

XXIX.—*On Absorption-bands in the Visible Spectrum produced by certain Colourless Liquids.*

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IN August last we published in *Nature* (vol. 22, p. 368, August 19th, 1880) a short statement of the results we had obtained by examining spectroscopically the light which had traversed considerable thicknesses of different colourless liquids, and we gave a diagram of the different visible absorption-bands produced. Since then we have extended and repeated our former observations.

The great advance made in this subject by the most important paper of Captain Abney and Colonel Festing on the absorption-bands in the infra-red end of the spectrum produced in colourless liquids, suggested our publishing in a connected form the results which we have obtained in the visible spectrum. All our observations are eye observations, made on columns of the liquids varying from 2 to 8 feet in length, and the spectroscope we used was one of Desaga's with a single heavy glass prism. The sources of light were a large argand burner, and the oxyhydrogen lime-light. In most instances both lights were tried, as it was found that with certain lengths and certain liquids, one light gave the best results, in the other case the other light.

In our communication to *Nature* we stated how we were led to this investigation, and how on examining a column of water 6 feet in length, we observed a distinct absorption-band. Its position is essentially between 600 and 610 (Fig. 1). The band is decidedly darkest on the more refrangible side, and ends sharply on that side, fading off far more gradually on the other side. When this band is

PLATE I.

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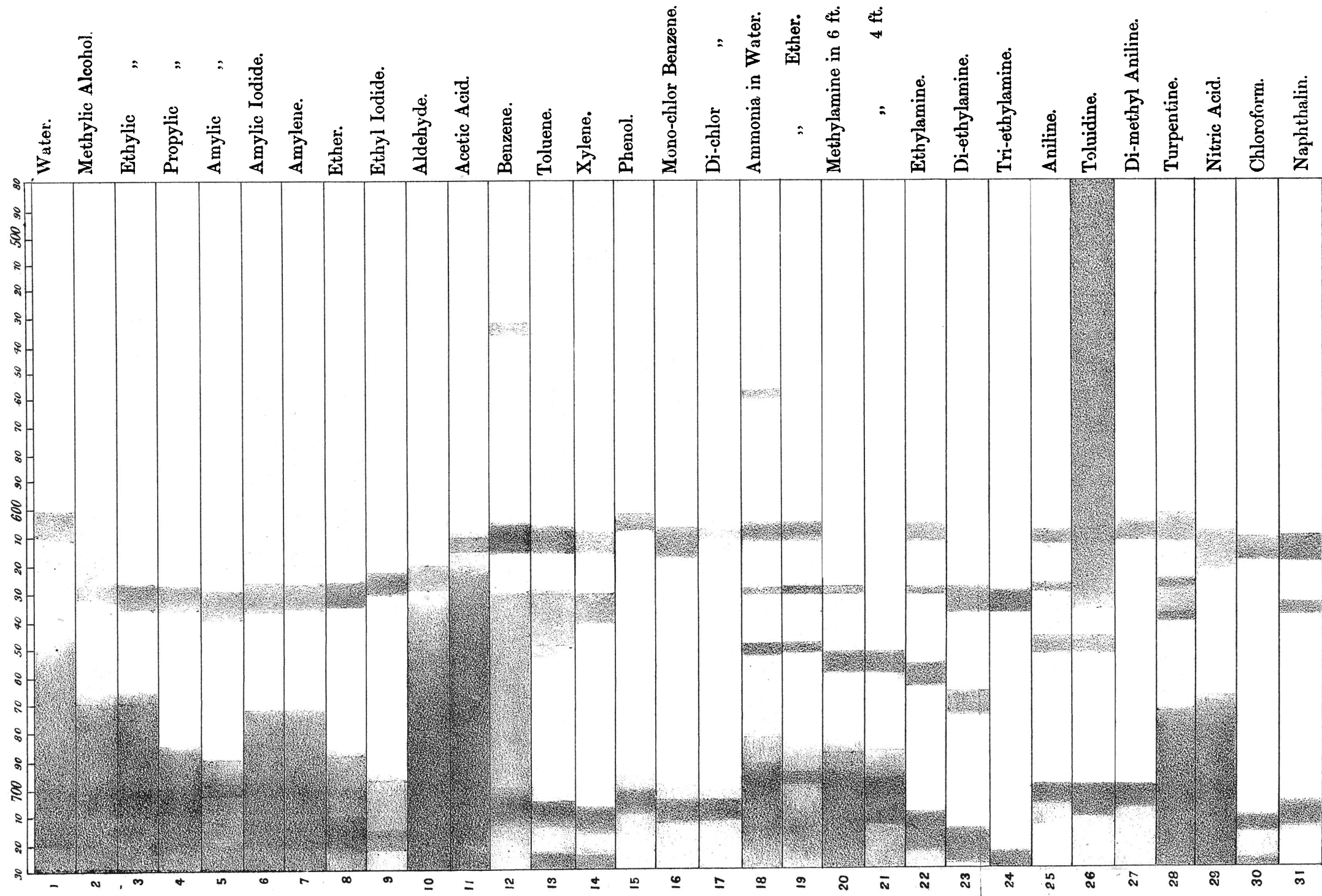
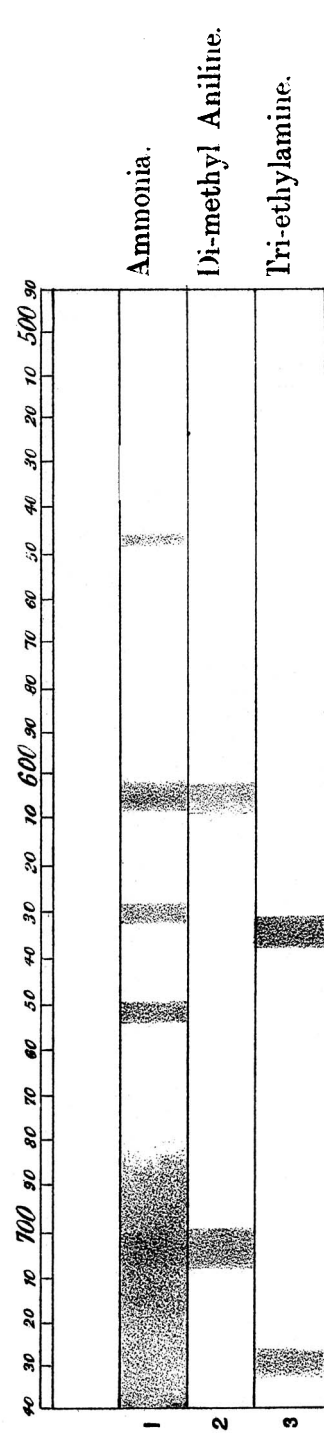


PLATE II.



distinctly visible, the general absorption in the red extends to about 655, and although too dark to allow us to speak with absolute certainty, we believe there is another band from about 705 to 723. We have also stated that on raising the temperature of the water from 20° to 60°, we saw no appreciable alteration in the intensity nor in the position of these bands, also whether ordinary or pure water was used, or even water saturated with ammonium chloride, or nitrate or carbonate, or potassium nitrate or lead nitrate or sodium chloride, or sugar, the intensity of this water-band was not altered. With a mixture of one volume of sulphuric acid and five volumes of water, it was also visible, but with ordinary pure commercial hydrochloric acid it required a column of 8 feet to see this band even faintly. Nitric acid (Fig. 29) gives a band visible in a column of 6 feet, from 605 to 620; it appears, therefore, to be a little nearer the red than the band given by water alone.

The colourless liquid in which we first recognised an absorption-band was ordinary alcohol, and we have since examined three other alcohols of this series, namely, methylic, propylic, and amylic alcohols. They all give a similar band; with each alcohol this band has a different position. The higher the alcohol in the series, the nearer is the band to the red end of the spectrum. Figs. 2, 3, 4 and 5 show these bands.

The saline ethers also give very interesting results; for in all the cases we have examined, we have found a band very similar to the alcohol one, but it is always slightly nearer the blue end of the spectrum. In the case of ethyl iodide another band is visible; this extends from 716 to 724. Probably this band is present in all the compound ethers, but in other cases it is hidden by general absorption. The spectrum given by the iodide is shown in Fig. 9.

In the amylic series we have experimented with the nitrate, acetate, and iodide. All these behave in exactly the same way as the compound ethylic ethers, viz., they all give bands similar to the alcohol band (Fig. 5), but slightly nearer the blue. With amylic iodide (Fig. 6) no second band is visible. It is also of considerable interest to note that amylene gives a band coincident with the one given by the compound amylic ethers. The same band running through each alcoholic series, shows that the band-producing body is unaffected by the acid radical.

Chloroform (Fig. 30) gives a faint absorption extending from 607 to 616, ending on one side very sharply. No band corresponding with the one in methyl alcohol is visible, there is, however, a very dark and sharp band extending from 711 to 717; judging from what occurs in the ethyl series probably this band runs through the whole of the methyl series.

Ether (Fig. 8) gives a spectrum which is remarkably clear and sharp; the most refrangible band coincides in position with the ethyl band (Fig. 3), but it is much darker and somewhat narrower—contracted a little on the less refrangible side, and the termination of the absorption on both sides is very sharp. The second band in ether is similar in position to the less refrangible band in ethyl iodide, but it is wider and darker.

Figs. 10 and 11 represent the absorption taking place with aldehyde and acetic acid; in both cases the absorption is but feeble, and it is only in lengths of 8 feet that we have been able to see these bands.

The next class of bodies examined were those belonging to the benzene series, and we found they gave very clear and interesting absorption-bands. Fig. 12 shows the absorption produced by 8 feet of pure benzene; both bands, the one from 606 to 616, and the other from 703 to 714, are remarkably sharp and dark; there is also a slight absorption extending as far as 678, and ending there so sharply that probably there is a line at that point, and further there is a still fainter shade extending up to 630, also ending sharply. The following drawing (Fig. 13) gives the visible absorption spectrum in 8 feet of the next member of this series, viz., methyl-benzene or toluene. There is much interest in the change which has taken place, the 606 to 616 band has become decidedly fainter, while the 703 to 714 band is as dark as before. Another band, or at all events an absorption ending very sharply at 725, is visible, and the absorption round the 703 benzene-band seems to have cleared away, but the faint absorption about 630 has intensified, and ends sharply at 631.

Fig. 14 gives the absorption produced by the next higher member of this series, xylene. The replacing of the second atom of hydrogen by methyl has carried on the same kind of change as that produced by the first substitution, for the 606 band is now fainter than it was in the toluene, and the 631 shade has developed to a complete band. The two dark bands in the red are as clear as ever. Another feature in the spectra of these compounds is the approach of the bands to the red; with the 703 band this is very marked and very regular. It would certainly seem that as the molecular weight of the compound is increased by the substitution of methyl for hydrogen, so does this band approach the red end of the spectrum.

In this connection we thought it would be of some interest to study still further the effect of substitution upon benzene. We therefore prepared the pure mono- and di-chlorbenzene; the latter was used dissolved in ether. Figs. 16 and 17 show the spectra given by these bodies. The two bands correspond exactly in position with those given by benzene, but the 606 band has become much fainter, exactly the same kind of change which occurred in the case of toluene and



xylene. The chlorine does not affect either the position or character of the less refrangible band.

In connection with these bodies it was of importance to examine naphthalene. A perfectly colourless sample of this body was fused in a 2-feet tube, closed at each end with a transparent glass plug, and having a tube fused into it to allow for the expansion of the contained liquid. The fused naphthalene gave a spectrum shown in Fig 31. There are three bands, and these correspond exactly in position with the two benzene-bands, and with the termination of the faint intermediate absorption. Further, the relative power of all these bodies to produce absorption is a matter of much interest and importance; for instance, a column of 2 feet of naphthalene produces about the same amount of absorption as a benzene column six or eight times as long, and benzene is a far more powerful absorbent than either toluene or xylene. In 2 feet of benzene the two dominant bands and the absorption from the red are distinctly visible. With the same length of toluene the most refrangible, the 606 band, has become decidedly fainter, and the least refrangible is less distinct than the corresponding benzene-band, and with the same length of xylene the only thing which is visible is a very faint indication of the least refrangible band, the other two bands have entirely disappeared.

Phenol gives two bands shown in Fig. 15; the most refrangible of the two agrees in position with the water-band, but it is smaller, and its sharp edge and dark side is on the less refrangible side, the reverse of what occurs with the water band. The least refrangible band is from 679 to 710, therefore a little nearer to the blue than the benzene-band.

In our former communication we described the several visible bands produced by a solution of ammonia, and the experiments we made to convince ourselves that all these bands did belong to ammonia. Fig. 18 shows the bands seen in a 6-feet column of a saturated aqueous solution. The band from 649 to 654 is the darkest; the position of the two more refrangible ones coincide very nearly, the one with the alcohol, and the other with the water-band, but differ in size and character; there is also a still more refrangible band, narrow and sharp, from 566 to 570. Clouded by the general absorption in the red, there is also an indication of a fifth band extending from 698 to 708. The next figure shows the spectrum given by ether saturated with ammonia. If alcohol in place of ether be the solvent a similar set of absorption-bands is obtained. On comparing the two spectra, Figs. 18 and 19, it will be evident that the most refrangible band is absent even in an 8-feet column, possibly in consequence of the mere absence of a sufficient amount of ammonia, the alcohol not taking up as much as the water. The band coincident with the water-band has become fainter in consequence, very probably not of the

absence of water, but of the absence of ammonia, the band coincident with the alcohol-band has become darker, and lastly the band in the red has become far more visible.

It was evidently of much interest to follow spectroscopically the changes which would ensue on replacing the hydrogen in ammonia by methyl, ethyl, &c.

Figs. 20 and 21 give the absorption produced by methylamine, the first by a column of 6 and the next by a column of 4 feet of a 33 per cent. aqueous solution of this body. Here clearly in Fig. 21 is a disappearance of the most refrangible band owing to shortening the length of the column.

On comparing this spectrum with that of ammonia (Fig. 18) it will be seen that the change which has taken place is a fading out of the more refrangible bands and a strengthening of the 649 band. In the shorter length the band in the red is quite visible.

Ethylamine also (Fig. 22) gives a spectrum very like that of ammonia. The dominant ammonia-band has become broader and darker, and a very clear and dark band is seen in the red. Both these bands, as compared with the corresponding ammonia-bands, are nearer the red end of the spectrum. We examined an aqueous solution containing 33 per cent. of ethylamine, and also the pure substance, and we found that they gave similar spectra. The next two (Figs. 23 and 24) give respectively the absorption produced by the di- and tri-ethylamine.

We would point out one or two curious facts which these experiments indicate. When ethyl or methyl is substituted for hydrogen in ammonia, the first thing which seems to occur is that the 649 band becomes broader, and is moved a little towards the red, also that the most refrangible ammonia-band disappears. When the second atom of hydrogen is replaced by ethyl, the 604 band disappears, the 649 band becomes much fainter, the 628 band becomes broader and darker, and finally when all the hydrogen in ammonia is replaced, the 649 band has entirely disappeared, and the 628 band has become very dark and sharp. Further, after each substitution it seems that the least refrangible bands are moved to the greatest extent towards the red end of the spectrum. Again, as far as the visible spectrum goes, ammonia gives the most complicated spectrum, triethylamine the least so, and it is important to note the similarity between the ethylic alcohol-band and those given by di- and tri-ethylamine.

Aniline, as shown in Fig. 25, gives bands similar to those given by ammonia. So similar are they in position that it might be difficult to distinguish these bodies by their visible absorption spectrum; the 649 band in aniline, however, is not so intense as the corresponding

ammonia-band. At the same time the least refrangible band appears always to be more conspicuous in aniline than it is in ammonia, and the next more refrangible band does not coincide exactly in position with the corresponding ammonia-band, but is a little nearer the blue its position being from 646 to 653.

On comparing the aniline spectrum with that of toluidine, it will be seen that as far as it goes there is a close resemblance; we have here another instance of the thickening of the dominant aniline-band. Unfortunately a little but a very persistent colour gave absorption in the green and blue, which rendered it impossible to see whether the two most refrangible bands which are in ammonia and in aniline, are also in toluidine. Judging from analogy we feel confident that they must be there, but that the absorption completely hides them.

The di-methyl-aniline, for which we have to thank Mr. Friswell, gives an interesting spectrum, which, like that of triethylamine, contains but two bands; both these bands correspond to aniline-bands, and therefore to ammonia-bands.

The simplification of the visible spectrum by the complication of the molecule, and the different relationships which exist between bodies formed on the same type, is shown in the last three figures, which give the bands produced by ammonia, dimethyl-aniline, and triethylamine. In the first case none of the hydrogen is replaced, in the other two all of it is.

Fig. 28 gives the spectrum of turpentine. Its most marked characteristic is the existence of two bands, one from 636 to 641, the other from 624 to 628; these bands are united by a considerable amount of absorption. There is also a faint band from 600 to 610, which is coincident with the water-band.

We have been able to find but few liquids which in columns of 6 or 8 feet do not give absorption spectra; in carbon tetrachloride and carbon disulphide we appear to have bodies which do not in these lengths give visible absorption-bands.