harazimj@seznam.cz

21_30_Harazim.pdf

CONTENS OF PHTHALIC ACID ESTERS IN FEEDING ADDITIVES AND THEIR PACKAGES

Jiří Harazim[1], Alžběta Jarošová[2],Lenka Krátká[2], Doubravka Kolenčíková[2], Pavel Suchý[3], [1]Central Institute for Supervising and Testing, Brno, [2]Mendel University of Agriculture and Forestry, Brno, [3] University of Veterinary and Pharmaceutical Sciences, Brno, Czech Republic.

Abstract

Samples of feeding additives (n=15) and others feeds (n=3) and their packages (n=18) were taken from the industrial producers in the Czech Republic in accordance with the National Law of Feeding Stuffs.
Packages of feeds consist of plastic material only, or plastic material and paper or aluminium (n=15) and paper and aluminium or aluminium only (n=3).
The concentrations of phthalic acid esters as di-n-butyl phthalate (DBP) and as di-2-ethylhexyl phthalate (DEHP) were measured in samples of feeds and their packages.
The highest/lowest concentration as a sum of DBP and DEHP of feed was detected in additive Niacin Amid (6,01 mg . kg –1) / in additive Vitamin A – No. 2 (0,11 mg . kg –1). The average content as a sum of DBP and DEHP was 1,80 mg . kg –1.
The highest/lowest concentration as a sum of DBP and DEHP of packages was detected in additive Vitamin E – No. 1 (526,80 mg . kg –1) / in additive Vitamin E No. 3 (6,21 mg . kg –1). The average content as a sum of DBP and DEHP was 73,06 mg . kg –1.
There was no evident relationship between the amount of DBP and DEHP and between feed and packages (P < 0,05). The work was supported by the Czech National Agency for Agricultural Research. Project No.: QG60066/2005.

Introduction:

Phthalate plasticizers have historically served as the preferred plasticizers to impart flexibility to PVC and several other polar polymers. They provide a desirable balance of cost and performance properties. Their acceptable and safe use is unmatched in medical appliances, food processing, and packaging applications, as well as in many other end uses KRAUSKOPF LG (2003).
PFORDT (2004) reported that all food samples analysed here had been sold in plastic packages; none of the packages, however, did contain phthalic acid esters as plasticizers.
JAROSOVA et. al. (1999) found that samples collected from commercial feed mixtures contained both DEHP and DBP (DEHP 0.24-1.77, DBP 0.06-2.37 mg/kg).
Among the civilization or household chemicals the ubiquitous phthalic acid ester (DEHP) is mentioned. This mechanism is called carry-over. The HACCP concept seems to be a very effective tool to control and eliminate hazards during production in the food industry reported HEESCHEN et al. (2004).
Literature data about phthalic acid esters are also considered in dairy products and possible sources of contamination (air, water, feed, microbial synthesis, migration from packaging materials) IMHOF et al. (1994).

Material and Methods:

Samples of feeding additives (n=15) and premixture, complementary feedstuff and feeding material (feeds) (n=3) and their packages (n=18) were taken from the industrial producers in the Silesian-Moravian Region of the Czech Republic in accordance with the National Law of Feeding Stuffs. The samples were being taken within the official inspections.

Packages of feeds consist of only plastic material, or plastic material and paper or aluminium (n=15) and paper and aluminium or only aluminium (n=3).

The concentrations of phthalic acid esters as di-n-butyl phthalate (DBP) and as di-2-ethylhexyl phthalate (DEHP) were measured in samples of feeds and their packages. Each sample of feed was measured for contain of DBP and DEHP, twice repeated; samples of packages were measured and repeated only once.

.Analysis was made by a method for the determination of di-2-ethylhexyl phthalate (DEHP) and di-n-butyl phthalate (DBP). Procedure consisted of extraction of phthalates (hexane : acetone, 1 : 1), separation of analytes from co-extracts using gel permeation chromatography in Bio-beads S-X3 gel (mobile phase dichloromethane : cyclohexane, 1 : 1), clean up of extracts or eluates with sulphuric acid and detection and quantification by HPLC (mobile phase acetonitrile : water, 99 : 1; flow 0,8 ml/min; Cogent e-Column, C 18, 150 x 4,6 mm, particle-size 5 µm) with UV detection (diode array detector) at 224 nm.

The statistical software Number Cruncher Statistical Systems (NCSS 2001), Kaysville Utah, USA, was used.

Results and Discussion:

The highest concentration as a sum of DBP and DEHP of feed was detected in additive Niacin Amid (6,01 mg . kg –1). The lowest concentration as a sum of DBP and DEHP of feed was detected in additive Vitamin A – No. 2 (0,11 mg . kg –1). The average content as a sum of DBP and DEHP was 1,80 mg . kg –1.

The highest/lowest concentration of DBP of feed was detected in feed material the wheat meal (1,21 mg . kg –1)/ the fewest in additive Niacin Amid (0,04 mg . kg –1). There were seven samples below limit of detection of DBP (< 0,03 mg . kg –1). The average content of DBP was 0,29 mg . kg –1.

The highest/lowest concentration of DEHP of feed was detected in additive Niacin Amid (3,28 mg . kg –1)/ the lowest in additive Vitamin D3 – No.1 (0,05 mg . kg –1). The average content of DEHP was 0,95 mg . kg –1.

The highest concentration as a sum of DBP and DEHP of packages was detected in additive Vitamin E – No. 1 (526,80 mg . kg –1). The lowest concentration as a sum of DBP and DEHP of packaging was detected in additive in additive Vitamin E No. 3 (6,21 mg . kg –1). The average content as a sum of DBP and DEHP was 73,06 mg . kg –1.

The highest/lowest concentration of DBP of packages was detected in additive Vitamin E – No. 1 (456,72 mg . kg –1) / the fewest in additive Vitamin E – No. 2 (3,59 mg . kg –1). The average content of DBP was 33,19 mg . kg –1.

The highest/lowest concentration of DEHP of packages was detected in additive Vitamin D3 – No. 1 (123,44 mg . kg –1)/ the lowest in additive Biotin – No. 2 (1,62 mg . kg –1). The average content of DEHP was 39,87 mg . kg –1.

The concentrations of DBP and DEHP of feeds and packages are shown on the table No. 1.
There was no evident relationship amount of DBP and DEHP between feed and packages ($P < 0,05$).

Concentrations of phthalic acid esters, which we found in feeding stuffs and premixtures were similar to those found by RASZYK et al. (1998) in feeds. They reported that mean concentrations of di-n-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) and the sum of DBP and DEHP were 0.207; 0.216 and 0.423 (mg . kg $^{-1}$ of original sample). Our results are similar to those found by JAROŠOVÁ, A. – MALYSZOVÁ, J. (2005). They reported that concentrations of DEHP 0,07 – 1,77 and DBP 0,06 – 2,36 mg/kg had been found in feeding stuffs for pigs, cattle and poultry.

Conclusion:

In spite of not founding any relationship between concentration of DBP and DEHP in feed and packages, the conclusions reached in this work will serve for monitoring esters of phthalic acid in feeds in the Czech Republic as well as for development of analysis method. This conclusion is the same as LATINI'S (2005) opinion, who said that the environmental phthalate monitoring should continue and its maximum allowed concentrations should be determined by regulations.

The work was supported by the Czech National Agency for searching in Agriculture. Project No.: QG60066/2005.

References:

HEESCHEN, WH. – BLUTHGEN, AH.: Carry-over OF environmental contaminants into milk and food hygiene assessment/management. Bulletin of the International Dairy Federation. No. 386, 29 ref. (2004), 28 – 39.
IMHOF, R. – GAUCH, R. – SIEBER, R. – BOSSET, J.: About some volatile organic pollutants in milk and dairy products. Mitteilungen aus dem Gebiete der Lebensmittelunterschung und Hygiene. 85 (6), 48 ref., (1994) 681 – 703.
JAROSOVA-A; GAJDUSKOVA-V; RASZYK-J; SEVELA-K.: Di-2-ethylhexyl phthalate and di-n-butyl phthalate in the tissues of pigs and broiler chicks after their oral administration. Veterinarni-Medicina. 1999, 44: 3, 29 ref.. 61-70.
JAROSOVÁ, A. – MALYSZOVÁ, J.: Esters of phthalic acid in chain of food. XX Meeting „Undesirable substances in food". Štrbské Pleso. 2005. 158 – 162 s.
KRAUSKOPF LG.: How about alternatives to phthalate plasticizers? Journal of vinyl and addive technology 9 (4); (2003), 159-171.
LATINI, G.: Monitoring phthalate exposure in human. Clinica Chimica Acta 361 (2005) 20 – 29.
PFORDT, J.: Levels of di(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalates in some foodstuffs with plastic packagings and in mother's milk. Lebensmittel-Rundschau 100 (11).: 2004: 431-436.
RASZYK, J. – GAJDUŠKOVÁ, V. – JAROŠOVÁ, A. – SALAVA, J. – PALAC, J.: Occurrence OF phthalic acid esters in combined feedstuffs and adipose tissues of swine and cattle. Veterinární Medicina. 43 : 3, 8 ref., (1998), 93 – 95.

The concentration of DBP and DEHP of feeds and packages **Table No.: 1**

Name of feed	Package	feed DBP mg. kg $^{-1}$	package DBP mg. kg $^{-1}$	feed DEHP mg. kg $^{-1}$	package DEHP mg. kg $^{-1}$	feed DBP+DEHP mg. kg $^{-1}$	package DBP+DEHP mg. kg $^{-1}$
Vitamin D3 - No. 1 additive	plastic + aluminium	<0,03 0,14	5,98	0,05 0,50	123,44	0,69	129,42
Vitamin A - No. 1 additive	plastic + aluminium	<0,03 <0,03	2,63	0,15 0,09	41,91	0,24	44,54
Vitamin A - No- 2 additive	paper + aluminium	<0,03 <0,03	5,58	0,11 <0,03	27,61	0,11	33,19
Vitamín E No. 1 additive	plastic + paper	0,08 0,18	456,72	<0,03 0,86	70,08	1,12	526,80
L-lysin additive	plastic + paper	<0,03 <0,03	12,22	1,97 1,76	96,06	3,73	108,28
Vitamin K3 - No. 1 additive	plastic	<0,03 <0,03	5,58	0,14 0,24	65,95	0,38	71,53
Biotin No. 1 additive	plastic + paper	0,19 0,22	6,75	1,63 1,74	36,93	3,78	43,68
Vitamin D3 - No. 2 additive	plastic + aluminium	<0,03 0,07	6,04	0,27 <0,03	112,54	0,34	118,58
Niacin amid additive	paper + aluminium	<0,03 0,04	4,35	2,69 3,28	27,47	6,01	31,82
Vitamin A - No.3 additive	plastic + paper	0,05 0,04	7,49	0,46 0,73	75,85	1,28	83,34
Vitamin E - No. 2 additive	plastic + paper	0,29 0,46	3,59	<0,03 <0,03	3,54	0,75	7,13
Vitamin K3 - No. 2 additive	aluminium	<0,03 0,27	10,10	0,36 0,22	15,87	0,85	25,97
Biotin - No. 2 additive	plastic + paper	<0,03 <0,03	8,91	0,49 0,58	1,62	1,07	10,53
Vitamin E - No. 3 additive	plastic	0,12 1,13	3,87	0,93 2,13	2,34	4,31	6,21
Pracid premix-	plastic + paper	<0,03 0,65	10,23	<0,1 0,77	3,38	1,42	13,61
Lipofish complementary feedingstuff	plastic	0,14 0,15	15,31	1,15 1,88	3,90	3,32	19,21
Wafolin additive	plastic + paper	0,05 <0,03	7,00	0,63 0,69	2,13	1,37	9,13
wheat meal feeding material	plastic	0,39 1,21	25,06	<0,03 <0,03	6,98	1,60	32,04

* bellow limit of detection

The limit of detection of DBP and DEHP of feeds was 0,03 mg. kg-1

The limit of detection of DBP and DEHP of packages was 0,1 mg. kg-1