Analyzing Freeze-Dried and Regular Milk for Dioxins and Furans using Pressurized Liquid Extraction and Automated Clean Up via EPA Method 1613

Introduction

Persistent Organic Pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs) are present in both human breast milk and regular (cow) milk. Studies of milk have been undertaken since the 1970s because of public health considerations. Such work requires the ability of a laboratory to analyze matrices, such as milk, at the trace level (pg-fg). US EPA method 1613 is typically used around the world for these analyses.

Manual Soxhlet extraction of milk and subsequent manual sample clean up using column chromatography can take a number of days and result in contamination and unreliable data. As an alternative to obtain faster and more reliable data, these various steps have been automated. This application note describes the automated Pressurized Liquid Extraction (PLE®) and automated column chromatography clean up (PowerPrep®) of milk.

Instrumentation

■ FMS, Inc. PLE®

■ FMS, Inc. PowerPrep®

■ FMS, Inc. SuperVap® 6 Concentrator

■ FMS, Inc. SuperVap® Vial Concentrator

■ FMS, Inc. 250 mL concentrator tubes (1 mL termination)

■ Thermo Trace GC Ultra with high res magnetic sector DFS Thermo mass spec

Consumables

■ FMS, Inc. High Capacity Acidic Silica column

■ FMS, Inc. Basic Alumina column

■ FMS, Inc. Carbon-Celite column

■ Fisher Optima® Dichloromethane

■ Fisher Optima® Hexane

■ Fisher Optima ® Toluene

■ 1613 $^{13}C_{12}$ spiking and recovery standards

PLE

■ 5 g of freeze-dried milk or 8 g of regular milk was mixed with 10 g inert Hydro-matrix® and spiked with surrogates

■ Sample placed in extraction cell

■ Capped with disposable Teflon end caps

■ Heated with 50% Dichloromethane/50% Hexane for 20 min at 120 ^{o}C and 1500 psi

■ 20 min cool down

■ Nitrogen flush to transfer analytes and extract to 250 mL collection tubes

SuperVap® Concentration

■ Pre-heat temperature: 55 ^{o}C

■ Pre-heat time: 15 min

■ Heat in Sensor mode: 55 ^{o}C

■ Nitrogen Pressure: 7-10 psi

■ Solvent exchange to hexane

PowerPrep Clean Up

■ Standard program

■ Install high capacity acidic silica, alumina and carbon/celite columns

■ Solvents used are hexane, dichloro-methane and toluene

■ Condition columns with hexane (60 mL)

■ Load sample

■ Elute silica/alumina with 160 mL hexane

■ Elute alumina/carbon with 70 mL dichloromethane

■ Elute carbon in reverse direction with 60 mLs toluene (collect PCDD/Fs)

FMS
Fluid Management Systems

SuperVap step (above)

Vial Evaporator
■ Reduce sample to 10 uL final volume under
1-1.5 psi nitrogen at 25 ^{o}C

Table 1 with native freeze-dried milk values and ^{13}C-labeled recoveries.

	native pg/g	recoveries %
2378-T4CDF	0.02	92%
2378-T4CDD	nd	93%
12378-P5CDF	nd	76%
23478-P5CDF	0.05	78%
12378-P5CDD	0.04	80%
123478-H6CDF	0.04	73%
123678-H6CDF	nd	75%
234678-H6CDF	nd	90%
123789-H6CDF	nd	98%
123478-H6CDD	0.03	87%
123678-H6CDD	0.05	84%
123789-H6CDD	0.04	
1234678-H7CDF	nd	78%
1234789-H7CDF	nd	86%
1234678-H7CDD	0.17	93%
OCDF	nd	
OCDD	0.67	85%

Table 2 with native regular milk values and ^{13}C-labeled recoveries.

	native pg/g	recoveries %
2378-T4CDF	nd	60%
2378-T4CDD	nd	63%
12378-P5CDF	nd	58%
23478-P5CDF	nd	60%
12378-P5CDD	0.18	43%
123478-H6CDF	nd	58%
123678-H6CDF	nd	55%
234678-H6CDF	0.11	57%
123789-H6CDF	nd	61%
123478-H6CDD	nd	60%
123678-H6CDD	nd	60%
123789-H6CDD	0.06	
1234678-H7CDF	nd	72%
1234789-H7CDF	0.03	79%
1234678-H7CDD	0.36	68%
OCDF	nd	
OCDD	1.04	79%

Conclusions

PCDD/F concentrations found in both kinds of milk are low with highest concentration around 1 pg/g. This low level of detection demonstrates the sensitivity of the method used. Freeze-dried milk gave better ^{13}C labeled recoveries than regular milk because of the absence of water. However, the combined PLE-PowerPrep sample processing method is suitable for both kinds of samples, assuring same-day analysis.

FMS, Inc. PowerPrep®, PLE® and SuperVap® Concentrator

For more information contact FMS:
FMS, Inc.
580 Pleasant Street
Watertown, MA 02472
Phone: (617) 393-2396
Fax: (617) 393-0194
Email: onlineinfo@fms-inc.com
Web site: www.fms-inc.com