Arsenite and Arsenate Levels in Wine

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Arsenic is receiving renewed attention because it is released to the atmosphere by coal-fired power plants as well as by smelters and agricultural pesticides. A portion of this arsenic that accumulates on agricultural land may be taken up by plants, animals, and ultimately by man. This study was conducted to establish amounts and chemical forms of arsenic in wines and the changes that occur during fermentation.

Arsenic-containing compounds have been used as fungicides in grape production and may lead to elevated arsenic levels in grapes and wine. In some European countries arsenical sprays are illegal in grape production, and arsenicals are no longer used in California grape production. However, arsenic compounds are widely used in the production of other agricultural products. It has been reported that during wine production most of the arsenic is removed in the fermentation process (AMERINE and CRUESS, 1960).

In this study, 19 samples of domestic table wines were analyzed for several species of arsenic. The samples included 13 varieties of white and red wines. The concentration of arsenite (As^{+3}), arsenate (As^{+5}), methylarsonic acid (MAA) and dimethylarsinic acid (DMAA) were determined using the technique developed by BRAMAN (1973) with modifications (CRECELIUS, 1974). The concentration of total arsenic was also determined on 4 samples by X-ray fluorescence (XRF) (MATHIES, 1974).

The concentration of As^{+3} ranged from less than 1 to 420 ppb, and the concentration of As^{+5} ranged from 1 to 110 ppb (Table 1). The majority of the arsenic was present as As^{+3} (Table 1). Both MAA and DMAA were below the detection limit of 1 ppb in these wine samples. The total arsenic concentration in 4 samples, as determined by XRF, was in good agreement with the chemical speciation technique which was employed in this study (Table 1).

The levels of arsenic in these wines are of particular interest because half of the samples analyzed greatly exceeded the maximum allowable drinking water standard of 50 ppb (U.S. DEPT. HEW, 1962). Also, most of the arsenic in these wines is present as the highly toxic As^{+3} form, which is more toxic to humans than As^{+5} (SCHROEDER and BALASSA, 1966). The United States does not have an arsenic standard for wine, but Great Britain's maximum tolerable arsenic level in wine is 100 ppb, and several other

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countries set the limit at 200 ppb (SCHNEYDER, 1973). A maximum value of 20 ppb was once recommended for the United States (AMERINE and CRUESS, 1960). By comparing the levels of arsenic in these wines with the U.S. drinking water standard of 50 ppb, it is apparent that half of the samples analyzed exceeded this standard (U.S. DEPT. HEW, 1962).

TABLE 1.

Concentration of arsenite (As^{+3}) and arsenate (As^{+5}) in wine. The results are given in parts per billion (ppb); the precision is ± 10%.

Total = sum of As^{+3} and As^{+5}; XRF = X-ray fluorescence.

Sample No.	As^{+3}	As^{+5}	Total	Total by XRF
1	106	24	130	140
duplicate	111	37	148	
2	263	39	302	
3	122	63	185	215
4	420	110	530	
5	267	47	314	294
duplicate	260	39	299	289
6	164	44	208	203
7	139	48	187	
8	40	28	68	
9	260	32	192	
10	22	<1	22	
11	87	35	122	
12	<1	1	1	
13	10	2	12	
14	76	29	105	
15	44	19	63	
16	7	7	14	
17	<1	<1	1	
18	6	4	10	
19	2	1	3	

An investigation of the agricultural practices in the area where the wine grapes were produced was not included in this study. The source of the surprisingly high arsenic levels in some of these wines is apparently from the use of arsenicals in the production of grapes.

The changes in the chemical species of arsenic that occur during the wine fermentation process were examined by adding As^{+3}, As^{+5}, MAA and DMAA to separate aliquots of concord grape juice. Montrachet wine yeast was added to these samples and the arsenic species were determined after 2 weeks, at which time the fermentation activity had stopped. The results shown in Table 2 indicate that the fermentation process reduced approximately 60% of the As^{+5} to the more toxic As^{+3}, but did not methylate As^{+3} and did not demethylate the MAA. A small fraction of the DMAA was converted to MAA. Only a small fraction of the arsenic was lost to residues as a result of the fermentation process.

TABLE 2.

Change in chemical form of arsenic during fermentation of grape juice by wine yeast. The results given in parts per billion (ppb) as arsenic; the precision is ± 10%.

MAA = methylarsonic acid; DMAA = dimethylarsinic acid.

Sample No.	Initial Conc. (ppb)		Final Conc. (ppb) As^{+3}	As^{+5}	MAA	DMAA	Total
1	As^{+3}	200	112	26	<5	<5	138
2	As^{+5}	200	125	33	<5	<5	158
3	MAA	200	<1	<1		<5	130
4	DMAA	200	<1	<1	11	133	144

This study brings to light some very interesting facts regarding the amounts, chemical forms and transformations in arsenic species which are possible during fermentation. The most stable form for arsenic in soils is probably As^{+5}. One would suspect that As^{+5} is the form taken up by plants, and in the case of grapes it is reduced to the more toxic As^{+3} during fermentation. Very little research has been conducted to determine whether significant changes in arsenic speciation occur in other cases during uptake by plants, transfer to animals, or during various types of food processing.

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