LC-MS/MS Analysis of Emerging Food Contaminants

Detection of Pesticide 1080 (Sodium Fluoroacetate) in Milk and Infant Formula

Matthew Noestheden and André Schreiber
SCIEX Concord, Ontario (Canada)

Introduction

Recently (November 2014), threats in the form of letters were sent to farming and dairy industry leaders in New Zealand. The letters were accompanied by small packages of milk powder that were shown to contain a concentrated form of the pesticide 1080 (sodium fluoroacetate). The sender demanded that the New Zealand government stop using 1080 for pest control. Sodium fluoroacetate is used to protect New Zealand's native flora and fauna against introduced pests like possums and ferrets. Opponents, however, argue that it also kills native animals and contaminates the environment.[1-2]

Such criminal threats are a potential danger and weaken consumers' trust in the food supply chain. Accurate and reliable analytical methods are needed to monitor food ingredients and final products to ensure food safety in light of this threat.

Liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) is an ideal analytical technique to detect polar analytes in complex food samples.

Here we present first results of method development to detect sodium fluoroacetate in milk and infant formula. The sample preparation protocol consists of a simple acetonitrile extraction and defatting using hexane. LC separation was achieved using a HILIC column in normal phase mode. The mass spectrometer was operated in Multiple Reaction Monitoring (MRM) mode. In MRM mode the transition of a molecular ion into a characteristic fragment ion is monitored. The monitoring of more than a single fragment ion allows not only quantitation but also highly confident identification based on the ratio between quantifier and qualifier transitions.

Initial studies show that sodium fluoroacetate can be detected at concentrations below 1 ng/mL (below 10 ng/mL in matrix) using the SCIEX QTRAP® 4500 system, with good accuracy and repeatability. Linearity for quantitation was achieved over 3 orders of magnitude (0.1 to 100 ng/mL). Future experiments are planned to further increase sensitivity, simplify sample preparation and to include an internal standard to correct low recoveries and matrix effects.

Experimental

Standards

Sodium fluoroacetate (Pestanal, analytical standard, Sigma-Aldrich #31220) was purchased from Sigma Aldrich.

Future studies will include the use of an internal standard which was not available at the time this study was conducted.

Sample preparation

10 g of infant formula was thoroughly mixed with 100 mL of water. Ready-to-feed samples were extracted directly.

Samples were extracted with acetonitrile and defatted using hexane. After pH adjustment the extract was phase-separated using QuEChERS salts, diluted and analyzed by LC-MS/MS.

LC Separation

LC separation was performed using a Shimadzu UFLC$_{XR}$ system with an Amide column (100 x 2.1 mm, 1.7 µm) and a normal phase gradient consisting of water with ammonium formate and acetonitrile. The injection volume was 50 µL.

MS/MS Detection

The SCIEX QTRAP® 4500 system with Turbo V™ source was operated using an ESI probe in negative polarity. The MRM transitions monitored were 77/57 and 77/33. Ion source parameters were set to the following values: CUR = 30 psi; Gas1 = 40 psi; Gas2 = 60 psi; TEM = 600°C; and IS = -4500 V.

Results and Discussion

An example chromatogram is shown in Figure 1. The selected LC conditions guaranteed separation from matric components (retention time > 2 min) to minimize potential matrix effects (i.e. ion suppression).

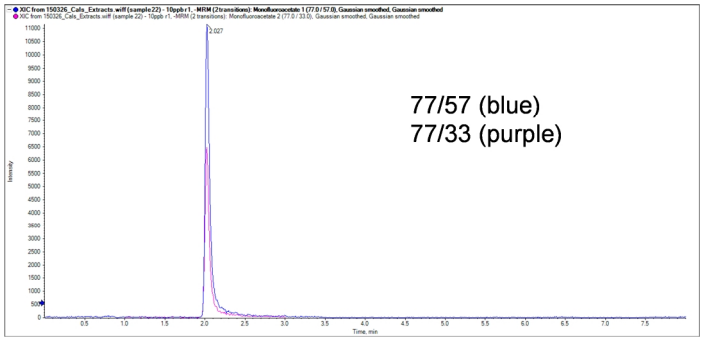

Figure 1. Example chromatogram of a 10 ng/mL standard of sodium fluoroacetate

Sodium fluoroacetate was accurately and reproducibly identified and quantified. The repeat analysis of a 1 ng/mL standard (n= 3) is shown in Figure 2.

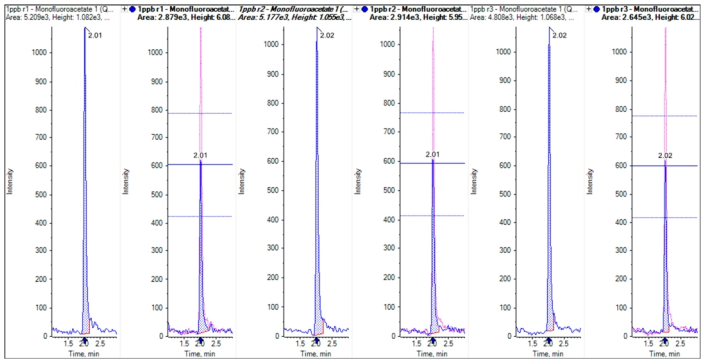

Figure 2. Repeat analysis at 1 ng/mL, 2 MRM transitions were monitored and the ratio of quantifier and qualifier transition (alternating from left to right, respectively) was used for compound identification (displayed MRM tolerances are 30%).

Identification was achieved using the ratio of quantifier and qualifier ion. The MRM ratio tolerances were well within the tolerance levels of 30% set by food testing guidelines (i.e. SANCO/12571/2013).

The MRM ratio is automatically calculated on MultiQuant™ software (version 3.0.2) and tolerance levels are displayed in the peak review window for easy data review (Figure 2).

Calibration lines for both MRM transitions are shown on Figure 3. The accuracy of all injections was between 92 and 109%.

Repeatability was excellent at all concentration levels and well below 10%, with the exception of 0.1 ng/mL for the quantifier MRM 77/33 (12.3%). Both coefficients of regression were larger than 0.999 using linear fit with 1/x weighting (Figure 3).

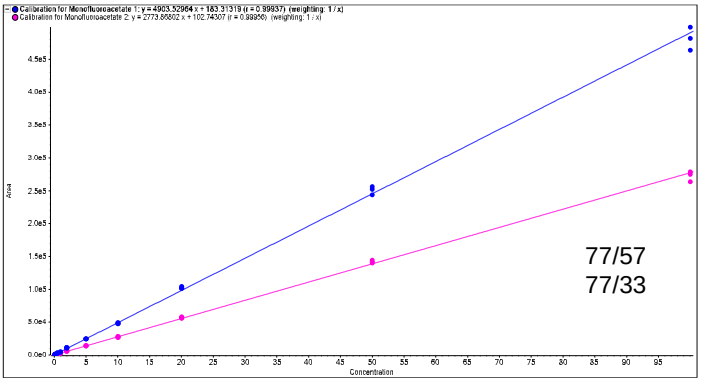

Figure 3. Calibration lines (0.1 to 100 ng/mL) for sodium fluoroacetate

Initial studies show that the developed method can detect sodium fluoroacetate in matrix samples at 10 ppb.

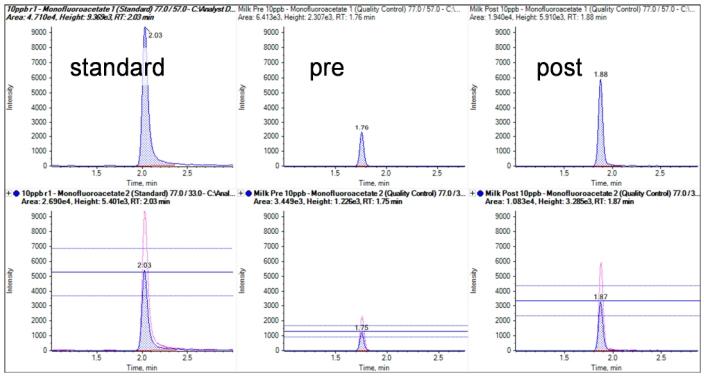

Figure 4. Chromatograms of standard at 10 ng/mL in comparison to the pre-extraction and post-extraction spike of milk at 10 ng/mL (the quantifier ion results are shown on the top row and the qualifier ion on the bottom row)

Figure 4 shows the pre-extraction and post-extraction spike of 1080 into milk at 10 ng/mL. The post-extraction spike indicates ion suppression of ~40% and the pre-extraction spike an additional recovery loss of 30%.

Summary

First results of method development were presented to detect sodium fluoroacetate by LC-MS/MS using the SCIEX QTRAP® 4500 system. Samples were prepared by simple acetonitrile extraction and defatting using hexane. LC separation was achieved using a HILIC column and normal phase chromatography. The MS/MS was operated in MRM mode, enabling detection limits below 1 ng/mL (below 10 ng/mL in matrix). Good accuracy, repeatability, and linearity for quantitation were achieved over 3 orders of magnitude.

Future experiments are planned to increase sensitivity, simplify sample preparation and to include an internal standard to correct low recoveries and correct for matrix effects.

References

1 http://www.nzherald.co.nz/business/news/article.cfm?c_id=3&objectid=11414980

2 http://www.nzherald.co.nz/nz/news/article.cfm?c_id=1&objectid=11415012

Publication number: 221015-01

Headquarters
500 Old Connecticut Path, Framingham, MA 01701 USA
Phone 508-383-7700
www.sciex.com

International Sales
For our office locations please call the division headquarters or refer to our website at
www.sciex.com/offices