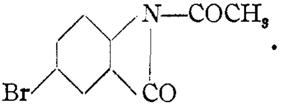
5-*Bromacetanthranil*,  .

—5-Bromacetanthranilic acid was boiled with an excess of acetic anhydride. The crystals which separated on cooling were filtered out, dried, and recrystallized from carbon tetrachloride.

The pure anthranil crystallizes in colorless scales, m. p. 131° (corr.).

The following figures were obtained on analysis: Found: C, 45.04; H, 2.50; N, 6.24 and 6.16; Br, 33.31. Calculated for $C_9H_6O_2NBr$: C, 45.01; H, 2.13; N, 5.83; Br, 33.32.

5-*Bromacetanthranilic Nitrile.*

5-*Bromacetanthranilic Nitrile*, $C_6H_3(CN)(NHCOCH_3)(Br)(1,2,5)$. —Acetanthranilic nitrile (m. p. 132.5° (corr.)) was brominated by suspending it in water and passing in a current of air laden with bromine vapor. Five or six hours were required to complete the bromination. The crude product was filtered out, washed, treated with bone-black, and recrystallized from water. Larger crystals were obtained from carbon tetrachloride. During the bromination the temperature of the liquid must not be permitted to rise above about 30°, or the product may be spoiled.

The pure nitrile forms clear, six-sided prisms, m. p. 158° (corr.); insoluble or difficultly soluble in cold water, carbon disulphide, cold benzene, or cold carbon tetrachloride; moderately soluble in cold dilute alcohol, hot water, cold toluene or hot carbon tetrachloride; easily soluble in 95 per cent. alcohol, hot dilute alcohol, acetone, ethyl acetate, hot benzene, hot toluene, or chloroform.

Bromine found, 33.52; calculated for $C_9H_7ON_2Br$, 33.46.

Columbia University and
Mississippi Agricultural and Mechanical College,
October, 1905.

ON THE OCCURRENCE OF ARSENIC IN WINES.

By H. D. Gibbs and C. C. James.

Received September 25, 1905.

While engaged upon the analysis of 100 samples of California dry, red wines, the frequent occurrence of coal-tar dyes induced us to test for arsenic which is often found in certain dyes. We were surprised to find that arsenic occurred in many samples which were otherwise free from unnatural ingredients. This led to a rather extended investigation of the subject, and in all 329 samples have been examined by various methods for the presence of arsenic compounds. The quantities found were in all cases small, and while in all probability the compounds of the element are not to be met in quantities sufficient to produce toxic effects, we have undertaken this investigation in the attempt to throw some light upon the source of this constituent, as it is undoubtedly an accidental ingredient. It is not beyond the realms of possibility that the source, if not discovered, might give rise to increasing quantities until the limit of tolerance would be reached. This in fact occurred in English beers some years ago when the brewers used glucose prepared with a sulphuric acid which contained considerable quantities of arsenic.

It is recognized that arsenic administered with alcohol[1] may be more toxic than when administered alone, owing to the more rapid assimilation caused by the stimulation of the gastric mucosa. Moreover, the system with continued use, becomes tolerant of large amounts of arsenic, and some individuals, owing to inherent idiosyncrasies, are much more resistant than others to its toxic effects. By employing special methods Gautier[2] has shown that arsenic is a remarkably uniform constituent of animal and vegetable organisms and a widely distributed element, but as we have not employed in this investigation his methods[3] for the estimation of minute quantities we do not consider that all of the arsenic which has been found is an unavoidable constituent of the wines examined.

Opposition to the use of artificial coloring substances in French

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[1] C. H. Tattersall (Report on Arsenical Poisoning, Borough of Salford, Eng.; H. Tappeiner: *Z.*, *Biol.*, **16**, 497 (1881), and "Physiological Chemistry," by A. Gamgee, 438 (1893)), as a result of experiments upon dogs and cats in which he had ligatured the pylorus before injecting into the stomach solutions of various alimentary and poisonous substances, came to the conclusion that the stomach absorbs only very small quantities of bodies which are introduced into it in aqueous solution, while, on the other hand, it appears readily to absorb dilute alcohol and substances dissolved in alcohol. When sulphate of strychnia was injected into the stomach of cats with ligatured pylorus, death from strychnia poisoning ensued in a period varying between one and one-half and three hours, while with unligatured pylorus death occurred from the same dose in eight minutes. If, however, strychnia were dissolved in dilute alcohol and injected into the stomach of a cat, with ligatured pylorus, death occurred in ten minutes.

[2] *Bull. Soc. Chim.* [3], **27**, 843 (1902); [3], **29**, 31 (1903); A. Gautier and P. Clausmann, *C. R.*, **139**, 101 (1904); V. Bordas: *Ibid.*, **139**, 234 (1904).

[3] *Bull. Soc. Chim.*, [3]. **29**, 859; *Ann. Chim. Phys.* [5], **8**, 384; Bertrand: *Bull. Soc. Chim.* [3], **27**, 847 (1902).

wines in 1876 led to the discovery that arsenic might thus be introduced into the wine, and Gautier[1] says that arsenic should always be looked for in wines containing aniline colors. In the same year C. Husson[2] published an article on "The Detection and Estimation of Fuchsine and Arsenic in Wines Which Have Been Colored with Fuchsine." J. Clouet[3] found that caramel, which is frequently used in conjunction with fuchsine, often contains large amounts of arsenic.

The outbreak of arsenical poisoning[4] at Manchester, England, in 1900 was traced to beer in which arsenic was introduced through the glucose. This epidemic led to an extensive consideration of rapid methods for the determination of arsenic, beginning with the Reinsch test and ending with the adoption of the electrolytic method of Thorpe[5] by the Royal Commission on Arsenical Poisoning. We have tried a large number of methods and various combinations and modifications and found none as satisfactory as the Marsh, using zinc and sulphuric acid.

Our investigations began with the analysis of 100 samples of dry red wines.[6] The ash obtained from the quantitative determination of the total solids and ash, by the method of the Association of Official Agricultural chemists,[7] using 50 cc. of wine, was dissolved in dilute sulphuric acid (1 to 3), filtered and introduced into the Marsh generator. By this rather rough method 15 of the 100 samples produced perceptible mirrors which were identified as arsenic by conversion into arsenious oxide tetrahedra. Twelve of these samples seemed to be pure wines, three contained in addition to the arsenic, coal-tar dyes, and one contained benzoic acid. Fourteen of these samples were bottled wines and one was taken from the cask. These results led to a systematic study of methods in order to assure ourselves that the arsenic was not introduced through the reagents or apparatus used, and that all the arsenic present in the wine was obtained in the mirror. The only methods employed were those by which the arsenic was finally obtained in the form of a mirror deposited upon the inner surface of a glass tube by the breaking down of arsine by heat.

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[1] *Bull. Soc. Chim.*, **25**, 483, 530 (1876).

[2] *C. R.*, **83**, 199. Report on Arsenical Poisoning, Borough of Salford, 1900, p. 47.

[3] *Annales d'Hygiène Publique*, 1878, p. 145.

[4] Report of Medical Officer of Health at Manchester, December, 1900.

[5] *J. Chem. Soc.*, **83**, 974 (1903); *J. Soc. Chem. Ind.*, p. 965 (1903).

[6] Bulletin San Francisco Board of Health, March, 1905.

[7] U. S. Dept. Agr., Bureau of Chem., Bull. **65**, 83.

The methods used for the conversion of the arsenic compounds into arsine include the electrolytic method of Thorpe[1] and the Marsh method, using zinc and hydrochloric acid and zinc and dilute sulphuric acid. After carefully testing the reagents for the Marsh method, hydrochloric acid was discarded in favor of sulphuric acid, and Kahlbaum's special granulated zinc was found on the whole to be most satisfactory. Twenty grams of this zinc were placed in the Marsh generator and completely dissolved in sulphuric acid (1 to 3), which required two and one-half hours. These reagents gave no signs of a mirror. The sulphuric acid employed was that manufactured by Baker and Adamson and, later in the investigation, acid manufactured by the Mallinckrodt Chemical Works was used with equal success. This test was repeated with zinc from each different lot employed and with several samples from each lot, with the same result. The action of the acid on the zinc was started with a few drops of a dilute solution of chlorplatinic acid.[2] Copper sulphate[3] and iron alloyed with the zinc have been used for this purpose, but it has been shown[3] that a part of the arsenic is retained in the generator by these reagents.

A Florence flask of about 250 cc. capacity was used as a container for the zinc and sulphuric acid. This was fitted with a two-holed rubber stopper, through one hole of which passed a separatory funnel for introduction of the sulphuric acid and the arsenic solution, the outlet tube passing through the other hole. As rubber will absorb arsine, care was exercised to have the exposed surface of the rubber as small as possible. The same rubber stopper and connections and apparatus were used throughout the investigation, with the exception of the Florence flask, which had to be renewed once. The outlet tube was connected with a 4-inch U-tube arranged so that the issuing gases first passed through a spiral of lead acetate paper and then through granulated calcium chloride, held in place by plugs of absorbent cotton. From the U-tube the gases passed into a Jena glass tube of 0.7 cm. internal and 1.0 cm. external diameter drawn down to a constriction from 10 to 15 cm. long[4] and 2 mm. external diameter.[5] These tubes were cleaned by standing in a mixture of nitric and

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[1] *Loc. cit.*

[2] Gautier: *Ann. Chim. Phys.* [5], 8, 384 (1876).

[3] Parsons and Stewart: This Journal, **24**, 1005 (1902).

[4] G. Bertrand: *Loc. cit.*

[5] W. Thompson: *Chem. News*, **86**, 179 (1902).

chromic acids, after which they were washed with water, alcohol and ether, and dried by aspirating a current of air through them. To decompose the arsine, this Jena glass tube, protected by wire gauze, was heated by two or three Bunsen burners for a space of 10 to 15 cm. before the constriction. The solution containing the arsenic was slowly added to the contents of the generator through the separatory funnel, after the air was completely expelled from the apparatus by allowing the action of the sulphuric acid on the zinc to proceed until the apparatus was full of hydrogen, or by running a rapid current of carbon dioxide through the apparatus before the sulphuric acid was introduced. The latter method seemed preferable as it avoids using up the zinc and the consequent concentration of the solution with salts, which, of necessity, retards the action of the acid on the zinc. If any oxygen is allowed to remain in the apparatus, the mirror will deposit white, probably due to the formation of the arsenious oxide. By this method when the amount of arsenic in the mirror was less than 0.1 mg. the formation of the mirror was practically complete in one hour and often in less time. However, the uniform time of one hour was adopted for each determination. After each determination the apparatus was thoroughly cleaned and a fresh quantity of zinc added.

Another generator used with less success was the electrolytic type described by Thorpe.[1] This method, although it is the official one in England, we discarded for the reason that samples of wine which we found by the Marsh method to contain arsenic failed to show even traces by the electrolytic method. Another disadvantage is that the arsenic must be in the arsenious condition before introduction into the generator.

The preparation of the solution for introduction into the generator offers some difficulty, and many methods were tried. Since the wine is acid in character, it might be supposed that there would be a loss of arsenic by evaporating the sample direct on the water-bath and then ashing the residue, as was done in the case of the first 100 samples. On evaporation, however, the wine loses its acid character and the ash is decidedly alkaline. To avoid the volatilization of the arsenic, several methods for destroying the organic matter were tried.[2] It was found imprac-

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[1] *Loc. cit.*

[2] Report of Royal Comm. on Arsenical Poisoning, *J. Soc. Chem. Ind.*, **23**, 159 (1904).

ticable to make the wine alkaline with sodium carbonate before evaporation, for the residue, on ashing, chars and fuses before a white ash can be obtained. The Chittenden[1] method was used for some time, but was finally discarded for the method finally adopted, as the mirrors obtained were not as heavy, and moreover it required more time and careful attention. The method finally adopted and used in the analysis of 229 samples of wine was that which had been used by Newlands and Ling[2] in determining arsenic in coal. In the case of the wines, 50 cc. are made alkaline with milk of lime, evaporated to dryness on the sand-bath and ignited at a low red heat. The method is very rapid and the condition of the ash is all that could be desired. There is no fusion or swelling and the method is particularly adapted to wines with a high per cent. of sugar. The ash is taken up with dilute sulphuric acid (1 to 3) filtered and the filtrate introduced into the generator.

Quantitative determinations were made by comparison with a set of standard mirrors ranging from 0.01 mg. to 0.1 mg. of metallic arsenic. These were made by adding the required amount of a standard solution of arsenious oxide to 50 cc. of arsenic-free wine and allowing this to run in the generator for one hour. Other mirrors were made by adding the arsenious oxide solution directly to the generator. The tubes were sealed off while the apparatus was still running, thus preserving the mirror in an atmosphere of hydrogen to insure permanency.[3] Little difference was discernible in the standards prepared by these different methods. However, a careful inspection of the mirrors reveals the fact that the 0.02 mg. standards are more than twice as heavy as those made by the introduction of 0.01 mg. of arsenic. The increase is more regular and uniform in the standards above 0.02 mg. We are led to believe that a small amount of arsenic is always retained in the generator. This amount seems to be uniform and uninfluenced by the amount of arsenic present in the solution tested. Perhaps it is retained by the platinum or by small amounts of iron which may be present in the zinc.

Two hundred and fifteen dry red wines, thirteen dry white wines and one sweet wine were tested by this method. Fifty cc. of the sample were employed in most cases but in a number of

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[1] *Am. Chem. J.*, **2**, 235.

[2] Newlands: *J. Soc. Chem. Ind.*, 1901, p. 736; 1904, p. 166.

[3] *Loc. cit.*

instances 300 cc. were used. We consider it a mere coincidence that the white wines and the sweet wine examined gave no mirrors, and it is to be regretted that the press of other work prohibited the examination of more samples. Of the dry, red wines nineteen showed less than 0.01 mg. of arsenic per liter and four gave mirrors showing the presence of larger amounts. Eighteen of these samples were taken from casks and five were bottled wines. We have no knowledge of the date of the bottling. Twenty samples contained arsenic, and no other unnatural substance was found to be present. Five contained arsenic and a coal-tar dye and one contained benzoic acid. The four samples highest in arsenic calculated as the metal are:

(1) 0.05 mg. per liter or one part in 20,000,000.

(2) 0.025 mg. per liter or one part in 40,000,000. Benzoic acid also found.

(3) 0.05 mg. per liter or one part in 20,000,000. Coal-tar dye also found.

(4) 0.013 mg. per liter or one part in 80,000,000.

The largest amount of arsenic found in wines by Gautier and Clausmann[1] is 0.009 mg. per liter, or about 1 part in 111,000,000.

In the examination of some 200 samples, representing about 30,000,000 gallons of wine, C. S. Ash,[2] has found some samples which contain larger amounts.

There are a number of sources to which it might be possible to attribute the introduction of the compounds of arsenic. Some of these, which appear to us to be the most probable, we have investigated in detail.

(1) The cultivation of vines on arsenical soils. It is an established fact that certain amounts of arsenic compounds are tolerated by plants. Stoklasa[3] concludes from experiments with oats that while arsenic can not replace phosphoric acid in the living cell it may increase the development of the organs of assimilation in the plant. Pot experiments[4] to investigate the absorption of arsenic by barley showed that most of the arsenic occurred in the grain. Arsenic was applied at the rate of eleven pounds per acre, but the soil itself was found to contain a greater

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[1] *Loc. cit.*

[2] Mr. Ash, chemist of the California Wine Association, has informed us that the amounts found in the three samples highest in arsenic are, 1 part in 6,000,000, 1 part in 8,000,000, and 1 part in 14,000,000.

[3] *Ann. Agron.*, **23**, 471; Abst. *Expt. Sta. Record*, 9, 1028.

[4] *Expt. Sta. Record*, **14**, 346.

amount. No data concerning grapes are at hand but it is possible that there may be a tendency for the arsenic to accumulate in the fruit. Gautier[1] has found that arsenic occurs in the largest proportions in the external covering of animals, the hair, skin and nails, and it is possible that the skin of the grape may contain larger amounts than the other portions of the plant. If this is true, the fact that larger amounts of arsenic were found in the red than in the white wines[2] would be in part accounted for, as the red wines are fermented with the skins while the white are not.

(2) The spraying of vines with arsenical insecticides, a practice which we are informed is rarely if ever practiced in California, would be a very probable source, especially in regions where there is little or no rainfall to wash away the arsenic compounds during the season in which the grapes are gathered.[3] A. M. Peter[4] reports that appreciable quantities of both copper and arsenic were found in tobacco which had been sprayed with Paris green. The practice of spreading upon the ground arsenical mixtures[5] for the purpose of poisoning grasshoppers and other insects is quite general in some localities.

(3) The use of sulphuric acid in cleaning vats used in the

[1] *Loc. cit.*

[2] Mr. Ash has also observed that the red wines show the larger amounts of arsenic.

[3] *Ann. Rep. State Vit. Comm.* (Calif.), 1887, 82. "Most of the enemies of the vine feed directly upon the foliage—the grasshopper, rabbits, squirrels, army worms, or sphynx-moth worm, beetles, scribe, false chinch bug, cut worms, etc. * * * The old—yes, the oldest remedy—Paris green or London purple, known to be destructive generally, has been brought into requisition. Extensive experiments have this year been conducted * * * to prove that a 'solution' of Paris green or London purple—one pound to one hundred and sixty gallons of water—may be used to spray the foliage of the vine, while the grapes are small, with perfect safety to the consumer of the grapes, wine, or raisins produced therefrom. The efficacy of the remedy as a destroyer, is not questioned; but to determine whether, in California where the summer rains do not fall, a condition dissimilar to that found in sections where the remedy is known—I say whether here, it could be used with the same guarantee of safety or not, seemed to me a question important enough to merit a trial. It is my pleasure to announce a perfect success; the products, grapes and wine, were carefully examined by Professor Rising, state analyst, and proved innocuous."

[4] *Ky. Sta. Rep.*, 1893, p. 14.

[5] W. B. Rising: *Loc. cit.* "As a final test, I myself picked in spots where the arsenic had been used most freely, from thirty to forty pounds of grapes in each of the different vineyards. These were examined for arsenic. In none did I obtain more than the faintest trace of this substance, an amount absolutely inappreciable, and too small to have any perceptible action upon the human body." "In this examination of the grapes they were carefully and repeatedly washed with dilute solution of caustic potash, and finally with pure water. The wash-water and alkali were evaporated to a small volume, and then tested by Marsh's apparatus for the presence of arsenic." "A few words of caution should be added to what I have said in regard to the use of this deadly poison. It is a poison, and this must always be kept in mind. It (referring to arsenic, mixed with bran, middlings and syrup, made into a stiff paste and then set upon the ground for the purpose of killing grasshoppers) should be gathered up and not left upon the land."

process of fermentation and casks used for storing and shipping. Sulphuric acid in its crude form invariably contains arsenic, and its use in cleaning vats, tanks, barrels and other wooden vessels may easily introduce small quantities of arsenic.

(4) The use of any substance in the manufacture of which sulphuric acid has been employed. This will include some coal-tar dyes, some preservatives and glucose. Glucose has in the past been a very notable source of arsenic and arsenical poisoning. No data are at hand concerning the extent of its use in the wine industry. Moreover, since the experience of the brewers in England, the glucose manufacturers are very careful to avoid arsenical compounds in their process. Our experience would lead us to believe that little or no arsenic is introduced by the use of coal-tar dyes and the common preservatives, except sulphur dioxide, for many of the wines which were found to be artificially colored and preserved failed to show any traces of arsenic.

(5) The use of sulphur in sulphuring casks and wines. T. L. Phipson[1] says that some samples of Naples sulphur contain a notable amount of arsenic and that some Silician sulphur is quite exempt. Japanese and French sulphurs are found in large quantities upon this market, the former in predominating amounts. The samples obtained were analyzed in two different ways: first by oxidation with fuming nitric acid, heating with sulphuric acid to remove the nitric acid and introducing the resulting solution into the Marsh apparatus; second by oxidation in a current of oxygen. For this purpose a hard glass tube was drawn down to a small size and bent to a right angle at the beginning of the constriction, so that it could be introduced into an absorption bottle, the point dipping below the water which was used to absorb the gases. The sulphur was introduced into the tube in a porcelain boat and heated gently in the current of oxygen until the combustion started, after which no heating was required. After the combustion was complete the boat and tube were washed with a dilute solution of sodium hydroxide which was added to the contents of the absorbing bottle. Aliquot parts of this solution were made acid and introduced into the Marsh apparatus after the sulphur dioxide was removed either by boiling or by oxidation with iodine solution. The reagents used were tested by a sufficient number of blank determinations. The two methods gave results which agreed in a satisfactory manner.

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[1] *Chem. News*, 83, 61 (1901).

Results.—Flowers of sulphur, Japanese. One gram, oxidized by means of fuming nitric acid, gave a mirror of 0.2 mg. One part arsenic in 5,000 of sulphur.

Japanese Sulphur.—1.9162 grams burned in a current of oxygen, the resulting solution made up to 300 cc., and 50 cc. portions introduced into the Marsh apparatus, gave 0.045 mg. mirrors. One part arsenic in about 7,000 parts of sulphur. One gram, oxidized with fuming nitric acid, the whole of the resulting solution being introduced into the Marsh apparatus, gave a mirror so heavy that it could not be accurately estimated quantitatively by comparison with our set of standards. A fairly close agreement, however, was apparent.

French Sulphur.—1.5586 grams burned in oxygen, the resulting solution made up to 250 cc. and 50 cc. portions introduced into the Marsh apparatus, gave mirrors of 0.01 mg. One part arsenic in about 30,000 parts of sulphur.

Three other samples analyzed showed smaller amounts of arsenic, one sample in particular showing merely traces.

These sulphurs are made into candles and burned in casks before wine is introduced in order to thoroughly disinfect the casks, one-half to one candle (containing about 30 grams of sulphur) being used to a cask of 62 gallons. After the sulphur is burned the cask is sometimes rinsed. In sulphuring the wines, in order to stop the fermentation, the sulphur candles are burned over the wine which is contained in a vessel only partially filled. Much of the sulphur dioxide escapes and is not absorbed by the wine but it is possible that all or nearly all of the arsenic present in the sulphur, the arsenious oxide being less volatile, will pass into the wine. It is difficult to estimate the amount of arsenic which may be introduced into the wine by this process. On the basis of four sulphur candles containing 30 grams of sulphur each and arsenic in the largest proportion (which we found namely one part in 5,000) being used for 500 gallons of wine, there would be thus introduced into the wine arsenic in the proportion of about 0.01 mg. per liter. There is no doubt that these figures are not excessive for some wines and in the case of white wines the amount of arsenic thus introduced may be double or treble this amount. Some of the arsenic which we have found present in the wine can thus be accounted for; however, red wines are rarely, if ever, sulphured and one would naturally suppose that more arsenic would be introduced in the process of sulphuring the wine than in sulphuring the cask and other receptacles.

(6) The use of clarifying agents (such as isinglass, gelatine and compounds of casein with soda) which contained arsenic was found[1] to introduce some arsenic into beer, and it is possible that some of the arsenic in wines may be traced to the same source. We have made no tests upon any of these substances.

(7) Yeast which has come in contact with arsenical solutions will take up arsenic and carry contamination to solutions in which it may afterwards be placed.[2]

(8) The glass of bottles in which wine is aged and shipped might be a source of some of the arsenic. Large quantities of arsenious oxide are used in the glass industry,[3] and this fact has suggested the possibility of the introduction of some arsenic into wine which has acted upon glass on long standing in the bottles.[4] Two bottles of the style in common use, one clear glass and one very dark, were tested for arsenic by several methods. The bottles were broken into small pieces, sampled, crushed quite fine, again sampled and ground in an agate mortar to an impalpable powder. One-gram samples were fused in platinum crucibles with fusing mixtures composed of sodium carbonate and potassium nitrate, sodium carbonate and potassium carbonate, the fused mass dissolved in sulphuric acid (1 : 3) and introduced into the Marsh apparatus. No traces of arsenic could be obtained from the dark glass, and only the very slightest traces from the clear glass. Repeated analyses gave the same result. Even though the entire amount of arsenic was not obtained in the mirror by this method it is evident that, as a source of arsenic in the bottled wines, the glass is not very promising.

(9) Lead shot used in cleaning bottles may account for the introduction of small quantities of arsenic. The practice of using

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[1] *Loc. cit.*

[2] Report beer, brewing and other materials, 1900 and 1901, Manchester, Eng., by S Delepine.

[3] W. Fresenius : *J. Soc. Chem. Ind.*, 1884. p. 263.

[4] Hovestadt : *Jena Glass. Trans.*, 1902, p. 412. "It is true that the substance put into the mixture (glass) is As_2O_3, but in all Jena glass oxidizing materials (nitrates) are added. These convert the lower oxide into the higher during melting, and in the glass as finally obtained the As_2O_5 is combined with alkali. Dr. Schott adds that, in many commercial glasses, such as plate and sheet glasses, As_2O_3 is employed without the addition of oxidizing materials, so that no As_2O_5 can be formed, but he adds that, in his opinion, no arsenic then remains in the glass—it is driven off in vapour and exercises no influence."

second-hand bottles is quite prevalent in the wine industry. These bottles are almost invariably cleaned by the use of lead shot. The peculiar shape of the common wine bottle with its hollow bottom, forms an ideal receptacle for the lodgement of shot, the dark glass completely masking their presence. The lead,[1] which invariably contains arsenic, will in time go into solution in the wine and thus introduce some arsenic. The largest arsenic mirrors which we have obtained were from the first lot of 100 samples almost all of which were bottled wines.[2] Some of these samples had undoubtedly been in the bottles for a number of years; one in particular, which gave an excellent mirror, bore an internal revenue stamp of the series of 1898. It is to be regretted that quantitative measurements of these mirrors were not made, the reason being that a set of standards was not then completed, and the mirrors were destroyed on further tests to prove the presence of arsenic. However, it is impossible to account in this way for more than a part of the arsenic found, for nineteen of the samples which were found to contain arsenic were taken directly from wooden vessels and remained in bottles especially cleaned under our direction, only a short time pending analysis.

(10) The metal pipes and pumps used in conveying the wines, and the filters may be the source of some very small quantities.

SUMMARY AND CONCLUSIONS.

(1) We find that arsenic, in small quantities, occurs as an accidental ingredient of some wines, and we have undertaken this investigation for the purpose of locating the source for the benefit of the wine industry. We are confident that as soon as the origin is discovered this ingredient will practically disappear as a menace.

(2) Total number of samples examined, 329; number in which arsenic was found, 38.

Of the samples containing arsenic, nineteen were bottled wines and nineteen were taken from the cask.

(3) The largest amounts found and measured quantitatively

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[1] Lead was not found in any of the wines. However, if present at any time in the wine, it may have been thrown out of the alcoholic solution as lead sulphate.

[2] It has been stated to us, in explanation of the occurrence of the largest amounts of arsenic in the older wines, that the use of arsenical sprays was much more common a few years ago than at present.

are one part in 20,000,000.[1] The limit of tolerance set by the British Commission on Arsenical Poisoning for beer is 0.01 grain per gallon, about one part in 7,000,000. This limit as applied to wine would undoubtedly be considered too exacting, for wine is usually consumed in much less quantities than beer.

(4) In all probability arsenic does not occur in quantities sufficient to ever produce toxic effects; however, much of that found can undoubtedly be excluded by care upon the part of those engaged in the wine industry.

(5) The arsenic which is present in some samples of wine can not in our opinion be attributed to one source.

(6) The most probable sources of the major part of that found are, arsenical sprays when used upon the vines, sulphur burned for the purpose of sulphuring the wines and receptacles, and perhaps to some extent the lead shot used in cleaning the bottles.

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[1] Subsequent analyses have revealed the presence of larger amounts of arsenic than any previous investigations of wines. Nine samples of dry, white California wines, selected from a winery which furnished us with a sample of sulphur containing arsenic in the proportion of 1 part in 5,000, gave the following results :

		Mgs. SO_2 per liter.	Arsenic, 1 part in
1.	Hock	126	25,000,000
2.	Sauterne	120	25,000,000
3.	White wine blend	7	trace
4.	Johannisberger	206	10,000,000
5.	Riesling	42	trace
6.	Sauterne	181	trace
7.	Riesling	79	15,000,000
8.	Hock	51	5,000,000
9.	White wine blend	77	10,000,000

It is not certain that all of these wines were treated with the same kind of sulphur. Fourteen samples of wines found upon the eastern markets and of eastern manufacture, gave varying amounts of arsenic, one sample in particular containing the largest amount yet discovered.

1.	Sherry	Contained salicylic acid.	trace
2.	Ives seedling		no mirror
3.	Catawba		trace
4.	Delaware		20,000,000
5.	Virginia seedling	Contained coal-tar dye and salicylic acid.	20,000,000
6.	Sweet catawba		15,000,000
7.	Catawba		10,000,000
8.	Port		10,000,000
9.	Catawba	Contained salicylic acid.	8,000,000
10.	Ives seedling		40,000,000
11.	Claret		2,500,000
12.	Delaware	Contained salicylic acid.	20,000,000
13.	Claret		trace
14.	Port		trace

FOOD LABORATORY OF THE BOARD OF HEALTH,
SAN FRANCISCO, CALIF.
September 7, 1905.