



## XX. On the nature and properties of indigo; with directions for the valuation of different samples

John Dalton Esq. F.R.S.

**To cite this article:** John Dalton Esq. F.R.S. (1825) XX. On the nature and properties of indigo; with directions for the valuation of different samples , Philosophical Magazine Series 1, 65:322, 122-128, DOI: [10.1080/14786442508628403](https://doi.org/10.1080/14786442508628403)

**To link to this article:** <http://dx.doi.org/10.1080/14786442508628403>



Published online: 27 Jul 2009.



Submit your article to this journal [↗](#)



Article views: 3



View related articles [↗](#)

of Ticsan which I have made known, leaves no further doubt respecting the existence of sulphur in the primitive districts. It has also been lately found in Brazil, that the chloritic quartz formation which covers, in the Capitania de Minas Geraes, the primitive clay-slate, contains both gold and sulphur. Laminæ of this rock strongly heated burn with a blue flame. Near to Villarica, in the district called Antonio Pereira, a schist, of the same age as that on which is superposed the itacolumite or chloritic quartz, contains a calcareous bed traversed by veins of quartz, which the Baron d'Eschwege (director of the gold and diamond mines of these countries) has found filled with little nodules of pulverulent sulphur. All these phænomena increase in interest, when we reflect that this learned geologist, and also another German traveller (M. Pohl) incline to the opinion that gold, micaceous iron, diamonds, euclases, platina, and palladium, which are peculiar to the alluvial districts of Brazil, have been derived either from the destruction of the great formation of chloritic quartz, or from that of a ferruginous bed (*itabarite*) which is placed above this formation.

---

XX. *On the Nature and Properties of Indigo; with Directions for the Valuation of different Samples.* By JOHN DALTON, Esq. F.R.S. &c.\*

WE owe the first good approximation to the chemical analysis of the indigo of commerce to Bergman. According to his experiments, the best samples of indigo yielded, by analysis, the following principles :

47	pure indigo
12	gum
6	resin
22	earth
13	oxide of Iron
<hr/>	
100	

A subsequent analysis of indigo made by Chevreul (*Annal. de Chimie*, t. 68), gives 45 per cent of pure indigo in the best Guatimala indigo, and the foreign matters much the same as by Bergman, but differing considerably in the proportions. Indeed it is most probable that the foreign matters will be found to differ materially, both in quantity and kind, from the various modes and circumstances of the manufacture as practised in different places, and perhaps from the various species

\* From the Memoirs of the Literary and Philosophical Society of Manchester.

of plants from which the indigo is extracted in different parts of the world.

It is to be understood that the part called pure indigo is the sole colouring matter, and that which gives value to the article. The rest may be considered as dross, doing no good, and being probably harmless to the use of the drug as a dye, but scarcely so to the printer, who meets with obstructions enough in the exercise of his art, without introducing such as may easily be avoided.

When we consider, however, that indigo is produced by a species of fermentation from vegetable matter, analogous to the vinous and acetous fermentation of saccharine matter, it is not improbable that the fermentation in many cases may be incomplete. And as the foreign matter found in the indigo of commerce is chiefly vegetable, and composed of the same elements as pure indigo, it may by a fresh fermentation develop more of the pure indigo than is found in it originally. This conjecture is countenanced by the practice of dyers, who, when the indigo is nearly spent, as the phrase is, put in other vegetable matter to the residue, and by certain processes obtain an addition to the quantity of colouring, which otherwise would not be acquired. In a similar way I conceive it is that vinegar made from sugar often contains a considerable portion of the latter, which has escaped the fermenting process.

There are two ways of obtaining pure indigo. The one is that commonly practised by dyers in their use of the article. On a small scale it may be effected as follows: into a two-quart bottle put 50 grains of finely pounded indigo, three or four times as much sulphate of iron, and hydrate of lime same weight as the salt of iron. Then fill the bottle with water, leaving little more room than what the cork or stopper will occupy. Mix up the contents by repeated agitation, and then let the insoluble matters subside. A fine transparent greenish-yellow liquid will appear in a day or two, which must be drawn off carefully by a syphon. As soon as this liquid is agitated in the air it becomes opaque, and a precipitate is formed, which is pure indigo; but it cannot be collected without some carbonate of lime in the first instance; it must therefore be submitted to water acidulated with muriatic acid, which dissolves the lime, and leaves the pure indigo to subside. Afterwards it may be collected on a filtre and dried. The theory of this process is now well understood. Pure indigo, deprived of a certain portion of oxygen, is known to be soluble in lime-water; the protoxide of iron, precipitated by the lime, deprives it of this oxygen, and hence the solution of the de-oxidized indigo. Such, however, is the affinity of indigo

digo in this state for oxygen, that it resumes it from atmospheric air the moment they are brought into contact.

Pure indigo thus obtained is called *precipitated* indigo: the solution may also be had from a blue-dyer's vat by plunging an empty phial into the liquid a few inches below the surface.

The other way of obtaining pure indigo is by sublimation. Take 20 or 30 grains of pulverized common indigo and place it in an iron spoon, which must be gradually heated to 500° or 600° Fahrenheit. A purple smoke will then exhale copiously, and at the same time a fine tissue of small, shining, silky needles will start up on the surface of the indigo. These may be withdrawn by the point of a knife; they are crystals of sublimed indigo.

*Precipitated* and *sublimed* indigo appear by the chemical tests to be constituted of the same elements; and no doubt is entertained that they present the pure colouring matter of indigo in its most concentrated form.

Three chemists have published analyses of pure indigo within the last three years; namely, Drs. Thomson and Ure, and Mr. W. Crum, all of Glasgow. The same plan was adopted by all three; namely, burning a small given portion of indigo in contact with the black oxide of copper in green glass tubes. The indigo being finely divided and intimately diffused through a comparatively large portion of the oxide, heat is applied sufficient to burn the carbon and hydrogen of the indigo, and to liberate the azote: hence from the quantities of carbonic acid and azote produced, and the loss of weight which the oxide sustains, the constituents of indigo are inferred. The results are below:

	Dr. Thomson.	Dr. Ure.	Mr. Crum.
Carbon	40·39	— 71·37	— 73·22
Azote	13·46	— 10	— 11·26
Oxygen	46·15	— 14·25	— 12·60
Hydrogen	0	— 4·38	— 2·92
	<u>100</u>	<u>100</u>	<u>100</u>

It is observable that the results of Dr. Ure and Mr. Crum present no remarkable differences, except in regard to hydrogen; whilst Dr. Thomson finds no hydrogen: and remarkable differences between his results and those of the other two are found in the articles carbon and oxygen.

The atomic constitution of indigo by the above authors is as follows:

	Dr. Thomson.	Dr. Ure.	Mr. Crum.
Carbon	7 atoms	— 16 atoms	— 16 atoms
Oxygen	6 do.	— 2 do.	— 2 do.
Azote	1 do.	— 1 do.	— 1 do.
Hydrogen	0 do.	— 6 do.	— 4 do.
	<u>14</u>	<u>25</u>	<u>23</u>

I am inclined to think the analysis of Mr. Crum as likely to be an approximation to the constitution of pure indigo as either of the other two; and I should adopt his atomic constitution, if he would modify it so as to adopt my weight of the atom of azote instead of its double, which has somehow got into common reception as a substitute without any sufficient reason that I can find. If we adopt my weight for azote, Mr. Crum's atoms will become 16, 2, 2, and 4; which, being all divisible by 2, become

8 atoms carbon
1 atom oxygen
1 atom azote
2 atoms hydrogen
<hr/>
12

This simplification of the atom of indigo I suggested to Mr. Crum in a conversation we had together, and he seemed inclined to adopt it. Referring therefore to my scale of atomic numbers, we shall have the atom of pure indigo to consist of

8 atoms carbon	5.4 = 43.2	.....	75.5
1 atom oxygen	7 = 7	.....	12.3
1 atom azote	5 = 5	.....	8.7
2 atoms hydrogen	1 = 2	.....	3.5
	<hr/>		<hr/>
	57.2		100

Mr. Crum, in his very ingenious essay above referred to, finds that a compound of one atom of indigo and one of water may be formed by means of sulphuric acid: he denominates it *phenicin*; it may perhaps be better designated by the name of proto-hydrate of indigo. The common product of sulphuric acid and indigo, or *sulphate of indigo* of Dr. Bancroft, he calls *cerulin*, and finds it to be a compound of one indigo and two of water, or the deuto-hydrate of indigo.

I have made no attempts myself to analyse pure indigo into its constituent elements, but have often tried, both recently and some years ago, to find the quantity of oxygen required to convert the green indigo solutions in lime-water into blue indigo. The results have been pretty uniformly the same—namely, that the oxygen which combined with the green indigo, to convert it to blue, was about one-seventh or one-eighth of the whole weight of the resulting indigo; and hence I concluded, on the supposition that one atom of oxygen was added to one of indigo, that the atom of indigo must weigh about 55, or 56; and this conclusion I pointed out to Mr. Crum, as corroborating his analysis. The quantity of oxygen required was much less, and of course the weight of the atom of indigo was much greater than I had anticipated.

We

We now proceed to the consideration of the best means of fixing a comparative value upon the different samples of the indigo of commerce. After numerous trials I find the method first suggested by Descroisille to judge of the strength of oxymuriatic acid to be preferred. The objects indeed are different, but the operations are analogous: he made use of a given solution of indigo to ascertain the comparative strengths of various solutions containing oxymuriatic acid; on the other hand, I propose to use a solution of oxymuriatic acid of known strength, to compare the relative quantities of pure indigo in different samples.

In the first volume of the *Annals of Philosophy* (1813) I pointed out a safe and easy method of estimating the quantity of oxymuriatic acid, in solutions of oxymuriate of lime, not by solutions of indigo, which must be variable from the quality of the indigo, but by solutions of proto-sulphate of iron, which can always be obtained of the same strength. I say *safe* and *easy* method, notwithstanding we are gravely told by one professor of chemistry that he had tried the method and was nearly killed by it; and another states that he had attempted to follow my method, but did not succeed. Any person who is tolerably skilled in chemical manipulations, and has the two liquids, sulphate of iron of a known strength, and oxymuriate of lime of a known specific gravity, before him, may determine the strength of the oxymuriate in the space of five minutes. In this time I found the strength of the oxymuriate of lime used on the present occasion. Having by me a solution of proto-sulphate of iron containing eight per cent oxide, I took 50 grain measures of it and poured them into a wine glass, then 100 of the oxymuriate, stirring the mixture, after which no smell was perceived; 100 more were poured in, still no smell; then dropped in ten grains at a time by a dropping tube, stirring the mixture each time; the fifth 10 grains produced a slight but transient smell; the sixth a strong and permanent smell. Hence 250 were required to saturate 50 of the sulphate. The oxide (four grains) being divided by nine, gives  $\cdot 444$  for the weight of oxygen in 250 oxymuriate, or  $\cdot 17$  parts of a grain of oxygen are imparted by each hundred of the liquid.

In the essay above referred to I mentioned another method of investigating the value of oxymuriate of lime solution; but, owing to the then prevailing erroneous notion on the proportion of the elements of nitric acid, no satisfactory application could be made of it. I now find that oxymuriate of lime converts nitrous gas into nitric acid immediately; and hence this operation may be used with great elegance and  
precision

precision to show the real quantity of oxymuriatic acid in solutions.

For example: I took a graduated tube of capacity equal to 300 grains of water; I filled it with pure nitrous gas, and then transferred it to a cup of the liquid oxymuriate, valued above by the sulphate of iron. After repeated agitation, covering the end of the tube carefully with my finger, I soon had 100 measures of liquid in the tube: then withdrawing it to a cup of water I agitated repeatedly, letting in water each time, instead of oxymuriate of lime, because I was aware that the 100 measures already in the tube were not saturated. Soon after, the process was at an end, no more nitrous gas being absorbed. The 100 measures of the oxymuriate took 168 measures of nitrous gas to saturate them. Now deducting one-sixteenth of this for the nitrous gas impregnating the liquid, and for loss occasioned by the free oxygen gas in the water which the nitrous gas had to combine with, there will remain 157 nitrous gas =  $\cdot 2$  grain weight, which was converted into nitric acid; but if we deduct one-eighth part from the weight of nitrous gas, we shall have the weight of oxygen requisite to convert it into nitric acid =  $\cdot 175$  parts of a grain; only differing  $\frac{2}{1000}$  from the other valuation by sulphate of iron.

To find the value of any sample of indigo, I take one grain carefully weighed from a mass finely pulverized. I put this into a small glass, a wine-glass for example; then by a dropping tube I put two or three grains of concentrated sulphuric acid upon it. The two principles are next well mixed together by trituration with the end of a small glass rod. Water is then poured in, and the colouring matter fully diffused through it. The liquid is now transferred into a tall cylindrical jar, of about one inch internal diameter; more water is poured in till the mixture becomes sufficiently dilute to show the figure of the flame of a candle through it. Then the liquid oxymuriate is mixed with the liquid gradually and by measure, agitating duly each time, and never putting any more in till the smell of the preceding has vanished. The liquid soon becomes transparent and of a beautiful greenish-yellow appearance; after the dross has subsided, the clear liquid may be poured off, and a little more water put to the sediment, with a few drops of oxymuriate of lime, and a drop of dilute sulphuric acid; if more yellow liquid is produced, it arises from particles of indigo which have escaped the action of the oxymuriate before, and must be added to the rest.

The value of the indigo I consider in proportion to the quantity of real oxymuriate of lime necessary to destroy its colour. The value also may be well estimated by the quantity and

and intensity of the amber-coloured liquid which the indigo produces, and this is found independently of any valuation of the oxymuriate of lime.

Some of the samples I have tried, and the results are as under :

1.—*Precipitated* and *sublimed* indigo, each one grain, gave nearly the same results. Each of these required 140 grains of the oxymuriate of lime solution, corresponding to 25 parts of a grain of oxygen. The yellow liquid obtained was 3600 grains.

2.—*Flora* indigo, one grain, required 70 of the oxymuriate = 125 parts of a grain of oxygen, or one half of the other.

The same result from a sample marked J. R. *best*.

3.—Indigos marked 1 P and 3 P required about 60 of the oxymuriate.

4.—Those marked J. R. *middle*, J. R. *worst*, and 4 P, required about 50 oxymuriate.

5.—That marked *Wood* was rather inferior to the above, but required above 40 oxymuriate.

6.—Those marked 2 P and 1194 were the lowest I have examined; one grain of each did not require more than 30 oxymuriate, or 35 at the most. A poor turbid yellow liquor was produced. The sample 2 P, when burned, yielded about 30 per cent of fine sand.

Upon a review of these experiments, I am persuaded that to destroy indigo by oxymuriatic acid, *twice* the quantity of oxygen is necessary that is required to revive it from the lime solution.

I hope the subject here taken up will not be considered as unimportant, when we are informed that the article *indigo* imported into this country annually, about fifteen years ago, amounted in value to upwards of two millions of pounds sterling; and it much exceeds that sum in all probability at the present time.

## XXI. On Aërial Navigation. By A CORRESPONDENT.

To the Editors of the *Philosophical Magazine and Journal*.

Gentlemen,

THE late passion for balloons has subsided without producing any improvement, except a sensible hint in one of the newspapers, that the *aëronaut* should carry with him a long line having a great number of ropes attached, so as to increase the chance of assistance from below. Yet I think it will appear that the direction of these machines, though