THE STUDY OF THE PHTHALTES REMOVING PROCESS FROM ALCOHOLIC PRODUCTS

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Abstract: In the laboratory of National Center for Quality Testing of the Alcoholic Beverages there were investigated phthalates sorption processes in the most widely applicable sorbents in alcoholic products. Among them – activated carbon, bentonite, kieselguhr. Also the sorption capacity and a number of other synthetic drugs were investigated. In addition to determining the level of phthalates sorption, the impact on other components of a complex matrix of alcoholic products was defined. The conclusions on the potential use of adsorbents for removal of phthalates range of products were done.
Keywords: Phthalates, alcoholic beverages, sorbents, gas-chromatography mass-spectrometry.

Introduction

With the appearance of problems of phthalates in alcoholic products, it was necessary to remove these contaminants. Studies of sorption processes - degradation of phthalic acid esters are not new, and most of them study the impact of natural microorganisms in the soil [1,2], water (sewage sludge) [3,4], also some studies of removal from the aqueous phase onto activated carbon [5], in addition photocatalytic degradation of phthalate in aqueous TiO_2 suspension under UV illumination has been investigated by Baoling Yuan *et all* [6]. Food stuff and alcoholic beverages in particular in this sense, were ignored. In the laboratory of National Center for Quality Testing of the Alcoholic Beverages some investigations in the field of processes of natural removing phthalates from alcoholic products in different stages of productions were done. Several sorbents, which commonly used in wineries and distillery, were studied. Among them: activated carbon, bentonite and kieselguhr. Additionally, few specimens were examined as sorbents, such as silicagel, synthetic adsorbent, ion exchange resin, also yeasts influence on phthalates content in fermenting mash were determined.

Experimental

Material and methods

Investigations were done on the base of wines: white - dry& sweet, red - dry& sweet (4 types), hydro alcoholic solutions (40% v/v) and eau de vie aged.

For samples contamination were used solvents of phthalates prepared from individual substances – DMP (dimethylphthalate 99.6%), DEP (diethylphthalate 99.6%), DBP (dibutylphthalate 99.8%), DEHP (Bis(2-ethylhexyl)phthalate 99.7%), DOP (dioctylphthalate 99.7%), DDP (didecylphthalate 99.8%) PESTANAL from SIGMA-ALDRICH.

As a sorbents used Bentonite (CLARIT PLV-45), activated carbon (FA SIHA), silicagel L 40/100µ (for column chromatography), kizelgur (BECOGUR-3500), furthermore three types of synthetic polymers were tested, - anion exchange resin RELITE

RAM1, synthetic adsorbent RELITE SP 411 (adsorbent based on styrene and DVB copolymer) and cation exchange resin FIBAN K-1.

Instruments

GCMS-QP-2010S (IS) (SHIMADZU) with a COMBI PAL autosampler (CTC ANALYTICS) with fused silica column RESTEK - Rtx-5MS (30m/0.25mm/0.25µm 5% diphenyl / 95% dimethylpolisiloxane phase).

Capillary Electrophoresis System – CAPEL – 105M (LUMEX).

Alcolyzer Wine (ANTON PAAR) plus density meter DMA-4500.

Gas chromatography–mass spectrometry

Measuring the concentration of phthalates in wine and base-wine was based on its elimination by chloroform extraction, chromatographic separation on a capillary column, identify by retention time and mass spectrum, and quantify with the characteristic ions m/z. Measuring the concentration of phthalates in alcoholic beverages such as vodka, brandy, cognac alcohol, rectified ethyl alcohol was based on chromatographic separation of the sample on a capillary column using aldrin with a purity above 99.3% and supplied by SUPELCO as an internal standard, the identification was made by retention times and mass spectrum, quantification – of characteristic ions m/z for phthalates and for aldrin respectively.

Results and Discussion

Activity of sorbents described below in relation to phthalates was studied on the different matrices. Firstly, sorption capacity was investigated for six phthalates in the base of hydro-alcoholic solution (40% v/v). With this purpose all types of sorbents were prepared in accordance with relevant procedures – INTERNATOINAL ŒNOLOGICAL CODEX – Bentonites COEI-1-BENTON: 2003, diatomite (kieselguhr) COEI-1-DIATOM: 2002, Oenological Carbon COEI-1-CHARBO: 2007. Three synthetic specimens were prepared conform manufacturer's recommendations. Silicagel has been washed with alcohol (not contain phthalates). Batch of phthalates solutions with sorbent was obtain. In this series ratio of phthalate to sorbent (by weight) were approx. 1:5000, 1:10000, 1:50000, 1:100000, 1:500000. Concentrations of phthalates in the solutions were equimolar to each other, and ranged from $0.05 \cdot 10^{-6}$ to $5 \cdot 10^{-6}$ $molL^{-1}$. Sorption mixture was agitated for a pre-determined time period (150min) using orbital shaker (BIOSAN PSU-20i), agitation - 120rpm, temperature - 25^0C. The residual phthalate concentration in the hydro-alcoholic phase was analyzed by gas chromatograph with mass spectrometer. Sorption capacity of different natural and synthetic sorbents is shown in tab.1. Capacities are given in ppm (mg of phthalates in kg of sorbent).

Tab.1. *Sorption capacity of different natural and synthetic sorbents*

Sorbent	DMP, ppm	DEP, ppm	DBP, ppm	DEHP, ppm	DOP, ppm	DDP, ppm
Carbon	0	0-8,5	4,85-180,0	16,0-675,0	31,5-2060,0	50,7-3670,0
Bentonite	0,2-3,0	0,2 - 4,0	0,25 - 4,7	2,25-12,5	4,9 - 24,4	6,6 - 41,2
Kiselgur	0 - 0,1	0 - 0,3	1,55 - 35,0	2,2 - 41,5	3,6 - 44,0	10,0 - 62,5
Silicagel	0 - 0,8	0 - 1,1	0 - 3,4	0 - 11,8	0,5 - 31,0	1,1 - 32,1
Fiban K-1	0	0	0,5 - 10,0	2,0 - 70,0	17,2 - 290,0	30,9 - 2910,0
RAM 1	0,9 - 11,0	0,95 - 45,0	1,6 - 85,0	5,7 - 495,0	16,1 - 810,0	37,8 - 9500,0
SP 411	2,4 - 70,0	3,0 - 13,0	3,2 - 55,0	14,7 - 975,0	30,0 - 2460	59,0 - 10100

The most of the capacities values are given in the form of intervals, because sorption depends on the concentrations of phthalates and phthalates content in the solutions – for one or all six together in the same solution. As it can be seen from the table, the most natural specimens do not have a high sorption activity with the exception of carbon. The highest activity was showed by synthetic materials. All examined sorbents showed a common tendency. Sorption capacity of each sorbent is proportional to molecular weight of phthalate isomers. Perhaps this is due to the labiality of the phthalate's molecules. This picture takes place in the case of hydro-alcoholic base only. With complication of this alcoholic matrix – to make it more closer to eau-de-vie or brendy by reproduction the mineral composition (basic cations) according to the Skourikhin I. M. [7], the picture changes significantly. For this purpose hydro-alcoholic solutions with phthalates (concentrations above) were prepared with addition of salts. Concentrations of basic cations (Na, K, Mg, Cu, Fe, Pb) were created by corresponding salts ($NaKC_4H_4O_6{\cdot}4H_2O$, $MgSO_4{\cdot}7H_2O$, $CuCl_2{\cdot}2H_2O$, $FeSO_4{\cdot}7H_2O$, $Pb(CH_3COO)_2{\cdot}3H_2O$). As a result, for a twenty-four hours in static conditions, T=25^{0}C, the sorption of DBP and DEHP decreased on 100% with carbon, kiselgur and bentonite. The following proportions sorbent / wine distillate were used – 0.25g/25ml, 0.50g/25ml.

The action of sorbents was subjected to real aged wines distillates in the similar conditions and with the same proportions. The degree of carbon's and bentonite's exposure on the aged wines distillates were established by capillary electrophoresis. The results of studies of sinapaldehyde, coniferaldehyde, syringaldehyde and vanillin are given in the tab.2.

Tab.2. *Effect of sorbents on the content of aromatic aldehydes, mg L^{-1}.*

		Sinapaldehyde	Coniferaldehyde	Syringaldehyde	Vanillin
Carbon	control	1,76	1,60	3,20	1,48
	0,25g/25ml	1,40	1,14	2,80	1,26
	0,50g/25ml	0,84	0,70	2,60	1,14
Bentonite	control	1,66	1,54	2,80	1,34
	0,25g/25ml	1,72	1,54	2,80	1,38
	0,50g/25ml	1,68	1,58	2,80	1,44

As a result, concentrations of DBP and DEHP were down on 3-5%, the most significant impact had a carbon to "heavy" phthalates – DOP and DDP.

By GC and GCMS methods were established that carbon, kiselgur, silicagel and bentonite did not affect the flavor of wine and eau-de-vie, due to the bad sorption of light ethers (esters) and aldehydes as well as the fusel alcohols.

Furthermore, the influence of some sorbents on phthalates in wine also was investigated. With this purpose samples of wines with six phthalates were created. Four types of wine were given for the experiment – white dry, white sweet (sugar - 80g L^{-1}), red dry and red sweet (sugar - 160g L^{-1}). Concentrations of phthalates were in the range of 0.01-0.03mg L^{-1}. On the basis of previous studies, the following proportions of the sorbent-wine were taken: bentonite, kizelgur, silicagel – 1/100, carbon – 1/1000. Process of sorption was carried out within 5 days in static conditions, T=25^{0}C. As a result the sorption by bentonite, kizelgur, silicagel and carbon of DMP and DEP were also close to zero. Sorption ability of bentonite, kizelgur and silicagel for DBP was approximately equal to 5-10%. In the case of carbon, despite the fact that carbon is 10 times less, sorption of DBP was 20-25%. DEHP was sorbed on the bentonite, kizelgur and silicagel by 10-15%, on the carbon (1/1000) – 40-50%. DOP and DDP were sorbed on the carbon by 40-50% too. Bentonite and silicagel showed high activity toward DOP and DDP – 70-80%, kizelgur – 40-60%. In general, we can conclude, that difference in the sorption of different types (four) of wines is not significant.

Research on the instrument by ANTON PAAR shows changes of density, total extract and alcohol content of wines in tab.3.

Tab.3. *Effect of sorbents on the density, total extract and alcohol content of wines.*

Bentonite 2g/200ml (1:100)	parameter before treatment/after treatment		
	alc % v/v	density g/l	total extract g/l
white/dry	11,88/11,09	0,9898/0,9909	18,90/18,88
red/dry	11,16/11,01	0,9927/0,9929	24,25/24,22
white/sweet	13,60/13,09	1,0178/1,0182	96,87/96,41
red/sweet	16,44/15,30	1,0448/1,0455	175,72/174,28
Carbon 0,2g/200ml (1:1000)	parameter before treatment/after treatment		
	alc % v/v	density g/l	total extract g/l
white/dry	11,88/11,81	0,9898/0,9897	18,90/18,73
red/dry	11,16/11,14	0,9927/0,9927	24,25/24,06
white/sweet	13,60/13,57	1,0178/1,0175	96,87/96,00
red/sweet	16,44/16,39	1,0448/1,0448	175,72/175,57
Silicagel 2g/200ml (1:100)	parameter before treatment/after treatment		
	alc % v/v	density g/l	total extract g/l
white/dry	11,88/11,50	0,9898/0,9904	18,90/18,81
red/dry	11,16/11,16	0,9927/0,9929	24,25/24,13
white/sweet	13,60/13,32	1,0178/1,0180	96,87/96,57
red/sweet	16,44/15,84	1,0448/1,0459	175,72/175,69
Kizelgur 2g/200ml (1:100)	parameter before treatment/after treatment		
	alc % v/v	density g/l	total extract g/l
white/dry	11,88/11,46	0,9898/0,9904	18,90/18,89
red/dry	11,16/11,16	0,9927/0,9929	24,25/24,17
white/sweet	13,60/13,40	1,0178/1,0178	96,87/96,28
red/sweet	16,44/16,09	1,0448/1,0456	175,72/175,62

Also, in the future, we plan to estimate the change of mineral composition of the wines and aged wines distillates after sorbents treatment.

Conclusions

As a result, it can be concluded that sorbents relatively effective show themselves on a simple matrix. Study of complex organic and inorganic bases, such as wines and real aged wines distillates, shows that besides target reactions with phthalates, there are many competing processes.

Also, it should be noted that in all cases sorption capacity of each sorbent is proportional to molecular weight of phthalate isomers.

In addition, at this point, we can conclude, that the most effective way to get the pure product is to prevent contamination.

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