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Determination of hazardous components in dairy products by chromatographic methods: a review

Abstract: Milk and dairy products takes an important place in human nutrition, being indispensable source of favorably balanced and easily digestible proteins, fats, carbohydrates, minerals and vitamins. Furthermore, it is a raw material for many dairy products, such as yoghurt, cheese, kefir and etc. Before the consuming of ready milk, it goes through production, circulation and processing. Each step reaches potentially unsafe factors, influencing to its chemical contamination that can affect milk quality. For the present time methods of determination the consistency of milk and milk products are sufficient. However not all methods are convenient and economically available to analyze dairy products with a high accuracy and expressively. During the research was collected the most effective analyzes of milk production due to the international sources data and it was approved that chromatography methods allow identifying hazardous components in dairy products through sensitive, less time-consuming and cheap analysis, than traditional methods that is particularly important for milk, which is a highly perishable food. It was established that according to complex compound of dairy products, 80 percent approximately of all researches were provided by gas chromatography and high performance of liquid chromatography methods which are highly sensible. This article reviews the essential chromatographic methods for the determination of harmful components in milk and dairy products approaching a special focus on sample preparation.
Key words: milk products, chromatography, gas chromatography, high performance of liquid chromatography.

Introduction

Milk and dairy products contribute an important role to human body. They are considered as the source of variety of nutrients, and influence on the exchange of calcium and phosphorus. Due to its medical properties, Avicenna used milk to treat many people and he had proved that cow's milk is the most suitable in treatment of humans [1]. Calcium in milk strengthens our bones and teeth; vitamins such as B2 and B12 cause effective metabolism and nerve function [2].

Demand for dairy products growth every year with the increasing population, and production of dairy products is increased respectively. But there is a great responsibility and resources are needed to produce a high qualitative milk product in big quantities. For example, with the aim of increasing the production rate of milk, all female ruminants are often treated with various kinds of medicines (e.g., antibiotics, urea, and hormones). In addition, animal feed is also subject to contamination, that source is considered to be different pesticide sprays that are used on the same farm. Thereby, bovines are endangered by various types and sources of anthropogenic contaminants, which, consequently, have a high possibility to remove to the milk [3].

The rations of ruminants usually consist of roughage, juicy and concentrated fodder, receiving by the technology of conservation of wet forage. Ruminant animals that consume plant food are more likely to be at the danger from exposure of mycotoxins, compared to animals that do not consume fodder grasses and their derivatives. Physiological and anatomical features of the digestive tract of ruminants determine the active metabolism of mycotoxins that transfers with feeds. It should also be taken into account that mycotoxin metabolites formed in the rumen can be more toxic in comparison with the original contaminants. For example, metabolite aflatoxin B1, such as aflatoxicol and aflatoxin M1 (AFM1) can be detected in milk after a few hours. The maximum concentra-

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tion in milk is observed after 24 hours. These results confirm the rapid absorption and metabolism of aflatoxins in the body of ruminants [4].

Other sources that decrease the quality of milk and may effect on the human body negatively: condition of technology of milk production. The process of technology is valuable part where all steps and additives are responsible for the quality of milk [12]. For instance, common hazardous materials may be assumed as unhygienic water, salt, blotting paper, melamine, caustic soda, urea, hydrogen peroxide, formalin, and others. In addition, in cattle farming a large amount of stimulus chemicals are injected routinely into the body of the ruminants to promote more milk production. These chemicals are then secreted along with the milk and may not be removed during pasteurization [5].

Also the harmful things in contamination of milk that transform it into cheap and available products can be chemicals such as emulsifiers, flavorings, colorants preservatives that are able to replace the natural products [3].

The milk market reaches in Kazakhstan today, the variety and quantity of production of milk products grows year by year [6]. However not all dairy contamination is detailed completely that concern scientists.

Many scientists consider the method of chromatography detection is the most suitable for the analysis of dairy products. In this review variety chromatography methods are presented with consideration of different sample preparation.

The analyzes of dairy products by chromatographic methods are given in Tables 1-6.

Table 1 – Determination of melamine in dairy products by chromatographic methods

№	Techniques	Products analyzed	Condition of analysis	Sample preparation	Reference
1	LPME-HPLC	Milk	2.0-5.8 ng mL−1 42 ., YL 9120 UV-Vis detector, column C18 (Hector, 5 μm, 250 mm × 4.6 mm	All the samples were dissolved in hot (40 °C)	[7]
2	HPLC	Milk, milk products	column 5 μm, 250 mm×4.6 mm	0.5 g sample + diethyl-water-ACN 10:40:50, t = 30 min, 200 mcl al., t=70°C + Sylon-BFT solution	[8]
3	HPLC	Milk, milk products	5 μm, 250 mm × 4.6 mm column	10 g sample + water, t = 10 min ultrasonic bath	[9]
4	C-gel fitation	Milk	Superdex 75 10/300GL column 10 × 300 mm and Superdex 200 10/300GL column 10 × 300 mm	10 g sample + 1.0 mL 0.1 M NaOH + water 100 mL, filtration	[10]
5	HPLC – derivatization by LLME	Milk	Supelcosil LC-18: 25cm × 146 4.6 mm, 5μm column	8.0 ml of 5% (w/v) trichloroacetic acid + 1.0 ml of 2.2% (w/v) lead acetate + 1.0 g of each homogenized raw milk, the mixed solution was centrifuged 163 for 10 min at 10,000 rpm	[49]
6	HPLC-FD	Milk	A Zorbax SB-C18 (150 mm× 4.6 mm, 5 mm) column connected to a Zorbax ODS (12.5mm×4.6 mm, 5 mm) pre-column	70 ml glacial acetic acid (HOAc) + 10 ml sample + 3 ml of ultrapure water. The resulting mixture (pH ¼ 4.6) was vortex-mixed for 3 min, centrifuged at 6000 rpm (2.012 g) for 10 min	[50]

Table 2 – Determination of antibiotics in dairy products by chromatographic methods

№	Techniques	Products analyzed	Analyte	Condition of analysis	Sample preparation	Reference
1	UHPLC-MS	Milk	β-lactam, macrolide, amide alcohol, forest amine	HSS T3 column (2.1 mm × 100 mm × 1.8 μm), scan range was m/z 100-1000.	1 ml sample + 4 ml CAN t=30 sec 3000 rpm t=10 min was centrifuged + 4,5 ml supernatant on SPE.	[11]

Continuation of table 2

№	Techniques	Products analyzed	Analyte	Condition of analysis	Sample preparation	Reference
2	LC-MS	Milk, cheese	Dicecyldimethyl, ammonium, chloride	Fusion-RP 80A column (75 mm × 2.00 mm, 4 m), cal: 5, 10, 20, 50, 100 and 150 g kg^{-1}	1 g sample + 10 ml deuterated solution + 20 ml (98-100%) HCOOH + 9 ml ACN / EtAc – 50:50 + 2 g $MgSO_4$	[12]
3	UHPLC-MS	Milk	Neomycin, genemycin, hygromycin, gouromycin	HILIC column, flow rate of 0.5 mL min^{-1} .	2 g sample + 250 µL CH_3OOH (15%) t=5 min was centrifuged +3.5 mL of 50 mM potassium phosphate buffer at pH 7.0	[13]
4	UHPLC	Milk	Theophylline, paracetamol	C18 column (250 mm x 4 mm; particle size 5 µm) and C18 pre-column (4 mm x 4 mm; particle size 5 µm)	0,1 g sample 2000 rpm t=10 min was centrifuged + 20 µL supernatant on SPE	[14]
5	GC-MS UHPLC	Milk	Diethyl phthalate bis(2-butoxyethyl) phthalate bis (2-ethylhexyl) phthalate	30 m × 0.32 mm i.d., 0.25-µm film DB-5 fused-silica capillary column	5,0 g sample +1,0 ml 10% CH_3OOH, t=10 min sand heating, 0,45 µm nylon filter. 5 ml filtrate + 1.0 ml ethylacetate by 3 times extracted + 0.5 ml methanol	[15]
6	LC-Q-Orbitrap-MS	Milk	Diethyl phthalate bis(2-butoxyethyl) phthalate bis (2-ethylhexyl) phthalate	C-18 aQ connected to a 10 mm × 2.1 mm, Accucore C-18 aQ guard column	15 f sample + 1% CH_3OOH + 10 ml MeCN + MgSO4 (6 g), + NaAc (1,45 g) t=5 min 4000 rpm was centrifuged + 1,2 g $MgSO_4$, 405 mg PSA and 95 mg C_{18}	[16]
7	LC-FD	Milk	CIP, LOM, DAN, FLE, OFL, ENR, NOR, MAR, LEV, ORB, FLU	C18 column (150 × 4.6 mm i.d., 6 µm) with gradient elution.	4.0 g sample into 10 ml polypropylene centrifuge tube + standard working solution. Then, the samples stand in the dark for 30 min at room temperature before centrifugation for 10 min at 10000 rpm	[51]
8	LC-MS	Milk	Enrofloxacin, Ciprofloxacin, Difloxacin, Danofloxacin, Sarafloxacin	C18 column (75 mm 4.6 mm; 3.5 mm particle diameter) from Waters. A Phenomenex C18 column (4.0 mm 3.0 mm)	5 ml sample + 6 ml ACN (0.1% formic acid). The mixture was vortexed again and kept at low temperature (20°C) for 30 min, tubes were centrifuged for 30 min at 12,000 rpm	[52]
9	SPME-GC-MS	Milk, milk products	NPX, KPF, TLF	J&W DB-5MS capillary column with dimensions of 30 m × 0.25 mm i.d., 0.25 m film thickness	To all samples 10 mL of ACN and 2 g of NaCl were added. The tubes were shaken in a vortex-mixer for 60 s and centrifuged at 5000 rpm for 15 min, at 5 ◦C	[56]
10	UHPLC-MS	Milk products	Nitroimidazoles, benzimidazoles, and chloramphenicol	C18 column (50 mm 2.1 mm i.d., 1.7 lm particle size)	1 g of sample + 3 ml of acetonitrile + 2 g NaCl were added and vortexed for 1 min. The mixture was centrifuged for 5 min at 10000 rpm, 4 C.	[61]

Table 3 – Determination of amino acids in dairy products by chromatographic methods

№	Techniques	Products analyzed	Analyte	Condition of analysis	Sample preparation	Reference
1	LC-Q-TOF-MS/MS	Milk	Glycinin G1 / G2, glycinin G20, glycinin G4 – allergic proteins	QTrap 4000 LC-MS/ MS system	Washed samples with ethanol were homogenized in 0.1 mol/L of aqueous ammonium 158 bicarbonate at 9500 rpm 159 for 2 × 20 s, followed by 13,500 rpm for 30 s and then, vacuum-dried using a CentriVap 160 micro IR.	[17]
2	LC-MS	Yoghurt	β-casomorphin	C18 column 100 mm × 2.1 mm, 100Å, 2.6 µm particle diameter with a guard column (2.1 mm x 10 mm)	Ph = 4,5 -20^{0}C	[18]
3	LC-MS	Cacao kefir. cheese	Tryptophan-2,3-thioxogenase (TDO), indolamine-2,3-22-dioxygenase-1 (IDO-1) and indolamine-2,3-dioxygenase-2 (IDO-2)	column (100 x 2.1 106 mm i.d., 1.9 µm) and Acquity UPLC HSS C18 column (150 x 2.1 mm i.d., 1.8 µm	Sample + methanol/water (60:40)	[19]
4	GC	Kefir	D, L-alanine, D- and L-valine, methionine and cysteine	column 25 m x250 µm	100 ml sample t=10 min was centrifuged pH=4,25 +7 M NH_3H_2O +3 M HCl	[20]

Table 4 – Determination of fatty acids in dairy products by chromatographic methods

№	Techniques	Products analyzed	Condition of analysis	Sample preparation	Reference
1	GC	Milk, cheese	column, 25 m x 0.32 mm	10 ml sample + 10 ml ethanol + 1 ml H_2SO_4 (2,5 mol/l t=10 min was centrifuged + 1 g Na_2SO_4 + 0,3 ml $MgSO_4$ (2,5 mol/l) + C_7H_{16} (1:1)	[21]
2	GC	Milk, cheese	Six-meter (0.25 mm i.d.)-fused silica capillary columns with chemically bonded DB-5 (0.1 pm coating thicknes	10 ml sample +10 ml ethanol + 1 ml H_2SO_4 2,5 mol/l t=10 min was centrifuged +1 g Na_2SO_4 + C_7H_{16} (1:1)	[22]
3	GC-MS	Milk	column coated with polyimide 60 mm x250 mm i.d., 0.25 mm film thickness column	1000 ml sample + 100 ml SS + 1180 ml ethanol + 200 ml pyridine pH = 5	[23]
4	GC	Milk, yoghurt	column (30 m × 250 µm i.d., 0.32-µm phase thickness;	All samples at -18 ° C was frosted.	[24]
5	GC-MS	Butter	C18 column (5 lm, 150 4.6 mm i.d.)	400 g sample to 500 ml was transffered t=75±2^{o}C + sediment, the precipitate was filtered and + Na_2SO_4	[25]
6	SPME-GC-MS	Milk	SLB-IL111 capillary column (100 m 0.25 mm i.d., 0.20 lm film thickness	25 mg of sample was derivatized to fatty acid methyl esters (FAME) by base-catalyzed methanolysis of the glycerides with KOH in methanol according to ISO-IDF procedure	[57]

Table 5 – Determination of hormones in dairy products by chromatographic methods

№	Techniques	Products analyzed	Analyte	Condition of analysis	Sample preparation	Refer-ence
1	UHPLC	Yoghurt, cheese	17-Estradiol	(10, 25, 50, 75 and 100 lmol L1, MIPs and NIPs were packed into 50x4.6 mm	500g sample + 150 ml methanol/acetone 1:1 t=5 min mix, + 15 ml water	[26]
2	UHPLC-MS	Cheese, kefir	β-zearalanol, β-zearalenol α-zearalanol,ethinyl estradiol, 17α-estradiol	Agilent 1909/S capillary column (30 m × 0.25 mm	3,1-12 g sample + 5 ml ethanol	[27]
3	GC	Cheese, kefir	formononetin, daidzein, entero-diol, Genistein	X-Bridge C18 column (50 mm x 2.1 mm, 1.7 µm)	100 g sample	[28]
4	GC-MS	kefir, yoghurt	Melatonin	SB-C18 column (50 4.6 mm i.d., 3.5 lm)	5 g sample t=3 min 20 000 rpm was centrifuged	[29]
5	GC-MS	Cheese, milk, yoghurt	17b-estradiol (17b-E2), 17a-ethynylestradiol (EE2), estrone (E1), estriol (E3)	MWCNTs (8–15 nm outer diameter (o.d.), 50 lm length) and MWCNTs (10–20 nm o.d., 10–30 lm length), and packed in a column	Sample +10 ml n-hexane + 10 MeOH + water, + 10 ml MeCN t=10 min was centrifuged	[30]

Table 6 – Determination of mycotoxins, preservatives, colorants and metal in dairy products by chromatographic methods

№	Techniques	Products analyzed	Analyte	Condition of analysis	Sample preparation	Refer-ence
1	GC-MS	Milk, yoghurt	Aflatoxin M1, aflatoxin G2, gliothoxin	100 mm × 2.1 mm, i.d., 2.6 m, Thermo Accucore C-18 aQ connected to a 10 mm × 2.1 mm	15 g sample + CH_3COOH + 10 ml MeCN/water (84:16)	[31]
2	UHPLC	Yoghurt	Aflatoxin M1	LiChrospher 100 RP-18, 5 Am column 25 4.6 mm	10 g sample + 10 ml CH_2Cl heated and + 5 ml water to dissolve.	[32]
3	SPE-UPLC-MS	Milk	Zarolenone, aflatoxin M1, Aflotoxin B1	C18 column (150 mm × 2.1 mm i.d., Thermo Fisher Scientific)	5 g sample + 25 ml water + t=10 min magnetic stirrer.	[33]
4	HPLC-MS	Milk	Oxystrerol	column Synergi Hydro, 4 µm, 250 162 x 2.0 mm	0,5 g sample + 40 µL CH_3OH + 5 ml 2 M KOH, t=30 sec mix, left on 16-18 hours.	[34]
5	UHPC	Milk	Phosphatidylserine	PS by the analytical column	0,75 g sample + 1,5 ml water + 9 ml methanol + 10 ml chloroform	[35]
6	UHPLC-MS	Yoghurt, cheese	Cr(III)	column (250 × 4 mm internal diameter (i.d.), 9 µm particles diameter) as well as an IonPac CG5A guard column	Ph = 8,5 + 6 ml 0,05 M EDTA 10000 rpm t =15 min was centrifuged.	[36]
7	SPME-GC-MS	Yoghurt	Acetaldehyde, 2-butanone, 2,3-butadione, hexanal	(Titanium alloy Ti-6Al-4V, length: 136 mm, tip diameter: 13 mm)	Sample was heated to 45 ° C	[37]

Continuation of table 6

№	Techniques	Products analyzed	Analyte	Condition of analysis	Sample preparation	Reference
8	HPLC	Yoghurt	Colorants: Y1 INS 110 NI MD2, NI MD3, MD4, E122, MD6, MD12, MD13 E102, E110, MD14, E123, E124	column oven CTO-20AC	5 g sample + 10 ml ethanol	[38]
10	HPLC	Milk	Kestosis, nystosis, fructofuranosyl nystosis	Atlantis dC18 (150 3 mm, 5 μm particle size	0,5 g sample + 1 g sediment t=5 min was centrifuged, 0,22 mm nylon filter.	[39]
11	HPLC	Cheese, milk, yoghurt	Benzoic, sorbic, propionic acids	Optimal wavelength 235 nm	10 g sample transfer into 250 ml + 100 ml extragent, t=10 min ultrasound bath + 5 ml Carrez I, Carrez II solutions + water	[40]
12	UHPLC	Yoghurt	Biogenic amines: cadaverine, spermidine, spermine, tyramine, putrescine	C18 column (150 mm length x 4.6 mm inner diameter, 5 μm particle size)	5 g sample + 10 ml $HClO_4$ Whatman n ° 1 was filtered(pH> 8, 12) + 2,5 ml NaOH 2 M t=10 min was centrifuged	[41]
13	HPLC-MS	Milk	Lactose	Carbohydrates NH2 (5 μm, 250 × 4.6 mm) and Luna NH2 (5 μm, 250 × 4.6 mm)	1 ml phosphotungstic acid + 5 mL of milk. shaking for 30 s and reacting for 15 min, the mixture was centrifuged at 4500 rpm (1920g) for 5 min	[46]
14	LC-FD	Milk	Drugs: NOR, OFL, FLE, CIP, DAN, LOM, ENR, ORB	C18 column (5 μm, 100 Å, 4.6 × 150 mm)	The sample was kept in the dark for 30 min and then centrifuged at 10,000 rpm (6950 g) at 20°C for 10 min.	[47]
15	HPLC–UV	Milk	formaldehyde	C-18 (250 X 4.6 mm; 5 μm; Supelco) column	2.5 ml + .0 mL of 0.1 g L-1 DNPH solution in ACN, pH = 4.0 + 0.2 and was vortex-mixed for 1 min and centrifuged at 6000 rpm (2.012 g) for 20 min.	[48]
16	SPME-GC-MS	Milk	NA, AcPY, AcP, FL, PHEN	HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25m film thickness)	5 mL of a liquid sample or 5 g of a solid sample were placed into a 15 mL SPME-vial. The vial was filled with water in order to avoid the headspace	[54]
17	SPME-GC-MS	Milk, milk products	Volatile compounds:	HP-5MS column (30 m length, 0.25 mm inside diameter, 0.25 μm film thickness	Sterile milk was prepared by reconstituting 10% (wt/ vol) skimmed milk powder in distilled water and autoclaving at 95°C for 5 min	[53]
18	SPME-GC-MS	Milk, milk products	Ink photo-initiators	Column (PDMS, 100 m film thickness), polyacrylate (PA, 85 m film thickness), Carboxen–PDMS (CAR–PDMS, 75 m film thickness)	All samples were homogenized and transferred into 20 ml vials	[55]

Continuation of table 6

№	Techniques	Products analyzed	Analyte	Condition of analysis	Sample preparation	Reference
19	GC-MS	Milk products	Dimethyl phthalate, diethyl phthalate, diallyl phthalate, diisobutyl phthalate, benzyl butyl phthalate	30 m × 0.32 mm i.d., 0.25-μm film DB-5 fused-silica capillary column	5 ml of sample was pipetted into a 10-mL glass centrifuge tube + 1.0 mL of 10% (vol/vol) acetic acid was added, mixed well, and heated in a sand bath at 70°C for 10 min and centrifuged for 10 min	[58]
20	GC-MS-AED	Milk products	Dimethylselenide, dimethyldiselenide	Capillary column DB-624 (30 m × 0.32 mm I.D. × 1.8 m) with G2350A microwave-induced plasma atomic emission detector	2 mL of sample were placed into a 15 mL SPME–vial, into which 0.6 g NaCl had been previously weighed.	[59]
21	HPLC	Milk, yogurt	Formaldehyde	5 μm particle sized octadecylsilyl (ODS) column (250 mm × 4.6 mm i.d.)	samples were pastoralized before the analyses and added 5 ml of acetonitrile	[60]

Sample preparation

Sample preparation takes almost 70% of all time of analysis, and has a great responsibility on the next step of analysis. Therefore in any process sample preparation is the important part to confirm components and identify quantities of them. The main products of the contamination of milk are included lactose (4.6%), proteins (3.2%), and lipids (3.9%). Even if these components are the homogeneous system, they are different in another animal's milk.

During the analysis protein and lipids complicate the treatment, substituting the ions of another component. Generally, it is suitable to use Mass-spectrometry method for purification of these components. However, in Mass-spectrometry method the water volume can disturb the extraction of analytes, affecting on their diffusion. Therefore, many scientists subjected the samples to sublimatic drying before the analysis [42]. As a result, Solid Phase Extraction (SPE) is used effectively in removal system components from the samples. But depending on the sorbents Liquid-Liquid Extraction (LLE) also can be useful [43]. As the sorbents were used acetonitrile, ammonium acetate, complex agent Na_2EDTA, and methanol, selecting suitable reagent by their organic class. For example, β-lactam is very sensible for methanol whereas tetracycline is able to be extracted only at pH=4, at another pH index it can participate for epimerization, dehydration, isomerization processes. Moreover, many antibiotics produce chelated complexes with metal ions and disturb the analysis of protein system [44].

High performance of liquid chromatography

HPLC analysis depends on the chromatography column, used sorbent and eluent. Due to its efficiency and time expressing HPLC method is highly demanded in the analysis of milk and dairy products. According to Governmental Standard no. 31504-2012 the optimum pH=4.5 to identify the preservatives in dairy products at 230-260 nm range. Analyzing all other researches, acetonitrile is the acceptable sorbent due to its non-selectivity to other components and easily accessible reagent that allows identifying analytes in 5-10 minutes. Moreover, for instance in Methodological instruction no.4.1.2420-08 was provided analysis where the rate of concentrations of melamine in milk compounds were 1,0-100 mg/kg. However, determination of melamine by Chromato-Mass-Spectrometry method consists of 2 parts: extraction of melamine and its derivatization. Mass spectrometry method allows determining the quantity of melamine even in very low concentration ranges undoubtedly, but it takes a lot of time for sample preparation, in addition, for derivatization is used t trimethylsilyl that interrupt the determination of other components [44].

Ultra high performance of liquid chromatography

The advantage of this method is highly sensitive column, as a rule it usually 50x4,6 mm with 1,7 μm size particles and expressive separation of components occurs within less than 2 minutes. In the tables provided above for the determination of components in milk products UHPLC method was used mostly. For example, in determination of estrogens Waters

Symmetry C18, 500 nm, 150 × 4.6 mm column was used, analyze time = 5 minutes, as a result 0.116–0.461 nmol/kg concentration rate – which is very small identified in 500 g sample [26]. However, in identification of synthetic colorants in yoghurt using special column and providing expressive time of analysis, pH of the analyzing solution should be equal to 7 which is not completely appropriate for us [30]. Also this method was used in amines detection [46]. The disadvantage of this method is expensive and inaccessible devices. In addition, this method is directed on the selectivity more not efficiency. Therefore UHPLC is appropriate to use only as combined method, for instance UHPLC-MS [30].

Gas Chromatography

Gas chromatography was used for analysis of dairy products, especially in identification of fatty acids. Gas chromatography is characterized by high selectivity, accuracy and also by its automated [45]. According to Governmental Standard no. 32915-2014, there was provided standard preparation of methyl ester, carrier gas was nitrogen, time of analysis was 50 minute. The main minus of this method is long duration of time for sample preparation. However the time of preparation and analyzing depends on analyte that is going to be tested, according to cognitive structure of dairy products [27]. For example, when amino acids were analyzed in dairy products with HP 6890 gas chromatograph the time of analysis was less than in previous research and as a result 3 amino acids were detected in kefir [38].

Quantitative determinations were provided by using the standard addition method. The identification of amino acid derivatization method by using chloroform in aqueous medium has been proceeding to the use of different alkyl chloroform and alcohols. These reactions provide an extremely fast and simple route for derivatization carrying out from aqueous samples in only one step [21].

Other procedures

LC–MS/MS method was optimized for determination of ammoniums in cheese and milk products at concentration levels in full obtains with the preliminary MRL setting as 100 g kg−1. In this method used 50:50 (v/v) proportion of ACN/EtAc defining it as the best sensitivity for. Because ACN is known to be a poor solvent for polar compounds otherwise increasing the volume of EtAc promotes the extraction of long-chain alkyl substances (especially DDAC C16 and C18) [13]. The similiar method was used for quantifying qualifiers of amino acids such as β-casomorphin in milk and yoghurts. The advantage of this method was useful sample preparation using SPE cartridges followed by LC–MS for the identification of low molecular weight degradation by-products of these β-CMs. However the limitation of this research was inadvertency of screening of all samples components [19]. Although, not all the researches were considered to do a detailed analyzes for all components [20].

Conclusion

In this paper was analyzed the techniques that was used for the determination of hazardous components in dairy products. During the research there was analyzed a large amount of information, research papers, statistics for the last 10 years from the international scientific portals such as Science Direct, Web of Science and other sources. More than 40 researches were considered; as a result all of the research papers were oriented on the determination of mycotoxins, amino acids, fatty acids, preservatives, colorants, hormones in the contamination of dairy products. Determination of these components in milk by chromatographic methods is a very terrible issue to ensure consumers ‘safety and to avoid, even removal company productions from the market of milk. Dairy products are highly complex compound that chromatography methods allow identifying the components even in very small concentrations that is why this method is acceptable for analysis of hazardous components in dairy products. For the sample preparation were considered Solid Phase extraction and Liquid-Liquid extraction were should be taken into account pH of the solution, in most researches it was equal to 4, and complete absorption of the main components so that they do not interfere with further analysis. Accordingly considered chromatographic methods almost 80 percent of analyzes were organized by gas chromatography and high performance of liquid chromatography methods, using available and cognitive mobile phase as ACN, in some cases it was dilution with another acids. In comparison with other methods for determination of hazardous components in dairy products, the most selective method was High Performance of Liquid Chromatography with high separation efficiency, having a good possibility to determine the composition of milk samples deeply. For the future time is required to provide the analyzes of dairy products due to this methods.

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