

[ADDED NOV. 28, 1902.—Since this paper was communicated to the Royal Society, I have seen a paper on the spectrum of lithium, by Hagenbach, in the 'Annalen der Physik,' No. 12, 1902, which was published on November 13. The experimental part of his paper deals almost entirely with the blue line, and the fact that there are other abnormal lines in the spectrum of lithium is recorded above for the first time. Hagenbach's conclusion that there are two lines near wavelength 4603 is not, I think, established; and I still hold that the views expressed in this paper are more probable. He has not been able to find the second line as a bright line, so the difficulties in the way of accepting the view that there is a second dark line, without a corresponding bright line, remain. He has not referred to Professors Liveing and Dewar's work,* and his evidence for saying there are two lines is, in fact, similar to the evidence they gave.]

'An Error in the Estimation of the Specific Gravity of the Blood by Hammerschlag's Method, when employed in connection with Hydrometers." By A. G. LEVY, M.D. (London). Communicated by Sir VICTOR HORSLEY, F.R.S. Received November 25,—Read December 11, 1902.

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Hammerschlag's method of estimation of the specific gravity of the blood is an application to clinical purposes of a physical method frequently employed when only a small quantity of the substance under investigation is obtainable. The method may be briefly described as the adjustment of the specific gravity of a mixture of chloroform and benzol by small successive additions of either constituent until it corresponds to the specific gravity of the blood, the test of the attainment of this condition being that a small drop of the blood, when immersed in the mixture, shall remain suspended without any very obvious tendency to rise or sink. The specific gravity of the mixture is then estimated by means of a hydrometer, the scale of which is graduated to register densities lying between the maximum and minimum densities of blood, *i.e.*, from 1.020 to 1.080.

In order to attain a rapid adjustment of the relative proportions of the chloroform and benzol, it is the general practice to use a comparatively small quantity only of these fluids and a small hydrometer, and, as will be hereafter seen, the size of the instrument is an important factor in the magnitude of the error.

This error was commented upon in a paper read by Dr. Baumann

* 'Phil. Trans.,' vol. 174 (1883), p. 215.

before a recent meeting of the Physiological Society, in which he recorded estimations by Hammerschlag's method which exceeded by 0.012 the estimation of the specific gravity of the blood by the picnometer method. Dr. Baumann also mentioned similar, but less considerable, excessive readings noted by certain other observers. I had myself, in the course of a series of experiments upon the blood of dogs,* occasion to remark upon the consistently high results yielded by Hammerschlag's method, the excess being, in my cases, from 0.007 to 0.008.

With the purpose of investigating the source of this error, I prepared two mixtures, the one (A) of chloroform and benzol, and the other (B) of glycerine and water, and, in each case, adjusted the relative proportions until identical readings were obtained on the scale of the same hydrometer. On immersing a drop of mixture (B) in a vessel of mixture (A), it rapidly sank to the bottom, thus indicating, in the absence of interfluid exchanges, an actually higher specific gravity of (B). This indeed could be demonstrated by other methods of finding the densities of the two liquids, *i.e.*, by the weighing bottle or picnometer, or by Westphal's specific gravity balance. The occurrence of a gross fault in the hydrometer method being established, it remained to investigate its extent and origin.

I proceeded by immersing four dissimilar hydrometers, all graduated from 1.000 to 1.060 to the test of immersion in a mixture of chloroform and benzol, which had been prepared, with the aid of Westphal's balance, of a specific gravity = 1.000, and the following table shows the point at which the lowest level of the fluid meniscus intersected each scale, *i.e.*, the *apparent* specific gravity for each hydrometer. The measurements of each instrument are included in the table for future reference.

The error, as set forth above, is explicable by a consideration of the differences between the values of the surface tensions of water and of chloroform and benzol. The exact experimental proof of this would, I find, involve an extended investigation into a complicated subject. This I have not attempted—it suffices to show how far the error, calculated from certain known conditions, agrees with my comparatively rough observations.

The action of surface tension of a fluid upon a floating hydrometer is evidenced in a downward pull upon the stem, so that a hydrometer becomes immersed, not only until it has displaced a weight of water equal to its own weight, but is still further immersed by the action of surface tension upon its stem until the additional weight of water displaced balances this surface tension pull. It is this point of ultimate

* "The Changes in the Blood of Dogs after Thyroidectomy," *Journ. Path. and Bact.* October 1898 p. 317.

Table I.

No. of hydrometer	No. 1.	No. 2.	No. 3.	No. 4.
Weight in grammes	15·3118	11·367	3·81	2·868
Diameter of stem in mm.....	3·95	4·37	3·55	3·13
Length of first division of scale (i.e., 1·000 to 1·001) in mm.	1·29	0·74	0·417	0·398
Reading of scale in a chloroform benzol mixture of specific gravity = 1·000	1·002	1·003	1·0095	1·010

No. 1 hydrometer is a more sensitive instrument than the ordinary urinometer, having a large barrel and a comparatively fine stem. No. 2 is an ordinary urinometer such as is in general use in hospitals. Hydrometers Nos. 3 and 4 are considerably smaller instruments, and are similar to those which have been employed in this laboratory for use in connection with Hammerschlag's method.

immersion which corresponds to the mark 1·000 on the stem when the hydrometer is floating in water.

If the same hydrometer is floated in a chloroform and benzol mixture of sp. gr. = 1·000, the same volume of mixture is displaced, but, as in this case the liquid possesses a lower surface tension, the pull upon the stem is less powerful, and hence less of it is immersed from this cause than in the case of water, the degree of surface tension immersion being, in the two instances, in direct proportion to the respective values of the surface tensions. The mark 1·000 on the stem, therefore, floats a little distance above the surface of the mixture, and the hydrometer hence shows a reading which is higher than the actual specific gravity.

The length of the divisions and the diameter of the stem of any hydrometer being known, the error due to surface tension may be calculated.

The value of surface tension may be readily expressed in milligrammes for each millimetre of the circumference of the stem on which it acts. The surface tension of water is estimated by Van der Mensbrugghe as 7·3 milligrammes per mm. Other observers have found higher values, but it is difficult to obtain water sufficiently clean to exhibit even the surface tension of 7·3 milligrammes, for an exceedingly slight contamination of the surface by greasy matter suffices to appreciably reduce the tension.

The surface tensions of chloroform and benzol are very nearly equal

in value, and may be taken in each case, for purposes of calculation, as 2.75 milligrammes per mm., the actual figures given by some other observers varying slightly.*

I further find, by experiment, that the surface tension of a mixture of the two fluids of any specific gravity between 1.000 and 1.080 is, for practical purposes, the same as that of the individual fluids.

The numerical difference between the values of the surface tensions of water and a chloroform and benzol mixture is therefore 4.55 milligrammes (7.3—2.75), and this, when multiplied by the circumference (expressed in mm.) of the hydrometer stem, is equal to the weight in milligrammes of a column of the mixture of the same diameter as the stem in question, and of a length which equals the extent to which the stem is exposed below the specific-gravity mark which should be the proper reading of the hydrometer.

This length may be calculated according to the simplified formula $h = 2T/rw$, where h is height, T is surface tension, r is the radius of the stem, and w is the specific gravity of the fluid.

Having calculated this height in the case of a hydrometer immersed in a chloroform and benzol mixture of sp. gr. 1.000, the division of this by the average length of the first divisions of the scale gives the theoretical error (at this specific gravity) of the hydrometer, expressed in scale units.

Example.—In the case of Hydrometer No. 4,

$$h = \frac{2T}{rw} = \frac{2 \times 4.55}{1.565 \times 1} = 5.8147$$

$$\frac{5.8147}{0.398} = 14.6$$

As each division represents 0.001, the error = 0.0146.

In the following table, the calculated errors are contrasted with the observed errors of Table I.

Table II.

Hydrometer.	Observed error.	Calculated error.
1	0.002	0.0035
2	0.003	0.0056
3	0.095	0.0123
4	0.010	0.0146

The not inconsiderable disparity between the two columns was, for a time, an unsolved problem, until I found by the following experi-

* Chloroform.				Benzol.		
Temp. 16° 6 C.	2.75	Quinke.		Temp. 15° C.	2.87	Schiff.
„ 12° 5 C.	2.813	Bedé.		„ 15° C.	2.76	Bedé.

ment that each instrument possessed an intrinsic error which tended to minimise the error of reading.

A hydrometer and its containing vessel were carefully cleansed with benzol and protected from contamination with greasy matter, and a sample of water taken, which was the cleanest readily obtainable, *i.e.*, tap-water which had been allowed to run through the pipe for some fifteen minutes. On immersing the hydrometer in this water, the mark 1·000 rested a slight distance below the surface. The water in which the hydrometer was standardised must have been contaminated, and hence possessed a considerably lower surface tension than that of the comparatively clean water in which my experiment was performed.

All the four hydrometers of my tables I found to possess this intrinsic error, which I estimated somewhat roughly, and have expressed in scale units. When these innate errors are added to the errors of Table I, the totals more closely approximate to the calculated errors. (See Table III.)

Table III.

Hydrometer.	Error due to difference between surface tensions of impure water and a chloroform-benzol mixture.	Error due to difference of surface tensions of impure and clean water.	Total error.	Calculated error.
1	0·002	0·0014	0·0034	0·0035
2	0·003	0·002	0·005	0·0056
3	0·0095	0·002	0·0115	0·0123
4	0·010	0·003	0·013	0·0146

There is thus sufficient agreement between the values of the observed and calculated errors to demonstrate that the disturbing influence of surface-tension is sufficient to cause the whole of the error in the hydrometer reading and to account for the inaccuracy of Hammerschlag's method. Taking into consideration the varying value of the surface tension of water, and the fact that no accurate determinations were made by me of each individual specimen of water or of chloroform and benzol, very exact calculations are precluded. Had this been done doubtless a more exact agreement between observations and calculations would have resulted. Furthermore, observations of this nature are replete with difficulties which can not be touched on here, but which may be gathered from a paper upon an elaborate investigation into a similar subject by Fridtjof Nansen.*

* "Scientific Results of the Norwegian North Polar Expedition," vol. 3, Part 10

The difference in the error of the several hydrometers is readily accounted for. A consideration of the facts already set forth shows that the error when expressed in scale units must vary directly as the radius of the stem, and inversely as the total weight of the instrument, so that when the stem is fine in comparison with the weight, the error is small. But in making a small hydrometer it is impossible to keep down the relative proportion of the stem. It thus follows that the smaller hydrometers exhibit a greater surface tension error than the larger ones.

The greatest discrepancy which I have *observed* in any hydrometer in chloroform and benzol was 0.014. This instrument was a small one, graduated from 1.020 to 1.080, and is not included in the above tables.

This source of error in Hammerschlag's method may be obviated by:—

(1.) The estimation of the specific gravity of the chloroform and benzol mixture by means of an instrument which excludes or minimises the surface tension factors. The most convenient is some such balance as Westphal's, in which the surface of the fluid is intersected by an exceedingly fine platinum wire only. The employment of hydrostatic bubbles is inconvenient on account of the long series required. The pycnometer method is not readily applicable in connection with very volatile fluids.

(2.) By employing a hydrometer which has been standardised or corrected in chloroform and benzol mixtures, the requisite specific gravities of which have been adjusted by an accurate method. In the absence of the above-mentioned appliances a rough method or correction may be applied to any hydrometer of which the highest mark is 1.000. The method consists of adjusting the proportions of a mixture of chloroform and benzol until a small drop of water immersed neither sinks or floats. The mixture being thus of the same specific gravity as water itself, the reading of the hydrometer in it is its error at this degree, and in the case of a well-constructed and accurately graduated hydrometer, this error holds good with only a negligible increase throughout the scale.

I have, in conclusion, to express my indebtedness to Professor Vaughan Harley for the resources of his laboratory, and to Professors Baly and Donnan, of the Chemical Department, at University College, for kind assistance and the loan of appliances.
