a 30 μl stainless steel external loop was used for injections. The injections were performed manually at room temperature. The mobile phase flow was 5 μl/min. The injection valve was switched back to load position after 4 min of injection, resulting in an injection volume of 20 μl. A Model 5730A GC system from Hewlett-Packard (Amsterdam, Netherlands) served as column oven. The temperature was 50°C. The column was connected to the injector with a fused-silica capillary of 25 cm×50 μm I.D.×375 μm O.D. by the use of a polyether ether ketone (PEEK) tubing sleeve (450 μm I.D.×1/16 in. O.D.; 1 in.=2.54 cm) (Upchurch Scientific, WA, USA). A Spectra 100 variable wavelength UV detector from Spectra-Physics (Fremont, CA, USA) was used for detection, which was performed at 260 nm. A fused-silica capillary (100 μm I.D.×375 μm O.D.) was used as the detection capillary. To avoid bubbling when operating at elevated temperatures, a fused-silica linear restrictor of 15 cm×15 μm I.D.×375 μm O.D. was connected to the end of the detector capillary. All fused-silica capillaries used in this study were purchased from Polymicro Technologies (Phoenix, AZ, USA). The chromatographic data were processed on a Shimadzu C-R6A Chromatopac

Integrator (Tokyo, Japan), and Excel (Microsoft) was used for regression analyses.

The mobile phase consisted of acetonitrile–10 m*M* ammonium acetate (85:15, v/v) while acetonitrile–water (40:60, v/v) was used as injection solutions.

2.1.3. Columns

The columns (320 μm I.D.×435 μm O.D.) were prepared in the laboratory as described by Trones et al., using supercritical carbon dioxide as the slurry medium [21]. The lengths of the columns were 25 cm for method development and 35 cm for method validation. Kromasil 100-C_{18} (Eka Nobel, Sweden) of 5 μm particle size was used as packing material.

2.2. Chemicals

All gases were supplied from AGA Gas (Oslo, Norway). CO_2 of 99.9992% and 99.998% purity were used for SFE and packing of the columns, respectively. Helium (99.998%) was used for degassing of the mobile phase and nitrogen (99.9%) was used for evaporation. Fenpyroximate (99.8%) was received from The Norwegian Crop Research Institute (Aas, Norway). Analytical-grade ammonium acetate was obtained from Merck (Darmstadt, Germany). HPLC-grade acetonitrile was purchased from Rathburn (Walkerburn, UK). The water was distilled and deionized.

Hydromatrix (HMX) was obtained from Varian (Harbour City, CA, USA). Acrodisc LC13 polyvinyl difluoride (PVDF) syringe filters with 0.45 μm pores and diameters of 13 mm were purchased from Gelman Sciences (Ann Arbour, MI, USA). Minisart-RC25 and Minisart-plus syringe filters with 0.45 μm pores and 26 mm diameter were obtained from Sartorius AG (Göttingen, Germany). A 5 ml gas-tight glass syringe (No. 1005) from Hamilton (Reno, NV, USA) was used for filtration.

2.3. Standard solutions

Five standard solutions containing from 0.10 to 0.99 μg fenpyroximate/ml acetonitrile–water (40:60, v/v) were made by appropriate dilution of a 99.2 μg/ml stock solution in acetonitrile, and used for examination of different syringe filters.

A 102.0 μg/ml stock solution of fenpyroximate in acetonitrile, made by dissolving 10.20 mg in a 100.0 ml volumetric flask, was used for preparation of standard solutions and calibration solutions for validation of the method. Solutions used for evaluation of linearity and the limit of detection (LOD) of the μLC–UV method, as well as establishing the calibration curve, were prepared by appropriate dilution of the stock solution using acetonitrile–water (40:60, v/v) as solvent. Standard solutions used for validation of the method were prepared by appropriate dilution of the stock solution using acetonitrile. Addition of 40.0 μl of five different spike solutions (5.10 (n=3), 10.2 (n=1), 25.5 (n=6), 35.7 (n=1) and 51.0 (n=3) μg/ml) to apple samples of 2 g resulted in spike concentrations of 0.102, 0.204, 0.510, 0.714 and 1.02 mg/kg apple. Quantification was done by external calibration using a three-point calibration curve.

2.4. Samples

Three types of apples from guaranteed untreated fields were obtained from the authors gardens. Norwegian Summerred apples from a field treated with different amounts of fenpyroximate were obtained from The Norwegian Crop Research Institute. The orchard had been divided into different sections, and the sections were treated once or twice with a formula consisting of fenpyroximate, azinophos-methyl and demeton-S-methyl. Some of the sections had been left untreated.

The apple samples were collected fresh, coded, chopped up in a food processor and kept frozen at –18°C

2.5. Procedure

After the apple sample had reached room temperature, a 2 g subsample was weighed into a 100 ml beaker. If the sample was to be spiked, spike solution was added at this stage. The sample was left for about 5 min for evaporation of some of the solvent before 2 g of HMX was added. The sample was homogenised manually for about 1 min and then filled into an extraction vessel of 9.7 ml in three portions, each compressed before the next was added. If necessary, the vessel was filled up with HMX.

The vessel was connected to the SFE instrumentation, and the temperature set to 90°C for 5 min for temperature equilibration before the CO_2 pressure program was started. When the vessel was filled with fluid, the restrictor was opened. The flow was set to 2 ml/min. Dynamic extraction at 100 bar was performed for 15 min and the effluent was collected in acetonitrile. The restrictor was closed, the collection vial changed and the pressure raised to 200 bar in 12 s. When the pressure reached 200 bar, the restrictor was opened and the extraction continued for another 15 min. A collection vial containing 10 ml of acetonitrile was used. The acetonitrile was subsequently evaporated to about 1.5 ml with N_2 gas and careful heating. The extract was transferred to a volume calibrated sample glass vial and the extraction vial was washed with about 3 ml of acetonitrile. The evaporation was continued to a volume of 0.8 ml, 1.2 ml water was added, and finally the solution was filtrated with Acrodisc LC13 PVDF syringe filter, resulting in a 2.0 ml solution with a 60% (v/v) water content. This solution was analysed by the large volume μLC–UV method.

3. Results and discussion

The thermolability of fenpyroximate prevented its direct determination by GC–NPD. Fenpyroximate could be chromatographed with neat supercritical carbon dioxide on packed capillary columns, e.g. with the Kromasil 100-C_{18} material, with NP detection (results not shown). Unfortunately, the low injection volumes compatible with the packed capillary supercritical fluid chromatography (SFC) system precluded the use of this technique for determination of fenpyroximate at the 0.1 mg/kg level. Since larger volumes can be injected in μLC, μLC–UV was utilised in this work.

3.1. Large volume μLC method

Capillary columns packed with Kromasil 100-C_{18} material of 5 μm particle size were found to be suitable for chromatography of fenpyroximate. A mobile phase composition, which gave a retention factor (*k*) of about 2.5, was sought in this study and a mixture of acetonitrile–water (85:15, v/v) was found appropriate (Fig. 2). Ammonium acetate (10 m*M*) was added for pH control. At 50°C the column efficiency measured as reduced plate height (*h*) was 2.7.

An injection volume of 0.06 μl is typically used in packed capillary LC. Injection of a larger volume will improve the limit of detection [22–25], and was therefore explored. Preliminary experiments showed that extraction of a 2 g apple sample and injection of 20 μl of the 2.0 ml extraction solution gave a LOD at the MRL. A larger volume was not used as it was desirable to keep the analysis time as short as possible. A mixture of acetonitrile–water (40:60, v/v) was found to be a sufficiently weak solvent to promote on-column focusing as no fenpyroximate eluted during a period of 2.5 h. An even weaker injection solution was not preferable because of the low solubility of fenpyroximate in water (0.021 mg/l at 25°C and pH 7 [4]).

Results recently presented by Molander et al. [23] show that better chromatographic resolution and peak shapes are obtained using time limited injections as compared to whole loop injection. Therefore a loop of 30 μl was used, and the desired injection volume of 20 μl was obtained by using an injection time of 4 min at a flow of 5 μl/min.

The retention time of a few compounds in the apple extracts was up to 1 h longer than that of fenpyroximate. These compounds could possibly interfere with the fenpyroximate peak in subsequent injections. Therefore these species had to be eluted from the column at regular intervals. This was done by injection of one loop-volume, which corresponds to about two column volumes, of acetonitrile between every second injection of sample. The baseline became stable in less than ten min after the acetonitrile injection and no memory effects were observed.

3.2. SFE

3.2.1. Extraction pressure

The restrictor temperature was set to 70°C to prevent plugging from ice and the CO_2 flow used was 2 ml/min. Preliminary results showed that fenpyroximate was extracted from apple samples at pressures above 150 bar at 90°C. However, a compound with retention time equal to fenpyroximate in the present μLC method was co-extracted at these

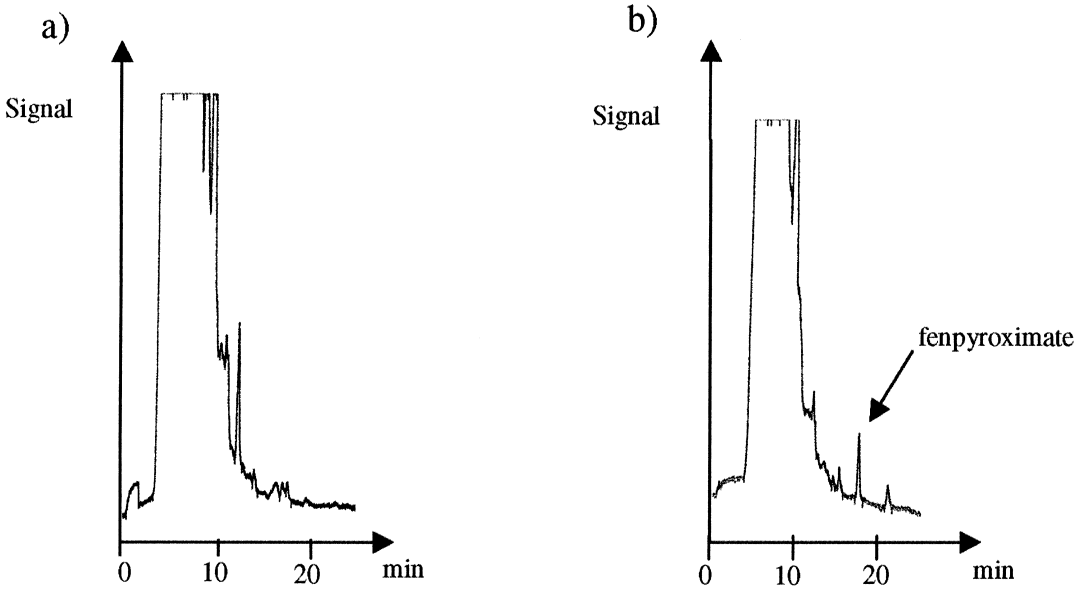

Fig. 2. Chromatograms of a) extract of apples from a field treated with fenpyroximate and b) extract of apples from untreated field. The sample was spiked with 0.198 mg fenpyroximate/kg apple. Apples samples of 2 g were extracted with supercritical CO_2. 20 μl of the final 2.0 ml acetonitrile–water (40:60, v/v) solution was injected on a 350×0.32 mm Kromasil 100-C_{18} column. The mobile phase was acetonitrile–10 m*M* ammonium acetate (85:15, v/v) at a flow of 5 μl/min.

conditions. This interference was found in two out of three apple types examined. The interference was extracted at a pressure of 100 bar and could therefore be removed before the pressure was increased and fenpyroximate extracted. A pressure of 200 bar was chosen for the extraction of fenpyroximate. Higher pressure was avoided because of the enhanced risk for co-extraction of other compounds.

3.2.2. Extraction time

Optimal extraction times regarding complete extraction were determined for both steps. An extraction time of 15 min for the first step and 10 min for the second step was sufficient. The extraction time for fenpyroximate was nevertheless chosen to be 15 min because the extraction of the analyte in spiked samples often is easier than in real samples [26,27]. Thus, including the μLC determination, the total analysis time was less than two h.

3.2.3. Sample to absorbent ratio

Apples contain about 85% water [28], and even a small amount of water (>1%, w/w) can cause problems in SFE, as water freezes in the restrictor tip [29]. Freeze-drying of the apple samples was examined, but was not pursued due to long drying time. Removal of water using a drying agent is another possibility. HMX, a commercially available diatomaceous earth, which absorbs twice its weight in water [30] has been investigated for SFE purposes [30]. The use of HMX also improves the dispersion of analytes in the matrix [31]. The fenpyroximate recovery using two different sample to HMX ratios was examined. Only the ratios 2:1 and 1:1 (w:w) were tested because these ratios fitted in the extraction vessels available. The 1:1 ratio gave the most reproducible results and was hence used for the rest of the study.

3.2.4. Effect of drying time

No significant difference in yield regarding the drying time after mixing of sample and HMX was observed. Actually, zero drying time gave the best results (results not shown) and was timesaving, and therefore chosen. Earlier SFE studies have also showed that completely dry samples gave slightly lower analyte recoveries than samples containing water [32].

3.2.5. Trapping solvent and volume

With the equipment available, solvent trapping was the only possible collection method. Acetonitrile was chosen as collection solvent because of the relatively good solubility of fenpyroximate (37.4 g/l at 25°C [4]) and because injection of the extracts could be performed with just a minimum of further sample preparation, i.e. dilution with water to obtain the appropriate elution strength for large-volume injection, followed by filtration. A collection volume of 10 ml acetonitrile was found to be the best with regard to repeatability and recovery (results not shown).

3.2.6. Syringe filters

After dilution with water, precipitates were observed in the extraction solution. To avoid column clogging, a filtration step had to be included. Three different syringe filters were tested using standard solutions of 0.10–0.99 μg fenpyroximate/ml of acetonitrile–water (40:60, v/v). The lowest concentration corresponded to the assumed MRL.

The filter types tested were Minisart-RC25 with a regenerated cellulose membrane, Minisart-plus with a cellulose acetate membrane and Acrodisc LC13 PVDF, with a polyvinyldifluoride filter. Varying recoveries of 70–90% were obtained for fenpyroximate solutions filtered with the RC25 filters. Using the Minisart Plus filters, compounds that interfered with fenpyroximate in the μLC method were extracted from the filters. Recoveries of about 90% of fenpyroximate were obtained using the PVDF filters (results not shown) and these were hence chosen.

3.2.7. Internal standard

An internal standard must behave similar to the analyte in the chromatographic system and during the sample preparation, while still being separated from the fenpyroximate and other species in the sample. The availability of a suitable internal standard increases the accuracy and the precision of the method. However, we could not find an appropriate internal standard for this method. Therefore, the method was validated using external standard calibration.

3.3. Validation

Due to the low expected concentration of fenpyroximate in the apple samples, it was most important that the method could quantify low concentrations. Hence, concentrations ranging from the limit of quantification (LOQ) to ten times the LOQ were chosen as the validation range.

3.3.1. Limit of detection and limit of quantification

LOD and LOQ were determined using a signal-to-noise ratio of 3 and 10, respectively. The LOD and LOQ of the μLC method were 0.02 and 0.08 μg fenpyroximate/ml of acetonitrile–water (40:60, v/v). Provided a recovery of >50%, this corresponds to LOD and LOQ for determination of fenpyroximate in apples of 0.03 mg/kg and 0.1 mg/kg apple, respectively. Quantification at the MRL was then possible with the developed method. The LOD of the present method is in the same range as the methods reported previously [4]. If a further improvement of the LOD is desired, larger volumes could be injected. However, injection of a very large volume is time consuming. Another approach is to use a low dispersion ''U'' or ''Z'' cell with an extended light pathway compared to conventional cell construction.

3.3.2. Linearity

The detector response was linear ($r=0.999$) in the concentration range 0.10 to 10 μg fenpyroximate/ml acetonitrile–water (40:60, v/v). The linearity of the off-line SFE μLC method was studied by extraction of apple samples spiked at five different levels as described in the Experimental section, covering a concentration range of 0.1–1 mg/kg apple. If the recovery is 100%, this range corresponds to a concentration range of 0.10–1.01 μg fenpyroximate/ml acetonitrile–water (40:60, v/v). The intercept was included in the confidence interval (95%) around zero and the linearity in the concentration range was satisfactory ($r=0.988$).

3.3.3. Repeatability

The average repeatability of the retention time of fenpyroximate was about 3.0%. The repeatability of the μLC method was better than 1% RSD (results not shown)

The repeatability of the method was determined on the basis of the results from concentration level one, three and five (0.102, 0.510 and 1.02 mg/kg) from the linearity study. The results are presented in Table 1.

Table 1
Repeatability of fenpyroximate determination at three concentration levels using the off-line SFE μLC–UV method

Amount added (mg/kg)	Within-day repeatability					Between-day repeatability			
	Amount found (mg/kg)	SD (mg/kg)	RSD (%)	*n*	Recovery (%)	Amount found (mg/kg)	SD (mg/kg)	RSD (%)	*n*
0.102	0.064	0.009	11	3	63	0.047	0.006	14	3
0.510	0.291	0.044	15	6	57	0.257	0.047	18	3
1.02	0.585	0.024	4.0	3	57	0.537	0.032	6.0	3

3.3.4. Reproducibility

The reproducibility of the method was evaluated by randomly selecting one replicate from each of the three levels from the repeatability testing. One replicate was further performed at each level for two more days. The spike solutions were stored at room temperature and all the apparatus except the pump, were shut down at the end of each day. The results are shown in Table 1.

3.3.5. Accuracy

Due to the lack of access to another validated and generally accepted reference method for determination of fenpyroximate, the results using this method could not be compared with other results. The accuracy determined as recovery was examined using the results from the linearity/repeatablity studies.

Table 1 shows that recoveries of approximately 60% were obtained. This is somewhat lower than expected.

3.3.6. Selectivity

In this off-line SFE–μLC system, fenpyroximate has been selectively determined in apple extracts. Even though the chromatograms from various apple types differed, no interference was seen in the μLC retention time window of fenpyroximate when the described two-step extraction and the washing procedure were followed.

3.3.7. Robustness

Control of the CO_2 flow-rate was important as the flow-rate slowly decreased during extraction. Too low flow-rate results in incomplete extraction of both the interfering compound and fenpyroximate. Too high flow-rates of CO_2 gave variations in the extraction yield between the extractions. Correct filling of the extraction vessel was of importance to avoid channel formation leading to poor extractions which occur if the packing is too loose or the vessel is not completely filled up.

All standard fenpyroximate solutions were stable at room temperature under exposure to daylight, during the time aspect of this validation study.

3.4. Application

Apples from fields treated with different amounts of fenpyroximate were analysed. Residue of fenpyroximate above the quantification level was not found in any of the eight samples received (Fig. 2). This is consistent with the observation that the degradation of fenpyroximate in aqueous environment is rapid [3,4].

4. Conclusions

This off-line SFE–μLC–UV method with large volume injection is the first to utilise SFE for extraction of fenpyroximate from apple samples. SFE was established as a promising alternative technique compared to conventional solvent based extractions due to shorter analysis time, less consumption of organic solvents, and the use of smaller amounts of sample. The method provides determination of fenpyroximate at a MRL of 0.1 mg/kg apple using 2 g samples. If necessary, lower concentrations can be determined by using larger injection volumes in combination with an extended light pathway cell.

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