

XLVI.—*The Detection of Foreign Colouring Matters in Wine.*

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IN January, 1876, I showed (*Analyst*, No. 2, p. 26), in a short note read before the Society of Public Analysts, that the true colouring matter of wine dialysed but very slowly, if at all, through parchment paper; whereas, on the other hand, various colouring matters, alleged to be used in the fraudulent coloration of wine, dialysed freely. A year later (*Analyst*, No. 11, p. 186) I showed that small cubes* of

* These cubes, about three-quarters of an inch side, are cut with a sharp wet

jelly, placed in the wine to be tested, could be substituted with advantage for the parchment paper. If, after a shorter or longer interval of immersion, such a cube is taken out, washed a little with water, and a central slice is cut out of it, in a direction parallel with one of the sides of the cube, it will be found, in case the wine be pure, that the colour has penetrated but a very little way into the cube (in the course of 24 to 48 hours the colour penetrates perhaps one-sixteenth of an inch), whereas many other colouring matters will have penetrated to the very centre of the cube.

Since then I have extended my examination, and have now, I believe, included all the more important colouring matters said to be used in the fraudulent coloration of wines, and several others besides. The broad fact, established formerly, remains unaltered, namely, that the colouring matter of pure wine and that of alkanet root (in the papers quoted rhatany root is printed in mistake) dialyse but very slowly into the jelly, while all the rest among those examined dialyse more or less rapidly. A wine, the colouring matter of which does not dialyse readily, is therefore presumably pure, or has only to be tested for alkanet root, while, if it dialyses readily, it must be pronounced impure; that is, artificially coloured. Fortunately, the colouring matter of alkanet root is readily distinguished from the colour of pure wine, and is, moreover, on account of its somewhat unstable character, not likely to be used. The colouring matter of a pure red wine shows a general absorption of light in all colours except the red, but, generally, no distinct absorption band. The red colour changes to a greenish-brown on addition of ammonia, becomes much darker in tint, and now shows a somewhat indistinct absorption band in the yellow and orange, besides the general absorption of everything except the red. The colouring matter of alkanet root shows, in an acid solution and of suitable concentration, three distinct absorption bands lying between the yellow sodium and the blue strontium lines, nearly equidistant from each other and from these lines. Ammonia turns the colour beautifully blue, and reduces the absorption bands to two, lying one over the sodium line, the other between that and the red lithium line, about two-thirds of the interval between these from the former. Both acid and alkaline solutions show a general absorption of the blue end of the spectrum, and indeed in moderately concentrated solutions absorb everything but the red.

In many cases it will be sufficient to show that the wine is artificially coloured, though sometimes it is necessary or desirable to go further. In such case the colour of the slice, or its absorption spectrum, or the action of ammonia on it, may lead to the discovery knife out of a plate of jelly of proper thickness, which can readily be cast in a paper mould of suitable size.

of the particular colouring matter present. As a general rule, the slice shows the proper colour of the added substance much more clearly than the wine itself. Indeed, it is a strong proof of the presence of a foreign colouring matter in a red wine if the colour shown by the slice differs from that of the wine. Indigo or logwood, for example, are thus readily discovered. The slice will also frequently furnish good results when examined by the spectroscope, as in the case of rosaniline, cochineal, beetroot, red cabbage, &c., &c. Lastly, the action of ammonia on the slice may yield characteristic results. Thus, a rosaniline slice, placed into diluted ammonia, becomes colourless; a red cabbage slice, dark green; a cochineal slice, purple; a logwood slice, brown. This latter effect, *i.e.*, a browning of the slice, is, however, frequently observed even if no trace of logwood is present, but with a little care this need not cause any difficulty. Tannin, which is always present in red wines, dialyses readily, and a gelatine slice cut from a cube which had been immersed in a pure wine, rich in tannin, gradually assumes a brown coloration when placed into ammonia. In these cases, however, the slice is colourless or nearly so, except close round its margin, as only the unoxidised tannin dialyses, and this nearly colourless slice gradually becomes brown. In the presence of logwood, this slice is coloured yellow or brown, to a considerable depth, before it has been acted on by ammonia.

If the nature of the foreign colouring matter present cannot be made out by these simple means, the wine must be submitted to a careful spectroscopic examination (*see* W. W. Vogel, *Ber.*, 1875, 1246), or be examined by the various precipitation and other tests described by Gauthier and others (*Bull. Soc. Chim.* [2], 25, 435—445, and *Chem. Soc. J.*, 1876 [2], 330). If these fail, as in my experience they very often do, more particularly if the wine under examination owes part at least of its colour to the true colouring matter of the grape, the following process may be adopted:—A foreign colouring matter having been proved to be present by means of the cubes of jelly, a larger quantity of the wine is submitted to dialysis in a parchment paper dialyser. When a sufficient amount of colouring matter has dialysed, the liquid may be examined, either directly or after careful concentration, by the spectroscope or chemically, and will now be found to answer to these tests uninfluenced, or nearly so, by the colouring matter of the grape, as this has remained inside the dialyser.

Formerly I employed jelly made with five parts of gelatine to 95 parts of water, but I find that in warm summer weather the jelly so made is not of sufficient solidity for use, and I now cut the cubes from a jelly containing 10 per cent. of air-dry gelatine.*

* I have quite recently been informed by Mr. Stansell that a jelly containing 10

The following are the colouring matters examined:—

Group a. Colouring matters that penetrate but slowly into the jelly:—

Colouring matter of pure wine.

„ „ alkanet root.

Group b. Colouring matters that penetrate rapidly into the jelly:—

<i>Althea officinalis</i> .	Currants, black.
„ <i>rosea</i> (hollyhock).	Elderberry.
Beetroot.	Indigo.
Bilberry.	Litmus.
Brazil wood.	Logwood.
Carnations (<i>Dianthus caryophyllus</i>).	<i>Malva sylvestris</i> .
Cherry, red, sour.	Raspberries.
„ black.	Red cabbage.
Clematis (purple).	Red poppy.
Cochineal.	Rhatany root.
Cranberry.	Rosaniline.
Currants, red.	Saffron.
	Strawberry.

In most cases an addition of colouring matter, equal to 10 per cent. of the total intensity of the colour of the wine, yields distinct results with these cubes. In some cases, as with logwood, 5 per cent., and in the case of rosaniline, even as little as 1 per cent. can be detected. In no case, I believe, could 20 per cent. (or four parts of wine with one part of a solution of the same depth of colour as the wine) be overlooked. It may be useful to state that, to the naked eye at least, the colour of the froth produced by shaking the wine is apparently influenced to a much greater degree by the presence of many of the above-mentioned colouring matters than that of the wine itself. If, therefore, a suspected wine yields a froth of like colour with a genuine wine of the same class, the presumption is in favour of its not being artificially coloured.

In conclusion, I would remark that if in the examination of a suspected sample of wine, the degree of dialysis shown seems somewhat great, though not sufficiently so to remove all doubt on the subject as to its purity or otherwise, it is advisable to procure a pure sample of a similar wine for direct comparison, when all doubt will generally be dispelled.

per cent. of glycerin, such as is used by microscopists, answers well, in some cases at least, and should it be found to answer generally it would have the great advantage that it will keep for a considerable length of time, and cubes cut from it could always be kept ready to hand.