

65225

ON THE ESTIMATION OF SMALL QUANTITIES OF PHOSPHORUS IN IRON AND STEEL BY THE SPECTRUM ANALYSIS.

BY SIR JOHN G. N. ALLEYNE, BART., BUTTERLEY.

INTRODUCTION.

THIS is not the first time that the subject of the spectrum analysis has been brought before the Iron and Steel Institute. At the London meeting of the Institute, in March, 1871, Professor Roscoe read a paper on the subject; that paper is included in the Proceedings, and will be found in Vol. II, 1871, of the JOURNAL. The Professor, after very fully describing the spectroscope itself, and exhibiting and experimenting with sundry apparatus, in speaking of the spectrum of the Bessemer flame, says, "Why do we not see the spectrum of phosphorus? I think the analysis of the slag will tell us why we do not see phosphorus in the flame, for the good reason that it is not there. A very small quantity of it is contained in the pig, and this we know quite well does not come out, though many people here wish it would, but it remains in the iron, so that I think it rather hard upon us to be told you cannot do us any good at all, because you cannot tell us anything about silicon or anything about phosphorus. In spite, however, of these shortcomings, I hope what I have said will show you that spectrum analysis is not wholly without its use, and that we may really believe it will, in time to come, be much more largely employed than it is at present, so that we may succeed, in the end, in doing what we originally intended to tell you: when to stop your blow, so as to have finished steel in your converters, without having added any spiegel at all."

Following at a very humble distance the great discoverers in Solar physics, Augstrom and Kirchhoff, in Germany, Huggins and

Lockyer, in our own country, the author has long been of opinion that, if they, by means of the spectroscope, can analyse the sun—if they can, by means of the cross prism or prism of comparison, prove to demonstration that most of, or all, the metallic elements and the various constituents of which this earth is formed, are found in a state of incandescence in the sun; if Dr. Huggins, by the displacement of the hydrogen line, can calculate whether a star is approaching to or receding from the earth,—we should be able to apply this system to our manufacturing operations. In bringing the subject again before the Institute, the author wishes to acknowledge the great advantage he has derived from the study of the published investigations of the gentlemen before mentioned, Dr. Huggins, Professors Augstrom and Kirchhoff, and Mr. Lockyer. He would especially point out to the Institute that, as practical manufacturers and engineers, it is their special business to apply, and apply rightly, the powers of nature to operations of the manufactory, it is the very basis of all improvement, the very charter of the Institution of Civil Engineers, of which the author and many of the members of the Iron and Steel Institute have the honour of being members. To quote the words of the late Mr. Thos. Tredgold, “A society for the general advancement of mechanical science, and more particularly for promoting the acquisition of that species of knowledge which constitutes the profession of a civil engineer, being the art of directing the great sources of power in nature for the use and convenience of man.” It is on this principle that the author invites the co-operation of the Institute, as well as that of, as it were, the parent society, the Institution of Civil Engineers, by whose kindness we are this day assembled in these rooms. The subject is very large, the field of enquiry and investigation which it opens is enormous—light, heat, and electricity. It is impossible to say into what ramifications a discussion may lead, bringing forward questions which in all probability the author would be unable to answer; and which are infinitely beyond the reasonable range of a single paper. It is with this view that it is proposed to confine the subject of the present paper to the estimation of phosphorus, by means of electricity of high tension, the power of absorption of hydrogen gas, and the spectroscope. The science of spectrum

analysis is a new one, one which will, if successful, be of the greatest advantage in our blast furnace, forge, and steel manufacturing operations, indeed to all manufactories where a qualitative or quantitative analysis of the materials is required. If the subject is brought before the Institute in too crude a state, the author would plead, as his excuse, that it was his ambition that the Institute should work it out for themselves, that a quantitative analysis should emanate from one of themselves, and that they should not wait until some of the great discoverers, before alluded to, had time to turn their attention to terrestrial investigations, and show us that the same law which applied to the absorption lines of the sun's atmosphere, and the effect of his rays passing through the atmosphere of the earth, could be applied to the quantitative analysis of the iron and steel as it passes from one process of manufacture to another. The author does not presume to come before the Institute and state that he has made a complete quantitative analysis of iron by Spectrum Analysis, but hopes that he will be able to show that he has made some progress towards that result. Taking up the subject, then, where Professor Roscoe left it in March, 1871, the author had first to get a spectrum of iron, and to find the requisite apparatus. Mr. Alfred Apps, of the Strand, furnished a powerful Grove's Battery, an induction coil capable of giving a spark of 12 inches between the secondary poles, and a Leyden Battery of 4 one gallon jars. The coil was of very much the same construction as that which he has now lent to further illustrate this paper, and which he has kindly offered to set to work, if the members wish to see it in operation. This offer the Council has accepted. A spectroscope, by Mr. John Browning, with a battery of 4 prisms of dense flint glass formed the first batch of apparatus. The author certainly has, after a great number of experiments and much study, formed an opinion of his own, but his wish and intention is to describe a number of those experiments, showing the results to which they lead, and leaving the members to form their own conclusions, inviting, nevertheless, their co-operation and assistance. Professors Augstrom and Thalén state that there are 460 lines in the spectrum of iron. Dr. Watts, in his index of spectrum, gives—Kirchhoff 71, Thalén 148, Huggins 101; but there are also present the atmospheric lines, which, in his index of spectra, give—

Huggins, 32 for oxygen, and nitrogen 78. The question first to be decided was, which of all that multitude of lines are atmospheric lines, which sulphur, calcium, manganese, phosphorus, &c., &c. It was very soon obvious that the spectra obtained from Geissler's vacuum tubes, although most beautifully made and contrived, gave the spectra under totally different conditions from those in which they exist in our iron. The curve recommended by Dr. Watts was tried, but the author found that the construction of the spectroscop was such that he could not work with certainty and accuracy. After many trials and experiments, with the details of which it is needless to trouble the Institute, he determined to work wholly by spectra of comparison. But considerable difficulty arose with silica, alumina, and sulphur, as well as phosphorus. First, as to the means of holding them as electrodes; secondly, they are very bad conductors. A piece of fire brick, held in the nippers, will give no spectrum, the spark jumps over it in the most clever way, and gives nothing but the spectrum of the nippers, be they brass or steel. Some of the small tubes, samples of which are on the table, were made—they are shown at No. 7 in the drawing. The object here was to bury the electrode in the pounded fire brick, and force the current to pass through it. These are obviously a modification of Geissler's tubes. The lines of silica and alumina shine out with splendour, but they do not last long, the glass gets coated with the material which is decomposed by the spark, and forms a conductor, the spark only passing in fitful flashes as at X, and giving but very little light; on the whole, the best way of charging the tube is, as shown at the drawing No. 8, letting the platinum electrode come through the throat of the tube, and burying the lower electrode in the powder under examination; this has the further advantage that the spectrum of the glass itself does not intrude, the lines of the platinum must, of course, be noted, and not confused with those of the powder. The spectra of iron ores come out very well by this method. The nozzles A B are for letting in gas. This being the most difficult spectrum with which the author has had to deal, he has thought it better to explain it before proceeding to phosphorus, which forms the main subject of the paper. The phosphorus lines were got in this way—a small hole was drilled into a piece of carbon and filled up with phosphorus, the

phosphorus worked over the carbon like the head of a rivet, so that the spark could not get from one carbon electrode to the other without volatilizing the phosphorus; but it is quite obvious that this method would not do in atmospheric air, the spectrum must be taken in a gas with which the phosphorus could not enter into combustion, or it would simply light in the spark, combine with the oxygen, and fill the cylinder with phosphoric acid. Carbonic acid, hydrogen, or the common coal gas, all do very well for this. A special apparatus, however, had to be fitted up, which is on the table, and is shown on the drawing at No. 2. The lines of phosphorus on a carbon point, taken in this way in coal gas, are shown on the spectrum on the drawing at No. 9. It will be seen at once that the characteristic features of phosphorus are seven broad bands in the green, there are also three very peculiar lines in the red, like a wicket with the middle stump thinner than the other two. There is also the same kind of group in sulphur, but in a different position in the red, by no means coincident. The lines of both sulphur and phosphorus are got by comparison, that is, one pair of electrodes were prepared with a phosphorus point, as before described, and another pair, from exactly the same carbon, were prepared without phosphorus; each pair was fitted into one of the glass cylinders, the cylinders were filled with coal gas, each with a separate branch pipe, and the gas lit, the pair of plain carbon electrodes were arranged in front of the slit of the collimator of the spectro-scope, and the phosphorus pair were arranged opposite the cross prism, or prism of comparison. The two spectra are seen—the phosphorus above, and the carbon below, in the usual way. The lines which coincide are those of carbon and coal gas, a beautiful spectrum well worthy of study, but one with which for the present we have nothing to do. The lines which do not coincide are those of phosphorus and anything the phosphorus may contain; the readings on the dividing plate must be carefully noted. We have now to look for phosphorus in our iron. The plain carbon points must be removed—the nippers replaced with a clean pair, the cylinder covers cleaned, and the iron electrodes, to be examined, put in. The iron is now in air, the phosphorus in coal gas, the lines which coincide are produced by phosphorus in the iron which is decomposed by the spark, taking

care to note which were the readings taken as phosphorus lines in the last experiment, for there may be silicon, sulphur, and other impurities in the carbon—there is certainly also carbon itself, all of which are present in the iron. There is, however, little or no risk of any confusion on this point. All the coincident lines in ordinary pig, puddled, or bar iron, are in the green, or very near to it. The seven lines or bands of the phosphorus are much broader, those of fairly good iron, very fine, sharp, and bright. The idea struck the author, are not those iron lines brighter than the phosphorus itself, because they are in an atmosphere containing oxygen? The question was soon put and answered, the coal gas was let into the iron cylinder, and the lines vanished entirely; but the spectrum of coal gas does not do very well for this purpose. It has numerous lines of its own, which have to be eliminated, the part of the spectrum—the green—where the characteristic lines of phosphorus occur, is ruled all over by the most extraordinary number of dark absorption lines, through the intervals of which the brighter parts of the continuous spectrum of the spark are seen. It is most difficult to determine whether these are, as supposed, bright spaces of a superimposed spectrum, or lines. Hydrogen gas is much better as an absorber, or as a gas in which, oxygen being absent, no combustion can take place. It is needless to point out here that, in using hydrogen, the greatest care must be taken to avoid explosions. The practice in these experiments has been to fill all the cylinders and pipes with coal gas, light it, and to displace this gas with hydrogen. It is found that, when there are twelve cubic inches of hydrogen, as measured by the graduated bottle hereafter to be described, the carbon rulings (if that can be accepted as a proper term) disappear. The lines of the spectrum, which in air are bright, and which coincide with those of phosphorus and sulphur, are completely blotted out or absorbed. The conclusion which the author has come to is that, when small quantities of phosphorus or other matters are present in the electrodes, they require oxygen in some form to bring them out as bright lines. He is confirmed in this view by other writers. In Schellen's *Spectrum Analysis*, page 162, after describing Professor Tyndall's discovery of another line in Lithium, in the intense heat of the Voltaic arc, he says: "If a few grains of common salt be dropped into the flame of a Bunsen burner, there is emitted

an intense light of one colour, producing the spectrum of a single yellow line. If the temperature of the flame be raised by a further supply of oxygen, the brilliancy of this line is immediately augmented, and the number of coloured lines so much increased, as to approach somewhat to a continuous spectrum." It may be that the lines are only obscured by the spectrum of hydrogen as a screen, or as a piece of coloured glass. If this should prove the correct explanation, it can, just as well as the first supposition, which the author has accepted as the true one, be used as a means of measuring the quantity present in the spark, and arriving at a correct estimation of that quantity by the spectrum analysis. By the first supposition, we calculate the quantity inversely, as the quantity of oxygen, or a compound of oxygen used; by the second, we alter the character and condition of the screen, it becomes less dense by admixture with the oxygen compound, until the line is able to penetrate. If a large quantity of phosphorus is undergoing deflagration at the electrodes, it will penetrate a screen of considerable density. If a small quantity only is undergoing decomposition, the density of the screen must be reduced, until the line can penetrate it; in either case the quantity can be estimated inversely, as the quantity of oxygen that has been used, or on same ratio as represented by the curve on the drawing, No. 1. In comparing a phosphide of iron with phosphorus, or a sulphide of iron with sulphur, the quantity of sulphur and phosphorus has power to penetrate the gas, but some of the lines at the red end of the spectrum are missing. To return, then, to the main subject of the paper. At No. 9 on the drawings, is shown by the characteristic lines of phosphorus, the lines were taken as before described on carbon electrodes tipped with phosphorus—some lines which are exceedingly fine have been omitted as doubtful. In this spectrum we have 21 lines; Dr. Watt's gives 47, as found by Plücker, but as to how the spectrum was taken, whether as a vapour at atmospheric pressure, or in a vacuum tube, he gives no information. The principle, which the author has introduced to the Institute, of course requires further investigation; but the fact does seem to him to be confirmed by such experiments as he has been able to apply, which is this, that an atmosphere of hydrogen gas, or a gas composed of the ordinary coal gas from the gas works, with

an admixture of hydrogen, has power to absorb completely the phosphorus lines in iron, even when there is as much as 3.334 per cent. of phosphorus present—that no sign of phosphorus is seen in the spectrum in an atmosphere of this gas—that on the admission of a very small amount of oxygen, the line does appear—that when very small quantities of phosphorus are present, a very much larger quantity of oxygen must be admitted, to make the line shine out as a bright line. The experiments which have led to this result have spread over many months, and have absorbed almost all the author's leisure time; they will, however, be explained in a few minutes. They extend over several samples of iron, from which a selection has been made, ranging from .550 of phosphorus to .021. From these samples, the curve shown at No. 1 on the drawings has been constructed; it will be observed that they do not proceed in a direct ratio, but in the form of a curve. If, as the author hopes, the principle is right—but on this he wishes to speak with great diffidence—he has lived to see many splendid inventions of the patent office and lecture room blown into thin air, when they get into the practical operations of the laboratory and the workshop, that he would use due caution. In the present state of his knowledge on the subject he would proceed to an analysis of iron, with the apparatus now on the table, and set forth on the drawings, in this way:—We propose, in this case, to deal with materials suitable for the Siemens steel furnace, either by Dr. Siemens' open-hearth furnace or by the Siemens-Martin process. For the quality we propose to make we will assume that we must not have more than .050 of phosphorus. A few pieces are chipped from the pig iron to be used, from these a pair of electrodes are filled up, they are placed in the nippers, and put into the glass cylinder shown at No. 2. We should place the phosphorus electrodes themselves in the cylinder shown at No. 3, let coal gas into No. 3, and turn on the current; when the spectroscope is adjusted, we should see that there are seven broad lines in the green, that the band marked $181^{\circ} 6\frac{1}{2}'$ in the green has a decided unmistakable coincident in iron. The current must not be kept on long, as the iron is in air it will be very rapidly coated with oxide, except to satisfy the observer that it is coincident, it is better not to turn on the current when the iron is in air, because the

oxide will be decomposed, and upset the subsequent calculations. Coal gas is next let into the cylinder and pipes, and lit at such portion of the pipes, and at the cylinder, as will ensure that all the atmospheric air has been driven out. The hydrogen gas holder is now connected, and the gas turned on. At No. 4 of the drawings the graduated bottle is shown; this bottle is drawn $3\frac{1}{8}$ in. diameter, so as to get 12 in. area. The bottle actually used in the experiments is an old barley sugar bottle, and can be graduated accurately to whatever its diameter may be, by weighing twelve cubic inches, marking the space on the bottle, and graduating it accordingly. This bottle forms a very important part of the apparatus. It is fitted with a syphon pipe, shown at No. 5. When the cock at the long leg is opened, and all the cocks to the cylinder and gas holder are also opened, the water runs out of the bottle into the bucket shown at No. 6. The coal gas in the cylinder, No. 2, flows out and takes its place, and the hydrogen from the gas holder follows and takes the place of the coal gas, or mixes with it. The practice in these experiments has been to let in, in this way, 12 cubic inches of gas as measured by the bottle, and to examine the spectrum for air lines; the practised eye will detect these in a moment. If the air lines are in the spectrum, this gas is not pure, oxygen is present, the hydrogen is unfit for use, or the pipes have not been properly cleared of air. With 12 inches of hydrogen which has been carefully prepared, the line, the reading of which on this particular instrument is $181^{\circ} 6\frac{1}{2}'$ is completely blotted out, a continuous hazy-looking spectrum with indications of lines at various parts, but the line $181^{\circ} 6\frac{1}{2}'$ has completely vanished. We have next to ascertain what quantity of oxygen will be required to make $181^{\circ} 6\frac{1}{2}'$ come out as a bright line. The hydrogen must be disconnected, and carbonic acid connected, taking care, of course, to exclude the air, 36 cubic inches are required to bring out a bright line. This iron may with confidence be passed and used, it drops on to the curve just at 36, showing that it has .021 per cent. Supposing that we are working the Siemens-Martin process—the next sample submitted to the spectrum analysis we will suppose to be puddled iron, it is tried with hydrogen and there is no line, the carbonic acid is let in as

before, at short intervals, and in quantities as measured by $\frac{1}{4}$ on the graduated scale, which is equal to 3 cubic inches, with the second admission of 3 inches, making in all, 6 cubic inches, the line is bright, the iron is very bad, it contains .550 of phosphorus, and may, with great confidence, be rejected. The curve was obtained by only 4 samples, containing—of phosphorus

.550 H.

.301 F.

.050 I.

.021 G.

Should this system come into general use, it is very probable that some such form of apparatus, as shown at No. 12 on the drawings, will be found the best, because greater quantities of the material under examination can be brought under the action of the spark. Iron, in the form of filings, gives a very fine spectrum in this way. Wishing to try on samples of iron containing larger quantities of phosphorus, the author asked Mr. Edward Riley to send him some of those from which he had made analyses—that gentleman kindly sent him five samples—ranging from 3.334 per cent. to .027, a sample containing .081 was tried and fell into its place in the curve in a very satisfactory way. The sample containing 3.334 was also examined, and it was found, that when such large quantities are present, other lines must be taken into account—the line $181.6\frac{1}{2}$ is wholly absorbed by the hydrogen, with six cubic inches of carbonic acid; it came out as a great broad band, nearly as broad as that of the phosphorus. Other lines came out which do not appear in iron, containing .550; these lines are nearer the blue. The special part of the apparatus for the examination of such materials as cannot be made into electrodes is also shown on the drawings. Samples of them are on the table. Figure 10 is a modification of Bequerell tube, which is used generally for the examination of solutions. A great objection has been found to using them as open tubes, with a fluid, quantities of it are scattered by the action of the spark, to the great injury of the slit of the spectroscope and the eyes of the operator. The same objection holds good with a powder. A plain glass, as shown at No. 12, would probably be a better form of apparatus than any before mentioned. It would be better to pass the platinum electrode

through a glass tube so as to insulate it from the stopper, because the deflagration from either a fluid or a powder so coats the glass and the face of the stopper that the current passes that way; the glass rod, should it also become coated, is easily cleaned by drawing it up through the cork and wiping the coating from it, and ensuring that the circuit can be made only by passing from the platinum electrode to the fluid or the powder. The subject of such large quantities as 2, 3, or more per cent., requires further experiment. The time of the Institute is valuable, and must not be taken up in dealing with suppositions. The author wishes to adhere to the subject of the paper—the estimation of small quantities of phosphorus in iron and steel by the spectrum analysis. As time goes on, should he be so fortunate as to gain more knowledge and experience, he will have great pleasure in bringing this matter forward again, hoping that other members who have taken up this most important subject, or who may be induced by this introduction of it to do so, will do the same.

through a glass tube as to insulate it from the stopper because
the diffusion from either a fluid or a powder coats the glass
and the face of the stopper thus the current passes the way
the glass rod, should it also become coated, it easily cleaves
by drawing it up through the cork and wiping the coating from it
and ensuring that the circuit can be made only by passing from the
platinum electrode to the fluid or the powder. The subject of such
large quantities as 2, 3, or more percent required, all a very important
The time of the instrument is valuable and must not be taken up in
dealing with suggestions. The author wishes to refer to the
subject of the paper—the estimation of small quantities of phos-
phorus in iron and steel by the spectrometric method. As this paper
should be so fortunate as to gain more knowledge and
experience, he will have great pleasure in bringing his matter
forward again, hoping that other members who have taken
in this most important subject, or who may be induced
this resolution of it to do so, will be the same.