Preparation of a dioxin containing candidate reference material milkpowder

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1. INTRODUCTION

In recent years the determination of dioxins in all kind of matrices was in the picture. When the Agricultural Division of the Commission of the European Union was confronted with trade problems, the BCR (Bureau Communeautaire de Reference) organized an intercomparison on the dioxin determination in natural and spiked milkpowder[1)]. This exercise proved that from the analytical point of view the preparation and certification of a reference material was feasable. Below information on the preparation of a candidate reference material milkpowder and its homogeneity testing is given.

2 MATERIALS AND METHODS

2.1 Preparation of milkpowder

End 1993 1650 liter cooled cows milk, known to contain dioxins, were transported to NIZO (Netherlands Institute for Dairy Research) in Ede and stored at 21°C. Before homogenisation, the milk was heated in 10 sec. to 74°C. Homogenisation occurred at 55°C at 200 bar; whereafter inline cooling to 5°C took place. The homogenized product was concentrated to 46% dry matter in four temperature steps in a falling stream evaporator from 74° to 46°C. The concentrate was sprayed with a nozzle atomiser at a temperature of 72°C to a final water content of about 2%. After mixing in a Nauta mixer the powder was filled into 6 sacks (25 kg each) and transported to IRMM (Institute for Reference Materials and Measurements) Geel, Belgium for bottling and labelling into 1500 bottles, each containing 100 g of milkpowder.

2.2 Method of analysis

The method is described in literature [2,3,4)] and very detailed described in internal RIKILT standard operation procedures. In principle, ^{13}C labelled dioxin internal standards are added to a known amount of milkpowder, after which fat is extracted, as complete as possible, from the milkpowder. By gelpermeation chromatography the native and labelled dioxin compounds are separated from the matrix. Hereafter cleanup over basic aluminina and a porous graphitized carbon column is carried out. Final determination is carried out with capillary gaschromatography and high resolution mass spectrometry. Together with the milkpowder samples, also internal control samples (blanks and dioxin containing fat samples) and chemical blanks were run.

3 RESULTS

3.1 Homogeneity

3.1.1 Homogeneity within samples

From two bottles milkpowder (# 15113 and # 15159) replicate analysis were carried out in five fold, resulting in a mean TEQ content of 1.94 pg TEQ/g milkpowder; sd = 0.03; CV = 1.4%. Spiking and fat extraction were carried out on 31-05-1994 resp. 01-06-994. Cleanup procedures were carried out in the period 20-24 June 1994. Final determination was carried out on 26-07-1994. In fig. 1 the results for the analyses in TEQ values are given. Table 1 presents the contents of individual dioxins compounds for the same samples, including mean and standard deviation.

3.1.2 Homogeneity between samples

For the homogeneity between bottles, 18 bottles were randomly taken and each analysed only once. Spiking and fat extraction was carried out in the period 26-04/30-05-1994; cleanup procedures were run during 08-06/20-06-1994 and the final determination with HRMS was carried out during 21-06/01-07-1994.
In fig. 2 the results for the 18 samples are given in TEQ values. The mean TEQ value is 1.83 pg TEQ/g milkpowder, sd = 0.09; CV = 4.8%.

4 DISCUSSION

From the homogeneity results in 3.1.1 and 3.1.2 the differences for the VC of the mean TEQ content are in agreement with results obtained with own internal control samples[1)]. For both homogeneity tests the period over which sample manipulation took place is the same. On the other hand HRMS analysis for the between homogeneity (18 sample analyses) was carried out in two sessions, the within homogeneity was carried out in one day.
The candidate reference material milkpowder was found to be suitable for a certification exercise.

5 LITERATURE

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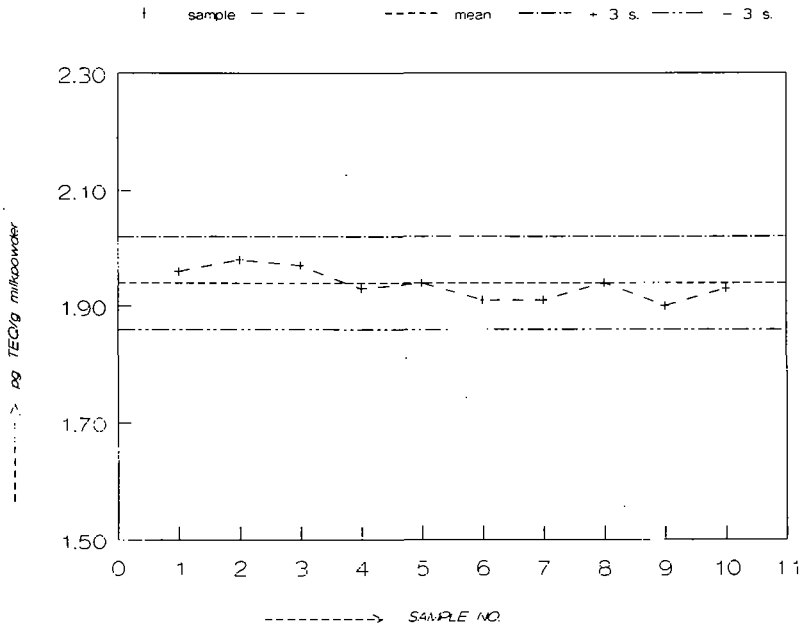
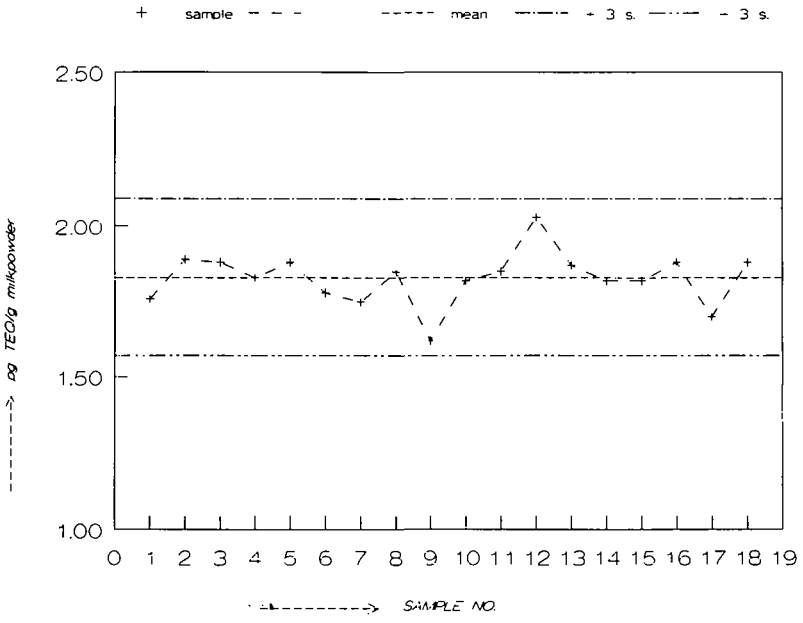
HOMOGENEITY WITHIN SAMPLE
MILKPOWDER BCR



HOMOGENEITY BETWEEN SAMPLES
MILKPOWDER BCR



RIKILT N0.	15113	15113	15113	15113	15113	15159	15159	15159	15159	15159	AVG	SD	VC%
2,3,7,8-TCDF	0.05	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.05	0.04	0.05	0.00	10.2
2,3,7,8-TCDD	0.23	0.23	0.22	0.23	0.22	0.23	0.22	0.24	0.21	0.22	0.23	0.01	3.1
1,2,3,7,8-PeCDF	0.04	0.05	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.00	8.9
2,3,4,7,8-PeCDF	1.65	1.69	1.66	1.64	1.65	1.71	1.66	1.68	1.68	1.73	1.68	0.03	1.6
1,2,3,7,8-PeCDD	0.79	0.78	0.81	0.77	0.78	0.78	0.78	0.80	0.78	0.79	0.78	0.01	1.7
1,2,3,4,7,8-HxCDF	0.82	0.85	0.82	0.82	0.79	0.84	0.81	0.82	0.84	0.81	0.82	0.02	2.0
1,2,3,6,7,8-HxCDF	0.85	0.85	0.85	0.86	0.83	0.86	0.84	0.85	0.89	0.88	0.86	0.02	2.0
2,3,4,6,7,8-HxCDF	1.01	1.03	1.05	1.00	1.05	1.14	1.09	1.07	1.03	1.07	1.05	0.04	3.9
1,2,3,7,8,9-HxCDF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
1,2,3,4,7,8-HxCDD	0.39	0.37	0.38	0.37	0.40	0.38	0.38	0.39	0.37	0.38	0.38	0.01	2.2
1,2,3,6,7,8-HxCDD	0.82	0.85	0.86	0.81	0.81	0.83	0.83	0.89	0.82	0.80	0.83	0.03	3.3
1,2,3,7,8,9-HxCDD	0.29	0.31	0.30	0.32	0.31	0.30	0.28	0.28	0.29	0.27	0.29	0.02	5.2
1,2,3,4,6,7,8-HpCDF	0.53	0.52	0.52	0.53	0.51	0.52	0.50	0.52	0.52	0.54	0.52	0.01	1.9
1,2,3,4,7,8,9-HpCDF	0.03	0.04	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.02	
1,2,3,4,6,7,8-HpCDD	3.64	3.16	3.07	3.01	3.23	1.52	1.49	1.50	1.51	1.42	2.36	0.93	39.5
OCDF	0.22	0.17	0.17	0.16	0.18	0.00	0.00	0.07	0.00	0.09	0.11	0.08	79.9
OCDD	52.09	46.47	41.06	41.92	44.33	13.55	13.86	14.12	13.44	13.83	29.47	16.82	57.1

Table 1. Homogeneity within milkpowder samples, contents expressed in pg/g milkpowder.