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SPECTROPHOTOMETRIC DETERMINATION OF METHANOL AND FORMALDEHYDE IN VINEGAR SAMPLES

SİRKE ÖRNEKLERİNDE METANOL VE FORMALDEHİT 'İN SPEKTROFOTOMETRİK TAYİNİ

NEJAT ALTINİĞNE* ŞENİZ ÇELİKÖZ

Ege University, Faculty of Pharmacy, Department of Food Analysis 35100 Bornova-İzmir Turkey

Twenty samples of vinegar were analyzed spectrophotometrically for their methanol and formaldehyde contents, for the evaluation of the quality of the samples, total acid and alcohol contents were analyzed and sediment occurrence was determined by Acetyl Methyl Carbinol (AMC) testing. Although 8 samples were estimated as artificial vinegar, the values measured were at normal range in all samples. Methanol and formaldehyde contents were found low enough to not produce any risk for human health. The methods applied for the determination of methanol and formaldehyde contents in vinegar were rapid, simple, inexpensive and gave results with high accuracy.

Yirmi sirke örneğinin metanol ve formaldehid içeriği spektrofotometrik olarak analiz edildi. Örneklerin kalite tayini için total asit ve alkol içeriği analiz edildi. Örneklarin kalite tayini için total asit ve alkol içeriği analiz edildi ve çökelti oluşumu Asetil Metil Karbinol (AMK) testi ile saptandı. 8 örneğin yapay sirke olduğunun belirlenmesine karşın, tüm örneklerde ölçülen değerler normal sınırlardaydı. Metanol ve formaldehit içeriği insan sağlığı açısından risk oluşturmayacak kadar düşük düzeyde bulundu. Sirkede metanol ve formaldehid analizi için uygulanan yöntemler hızlı, basit ve ucuzdur ve yüksek doğrulukta sonuçlar elde edlimiştir.

Keywords: *Vinegar; Formaldehyde; Methanol; Spectrophotometric analysis*

Anahtar kelimeler:*Sirke; Formaldehit; Metanol; Spektrofotometrik analiz*

Introduction

Vinegar, a widely consumed product in Turkey, is produced exclusively from several fruits including grape, and also from wine, spirit, cider, etc. by fermentation (1-4). Vinegar is also obtained artificially by dilution of synthetic acetic acid, which is allowed in some countries, but not in Turkey (5,6). The essential composition of natural vinegar and quality criteria were defined by food product regulations (6,7). However, several products with unknown origin and those produced artificially are sold illegally in Turkey as well as in other count-ries. These products are not prepared in accordance with the general regulations as well as general principles for food hygiene. Subsequently, they may contain some impurities in addition to qualitative/quantitative differences in the composition, and they possibly cause hazard to human health (1,8,9). Therefore, the analysis of vinegar products in regard to their ingredients and the quality, and also to improve simple methods for routine measurements are getting more important for human health.

Methanol and formaldehyde are formed naturally in limited amounts during the production of vinegar from biological origin (10-12). Both substances are toxic to human health in a concentration-dependent manner (13). It has been demonstrated that methanol levels formed naturally in orange juice and wine may increase to toxic levels and pose a hazard to health (14 - 17). There are no spesific regulations for methanol and formaldehyde levels in vinegar products and there is no study on this subject in the literature.

* Correspondence

Therefore with regard to hazards of these subtances to human health, we aimed to analyze methanol and formaldehyde contents of vinegar samples in the present study. For this purpose, we used a simple and suitable spectrophotometric method for routine analysis of these substances in vinegar.

Materials and Method

All chemicals used in the study were of analytical grade. A Shimadzu Model UV-1208 type UV-visible spectrophotometer (Japan) was used. Other instruments were Hanna Instrument pH-meter (HI 9321) with HI 1131 type electrode (Portugal), magnetic stirrer IKAMAG-RH (Germany) and several glasware, etc.

Twenty vinegar samples, each representing different commercial products, were collected from markets in İzmir. The analysis of total acid and alcohol contents, and application of AMC testing were based on the methods defined by Turkish Standards Institute (TSI) (6).

For determination of formaldehyde content, we applied the method used for formaldehyde analysis in wine by Diemar et al., and modified the same method for methanol analysis in vinegar samples (18).

For formaldehyde analysis, 50 ml sample was distilled and 40 ml distillate collected. 1 ml of distillate was transferred into a tube with glass cover. 1 ml sodium salt of chromotropic acid (500 mg/100 ml), and 8 ml 81 % sulphuric acid added respectively. The mixture was kept at 60°C in water-bath for 20 min. After cooling to room temperature, the absorbance of the solution with blue-violet colour was read at 570 nm against the blank. Formaldehyde concentrations were calculated by a calibration curve obtained by using 8 different concentrations of formaldehyde standart solution in distilled water, ranging from 0.0 to 42.2 µg/ml (r=0.99). For the recovery rate estimation, 16.7 µg/ml formaldehyde solution was added to 4 different samples; the test was repeated 5 times for each sample. The recovery rate was 92.81±0.40% (mean±standard eror). Method precision was acceptable because coefficient of variation of assays was found as ±5%. For methanol analysis, 50 ml sample was steam distilled following the neutralization by 30% of sodium hydroxide, and 40 ml distillate collected. 1 ml of distillate was transferred into a tube with glass cover and 2 ml $KMnO_4$ solution (3% in distilled water, including H_3PO_4) was added. The mixture was kept on an ice-bath for 30 min and sodium bisulphide (5%) was added dropwise until the mixture was decolorized. Following the addition of 1 ml sodium salt of chromotropic acid and 8 ml concentrated H_2SO_4, respectively, the mixture was heated at 65°C for 15 min. After cooling at room temparature (20±1°C), the absorbances were read at 570 nm against the blank. Methanol concentrations were calculated by a calibration curve obtained by using 8 different concentrations of methanol standart solution in distilled water, ranging from 0.0 to 316.0 µg/ml (r=0.98). For the recovery rate estimation, 32.66 µg/ml methanol solution was added to 4 different samples and the test was repeated 5 times for each sample. The recovery rate was 94.54±0.41% (mean±standard error). Coefficient of variation of the assays was found as ±5%.

Results and Discussion

The results are presented in the table. AMC testing results were negative for 8 samples indicating the products originated from synthetic acetic acid. Alcohol and total acid contents were at the normal range (5,6). Therefore, we can conclude that the commercial vinegar samples analyzed in this study were in accordance with the statement of TSI and regulations of food products, but 8 of the samples were estimated as artificial products (5-7).

We applied the spectrophotometric method demonstrated by Diemar et al. for formaldehyde determination and modified the method for methanol quantification. Preceeding these methods, we also tested other spectrophotometric mehods demonstrated by Rebelein (10) and Uino et al. (19); however, in our case, these methods did not give satisfactory results for quantitative analysis of related substances in vinegar. The methods used in this study allowed us to obtain reliable quantification of formaldehyde and

Table: The results of analysis of vinegar samples

Sample no	AMC*	Alcohol% (v/v)	Total acid** (g/100 ml)	Formaldehyde (mg/l)	Methanol (mg/l)
1	(+)	0.34	3.6	11.14	35.66
2	(+)	0.67	3.6	16.19	45.90
3	(+)	0.55	3.7	3.66	56.31
4	(-)	0.67	3.3	1.92	15.18
5	(+)	0.94	4.1	18.45	160.82
6	(+)	0.61	3.7	25.24	72.38
7	(+)	0.87	3.9	25.59	189.60
8	(-)	0.34	3.8	22.11	9.36
9	(-)	0.41	3.6	32.21	8.30
10	(+)	0.26	3.8	21.76	66.73
11	(-)	0.14	3.3	53.45	2.82
12	(+)	0.55	3.8	10.45	73.97
13	(-)	0.14	3.4	9.23	20.30
14	(-)	0.14	3.4	5.57	4.41
15	(+)	0.14	3.4	5.22	135.23
16	(+)	0.67	3.5	2.96	67.97
17	(+)	0.94	4.0	6.62	280.16
18	(+)	0.81	4.1	8.70	203.37
19	(-)	0.21	3.6	19.50	5.83
20	(-)	0.14	3.8	8.88	11.65

*Acetyl methyl carbinol
** Calculated as acetic acid

methanol in vinegar samples as recovery rates were 92.81±0.40 % and 94.54± 0.41 % respectivey and coeffici-ents of variation of the assays were in the acceptable range(±5%). The detection limit of both methods was 0.8 ppm.

As shown in Table 1, formaldehyde and methanol levels in vinegar samples were low. These substances are present in vinegar naturally resulting from degredation of pectin (10,14). No study related to the levels of methanol and formaldehyde in vinegar was encountered. Because the amounts of these substances in vinegar are minimal, they may be negletted. Reported literature levels for methanol ranged from 4 to 420 mg/kg in orange juice and from 0.014 to 0.420 ml per litre of wine (14-420 ppm) (14,17) Maximum intake of methanol allowed by the Department of Health is 600 mg per day for a 60 kg adult (14). Methanol levels demonstrated above were considered as nontoxic for human health, in regard to the estimated maximum intake of methanol by extreme consumers of drinks, and that the assumptions based on the literature (14). In another study carried on with tea-bag tissue, maximum formaldehyde levels were 0.240 mg/kg of tea and considered as nontoxic (20). In this study, methanol and formaldehyde contents of vinegar samples were lower than the levels produced naturally in vinegars, and considered as nontoxic for human health with regard to the literature (11, 14,17,20).

In this study, the spectrophotometric methods applied for formaldehyde and methanol analysis were simple, rapid and

inexpensive. Further they gave results with high accuracy. These methods can be used successfully in routine analysis of methanol and fomaldehyde in vinegar samples.

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