

DETERMINATION OF SODIUM BENZOATE, POTASSIUM SORBATE, NITRATE AND NITRITE IN SOME COMMERCIAL DAIRY PRODUCTS

BAZI TİCARİ SÜT ÜRÜNLERİNDEKİ SODYUM BENZOAT, POTASYUM SORBAT, NİTRAT VE NİTRİTİN BELİRLENMESİ

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ABSTRACT: The aim of this work is to determine the sodium benzoate, potassium sorbate, nitrate and nitrite contents of commercially available dairy products in Turkey. Seventy-four per cent samples of strained yoghurt, seventy per cent samples of kasar cheese, eighty-five per cent samples of tulum cheese and eighty per cent samples of ayran had sodium benzoate. All cheese samples had potassium sorbate levels inside the legal limits (1000 mg/kg in the sample). All values for nitrates and nitrites that have been found were fairly low. According to Turkish Food Codex, the presence of sodium benzoate, and potassium sorbate (except cheese) in dairy products is prohibited. It is clear that new training and checking programs for the most of dairy producers are necessary.

Keywords : Sodium benzoate, potassium sorbate, nitrate, nitrite, dairy products

ÖZET: Bu çalışmada, Türkiye'de ticari olarak mevcut olan süt ürünlerinin sodyum benzoat, potasyum sorbat, nitrat ve nitrit içeriklerinin belirlenmesi amaçlanmıştır. Süzme yoğurt örneklerinin %74'ü, kaşar peyniri örneklerinin %70'i, tulum peyniri örneklerinin %85'i ve ayran örneklerinin %80'i sodyum benzoat içermektedir. Bütün peynirlerde tespit edilmiş olan potasyum sorbat miktarı yasal sınırlar içerisinde (1000 mg/kg örnek). Örneklerde bulunan nitrat ve nitrit miktarları oldukça düşük düzeydedir. Türk Gıda Kodeksi'ne göre peynir dışındaki süt ürünlerinde sodyum benzoat ve potasyum sorbat bulunması yasaktır. Süt ürünleri üreticilerinin pekçoğu için yeni eğitim ve kontrol programlarına gereklilik duyulduğu açıktır.

Anahtar kelimeler : Sodyum benzoat, potasyum sorbat, nitrat, nitrit, süt ürünleri

INTRODUCTION

Food preservatives have become an increasingly important practice in modern food technology with the increase in the production of processed and convenience foods (1). These preservatives are added to stop or delay nutritional losses due to microbiological, enzymatic or chemical changes of foods and to prolong shelf life and quality of foods (2, 3). The most commonly used preservatives in many types of foods are benzoic and sorbic acids, nitrate and nitrite (4, 5, 6).

The importance of food preservatives to consumers has always been a health safety issue (7). For these reason, the use of food additives in different countries is limited by specific regulations (8). These preservatives are allowed by legislation but their use demands special care (9). Turkey follows regulations of Turkish Food Codex on the safe use of food additives. According to Turkish Food Codex, maximum legally allowable limit for potassium sorbate in cheese is set at 1000 mg/kg in the sample. The usage of potassium sorbate in yoghurt and ayran and of sodium benzoate in dairy products is prohibited. In Turkey where the addition of potassium nitrates in the cheeses is permitted up to the level of 50 mg/kg. Moreover, the Turkish Food Codex doesn't accept the use of nitrate in other dairy products (10).

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Strained yoghurt, kasar cheese, tulum cheese and ayran, traditional milk products, are widely consumed in Turkey. Although these products have been manufactured in the industrial plants, many of low-income consumers prefer the lower priced dairy products from small-sized producers, which predominate in the local markets (11). To inhibit yeasts, moulds, and bacterial growth, some dairy producers have been using sodium benzoate, potassium sorbate and nitrate with no guidelines to regulate their use. Although several articles pertaining to chemical composition and preparation of strained yoghurt, kasar cheese, tulum cheese and ayran, published reports on detection the presence of sodium benzoate, potassium sorbate, nitrate and nitrite in the products are not available from literature.

The purpose of this study was to investigate the occurrence of sodium benzoate, potassium sorbate, nitrate and nitrite in strained yoghurt, kasar cheese, tulum cheese and ayran commercially available on the local markets in Antalya, Turkey in order to compare their levels respective allowable limits.

MATERIALS AND METHODS

Sampling

The samples of strained yoghurt, cheese and ayran produced from cow's milk were purchased from 35 vendors in 7 districts of Antalya, Turkey. A total of 90 samples of strained yoghurt (35), kasar cheese (20), tulum cheese (20) and ayran (15) were aseptically taken and placed into sterilized jars. Each analysis was performed in duplicate.

Standards and Chemicals

HPLC grade methanol and other reagents (analytical grade) purchased from Merck (Darmstadt, Germany). Water used for chromatography processing was obtained from an Aquamax-ultra water purification system (Younglin Inst., Kyounggi-do, Korea).

Analysis of Sodium Benzoate and Potassium Sorbate

Sample preparation

The liquid chromatography technique was used to determine the concentrations of sodium benzoate and potassium sorbate in the samples following the procedures described by Anonymous (12). Approximately 20 mL of water added to 5 g each of the samples and then homogenized on Stomacher 80 (Seward Medical, London, UK) for 10 min at medium speed. The extraction of sodium benzoate and potassium sorbate was made by methanol. The mixture was thoroughly mixed with 35 mL of methanol. The volume was brought up to 100 mL with water and filtered through Whatman paper No.1. For the filtration of the samples prior the injection, a Millex HV 0.45 µm filter (Millipore) was used.

HPLC Conditions

The chromatographic analysis was carried out in a HPLC (Agilent Technologies, Waldbronn, Germany) equipped with a type G1311A pump, a type multiwavelength diode array detector G1315B (190-380 nm), a type G1379A vacuum degasser, a type G1313A automatic sampler, a type G1316A column oven and Agilent ChemStation controller software. The chromatographic separation was achieved with a C18 column (Hypersil, 25 cm x 4.6 mm i.d., 5 µm particle size). The mobile phase was 65:35, acetate buffer (pH 4.74) and methanol. The analysis was performed at room temperature using flow rate of 0.8 mL/min. The injection volume was 20 µL. The chromatogram was recorded for 20 min. The detection of sodium benzoate and potassium sorbate was carried out at wavelength of maximum absorption of the compounds, 235 nm.

Preparation of The Standard Curve

The external standard plot method was used. Duplicate injections of 20 µL sodium benzoate and potassium sorbate standard solutions were used to construct linear regression lines (peak area versus concentration).

The peaks were identified based on the retention time. The standard curves were obtained with five points for both of sodium benzoate and potassium sorbate. Concentrations were 5, 10, 20, 40 and 80mg/L for sodium benzoate and 1, 2, 4, 8 and 16mg/L for potassium sorbate.

Recovery Study

In order to verify to accuracy and precision of the analytical procedure, the recovery studies were carried out. The recovery of sodium benzoate and potassium sorbate added to the samples free of the two preservatives was carried out. Two samples of strained yoghurt, kasar cheese, tulum cheese and ayran were analyzed before and after addition of 100 and 200 mg of sodium benzoate and potassium sorbate to 100 g of the samples.

Analysis of Nitrate and Nitrite

Nitrates and nitrites were determined according to the International Dairy Federation standard method (13). The method involves dissolution of the dairy product in warm water, precipitation of the fat and proteins, and filtration. Nitrites were determined directly and nitrates were determined after reduction to nitrites by copperized cadmium in the filtrate. In both the reduced and unreduced parts, the intensity of red colouring elicited by addition of sulphanilamide and *N*-1-naphtyl-ethylenediamine dihydrochloride was measured at a wavelength of 538 nm by UV-160A Spectrophotometer (Shimadzu, Japan). The content of nitrites was calculated as the difference in concentration between the reduced and unreduced parts. The method was continuously tested by standard addition of nitrates and nitrites in each type of dairy product studied.

RESULTS

The approximate retention time was 10.2 min for sodium benzoate and 16.4 min for potassium sorbate. The limit of detection (LOD) for sodium benzoate and potassium sorbate were 1.68 mg/kg and 0.69 mg/kg in the samples, respectively. The limit of quantitation (LOQ) for sodium benzoate and potassium sorbate were 5.6 mg/kg and 1.3 mg/kg in the samples, respectively. Recoveries ranged from 91 to 103%. Linearity between the concentration of sodium benzoate and potassium sorbate and the UV absorbance at 235 nm was maintained over the concentration range of 5-80 mg/L for sodium benzoate and 1-16 mg/L for potassium sorbate. The mean regression equations for concentrations of sodium benzoate and potassium sorbate versus arbitrary units of peak area were $Y = 48.92 X + 34.51$ (Y represents peak area, X represents concentration in mg/L) and $Y = 134.04 X + 11.30$, respectively. The correlation coefficients for standard curves of sodium benzoate and potassium sorbate were 0.9993 and 0.9988, respectively.

Table 1 shows mean concentrations (mg/kg) of sodium benzoate and potassium sorbate in commercial strained yoghurt, kasar cheese, tulum cheese and ayran samples, whereas the typical chromatogram of standard mixture of sodium benzoate and potassium sorbate are shown in Figure 1.

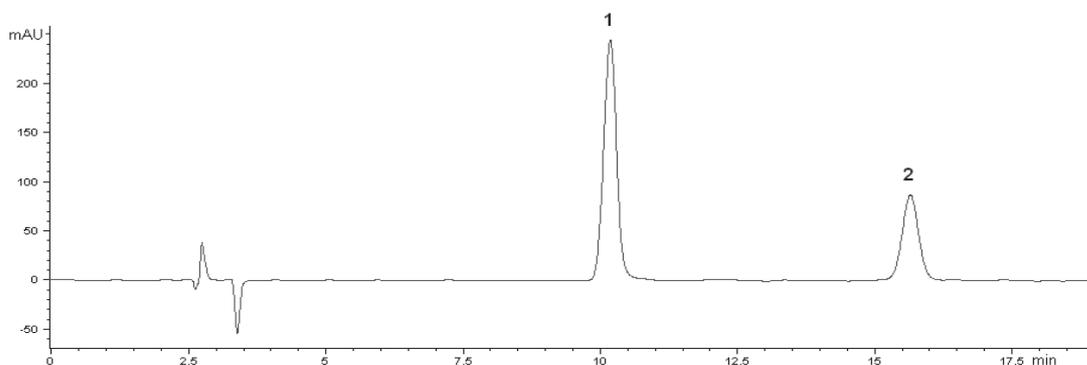


Figure 1. Typical chromatogram of standard mixture of preservatives containing 40 mg/L of sodium benzoate (1) and 8 mg/L of potassium sorbate (2).

Twenty-six (74%) of strained yoghurt samples contained sodium benzoate in the range of 28.6-425.3 mg/kg, 14 (70%) of kasar cheese samples contained sodium benzoate in the range of 72.3-814.7 mg/kg, 17 (85%) of tulum cheese samples contained sodium benzoate in the range of 33.4-754.1 mg/kg and 12 (80%) of ayran samples contained sodium benzoate in the range of 23.1-698.8 mg/kg, which are not acceptable according to Turkish Food Codex. Four (11%) of strained yoghurt samples contained concentrations of potassium sorbate between 321.9 and 612.4 mg/kg, which was not in compliance with the Turkish legislations. Potassium sorbate was detected in three (15%) of kasar cheese samples at levels ranging 112.7-688.1 mg/kg. The potassium sorbate levels of kasar cheese samples were determined below the maximum permitted concentration (1000 mg/kg in the sample) of Turkish Food Codex. Only one (5%) of tulum cheese sample had potassium sorbate level (911.7 mg/kg) inside the legal limits. Potassium sorbate was not detected in any of the ayran samples. Only three (9%) of strained yoghurt, two (10%) of kasar cheese and one (5%) of tulum cheese samples contained both of sodium benzoate and potassium sorbate.

Table 1. Concentrations (mg/kg) of sodium benzoate and potassium sorbate in strained yoghurt, kasar cheese, tulum cheese and ayran

Product	n	Sodium benzoate		Potassium sorbate	
		Mean	Range	Mean	Range
Strained yoghurt	35	112.1	nd-425.3	50.3	nd-612.4
Kasar cheese	20	280.4	nd-814.7	49.7	nd-688.1
Tulum cheese	20	187.5	nd-754.1	45.6	nd-911.7
Ayran	15	166.1	nd-698.8	-	nd

n: number of analyzed sample, nd: not detected

Mean values were calculated assuming nd as zero

Kucukcetin et al. (14) found that 28 of 45 yoghurt samples contained concentrations between 37.0-233.9 mg of sodium benzoate/kg, and 7 of 15 white pickled cheese samples contained concentrations between 42.4-441.9 mg of sodium benzoate/kg. They also observed that 3 of 45 yoghurt samples contained concentrations between 28.9-577.9 mg of potassium sorbate /kg, and only one of 15 white pickled cheese samples contained potassium sorbate with a mean value of 946.5 mg/kg. In comparison with data of Wang et al. (15), who had not detected benzoic acid in the yoghurt samples and found a mean content of 157.7 mg/kg sorbic acid in the samples. Tfouni and Toledo (8) observed that yoghurt and cheese samples contained sodium benzoate in the range of 126-213 mg/kg and in the range of 376-1371 mg/kg, respectively.

During the nitrate and nitrite analysis, special attention was paid to reducing capacity of the cadmium column and to adherence to the method protocol. The reducing capacity of the column was more than 98%. The method was continuously monitored by standard addition of nitrites and nitrates. Recoveries have been found to be between the acceptable limits of 98 and 101%.

The nitrate and nitrite contents of the samples are given in Table 2. Eight (23%) of the 35 samples of strained yoghurt had no detectable amounts of nitrates, 12 (34%) samples had nitrates between 3 and 15 mg/kg, and 15 (43%) samples had nitrates between 20 and 50 mg/kg. Seven (35%) of the 20 samples of Kashar cheeses had no detectable amounts of nitrates, 7 (35%) samples had nitrates between 4 and 20 mg/kg, and 6 (30%) samples had nitrates 22 and 50 mg/kg. Four (20%) of the 20 samples of Tulum cheeses had no detectable amounts of nitrates, 11 (55%) samples had nitrate between 2 and 20 mg/kg, and 5 (25%) samples had nitrates 22 and 50 mg/kg. Five (33%) of the 15 samples of ayran had no detectable amounts of nitrates, 9 (60%)

samples had nitrate between 4 and 20 mg/kg, and only 1 (7%) sample had nitrate (21.1 mg/kg) above 20 mg/kg. The values of nitrates that have been found were fairly low. All values for nitrates of cheese samples were lower than the maximum legally allowable limit.

Eight (23%) of the 35 samples of strained yoghurt, 14 (70%) of the 20 samples of Kasher cheese, 7 (35%) of the 20 samples of Tulum cheese and 9 (60%) of the 15 samples of ayran had no detectable amounts of nitrites. The detectable nitrite content in the rest of the samples was below 5 mg/kg.

Our results are in agreement with previous studies (16, 17). Daglioglu and Gunduz (16) found that 9 of 25 cheese samples had nitrates with a mean value of 10.8 mg/kg. All the analyzed samples of cheeses had no detectable amounts of nitrite. Dogan et al. (17) found that 46 of 60 cheese samples had nitrates between 0.1 and 21.9 mg/kg and 53 of 60 cheese samples had nitrites between 0.01 and 1.4 mg/kg.

Table 2. Concentrations (mg/kg) of nitrate and nitrite in strained yoghurt, kasar cheese, tulum cheese and ayran

Product	n	Sodium benzoate		Potassium sorbate	
		Mean	Range	Mean	Range
Strained yoghurt	35	16.6	nd-40.1	2.1	nd-4.8
Kasar cheese	20	13.4	nd-47.8	1.1	nd-4.2
Tulum cheese	20	11.3	nd-44.0	1.9	nd-4.9
Ayran	15	6.6	nd-21.1	0.6	nd-2.2

n: number of analyzed sample, nd: not detected

Mean values were calculated assuming nd as zero

DISCUSSION

All values for nitrates and nitrites that have been found were fairly low. The nitrate content of the examined samples could be attributed to external sources such as contamination by nitrate fertilizers, forage, and agricultural drinking water. But the general detections of sodium benzoate and potassium sorbate in most of the samples, lead to the conclusion that they are commonly used as preservatives in most of strained yoghurt, kasar cheese, tulum cheese and ayran available in the retail market. The usage of sodium benzoate in all dairy products and of potassium sorbate in strained yoghurt and ayran is prohibited by the legislation in force in Turkey. The detections of sodium benzoate and potassium sorbate in these products made by some local manufacturers indicate an application without knowing Turkish food legislation. To ensure compliance with national standards, more cooperation among producers, processors and the regional administration is essential.

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