THE USE OF QUARTZ COMBUSTION TUBES ESPECIALLY FOR THE DIRECT DETERMINATION OF CARBON IN STEEL.

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During the last two years a new material, fused quartz, has come into use in analytical laboratories. The present paper deals with some applications of fused quartz tubes to high-temperature work, for which their great resistance to sudden changes of temperature renders them very suitable. Quartz ware is obtainable in two varieties: in the transparent, fully fused state, and in the opaque, partly fused

form. The first of these varieties is distinguished chiefly by the ease with which apparatus of any shape, not too large, can be made, and by its high price. The second, so-called "vitreous," variety is a much less costly material, but possesses the disadvantage that particles flake off; hence it is not suitable for crucibles out of which precipitates are brushed before weighing.

Analysis of a sample of each kind of quartz tube gave the following results:

	Clear. Per Cent.	Vitreous. Per Cent.
Silica (by difference)	99·77	99·77
Alumina and iron oxide	0·12	0·15
Lime	nil	0·04
Magnesia	nil	trace
Sodium oxide	0·11	0·04
	100·00	100·00

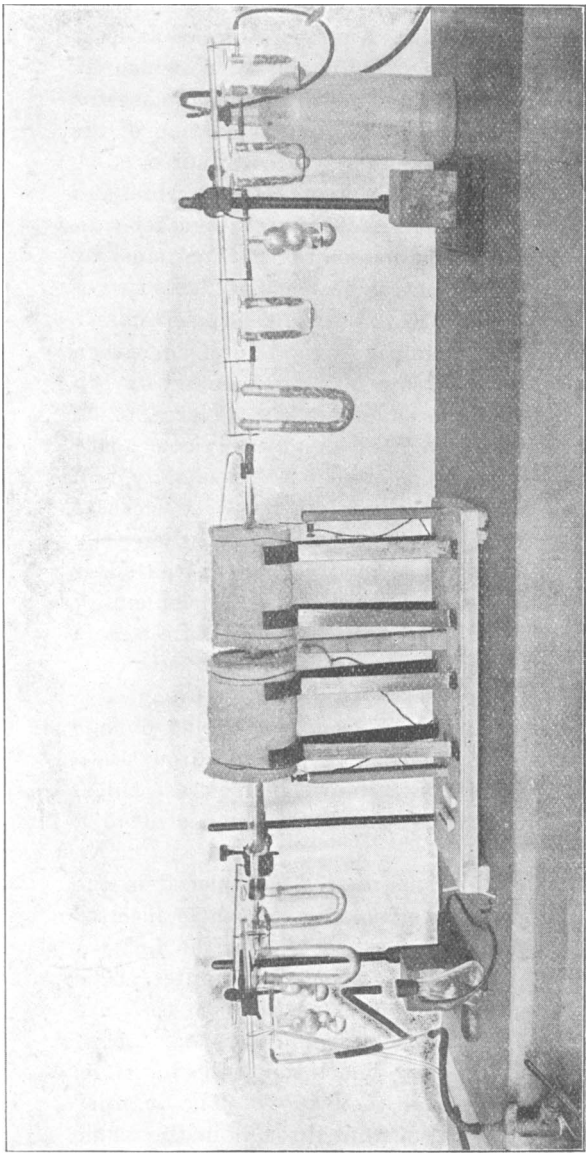
Organic Combustion.—The first use to which we put quartz was to replace the tubes commonly used for organic combustions. It was found that tubes of clear silica were well suited to this purpose, they being much longer-lived than glass tubes. The higher temperature possible also renders combustion of volatile liquids, the vapours of which need rapid oxidation, a much easier matter than with glass Unless an altogether excessive temperature is reached, silica withstands the action of the usual packing agents, such as copper oxide and lead chromate, very well—better, in fact, than does glass. It was found, however, that at about 900° C. copper oxide rapidly attacks and destroys quartz tubes, so that some care is necessary in regulating the temperature.

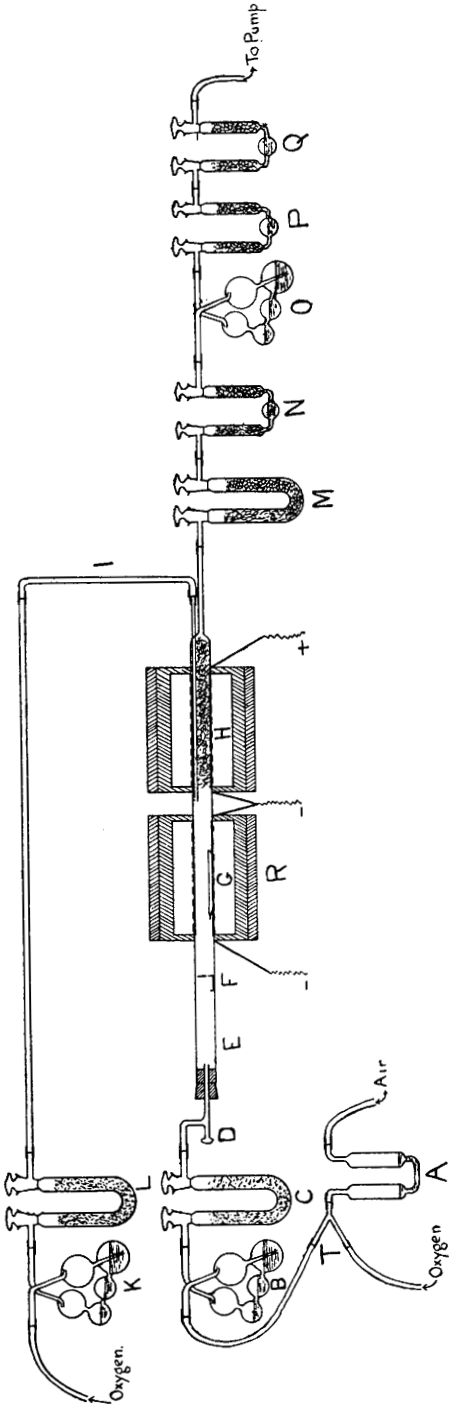
Determination of Oxygen in Copper.—We next proceeded to use quartz tubes for the determination of oxygen in copper by fusion in hydrogen. For this purpose a tube of clear silica, 275 mm. long by 13 mm. bore, joined at one end to a quartz tube 25 mm. long by 4 mm. bore, is wound with very thin platinum foil obtained from Heræus—a strip of foil about 1,500 mm. long, 4 mm. wide, and 0·007 mm. thick, being used. The resistance of this winding, when cold, is about 15 ohms, and when heated to about 1,200° C., 26 ohms. The leads at the ends are made of stout platinum wire. The tube is supported by uralite discs in the centre of a fireclay cylinder 75 mm. in diameter with walls about 6 mm. in thickness. This cylinder is wrapped round with asbestos cloth. The furnace is constructed for a 200-volt circuit; it is started in series with an adjustable resistance of not less than 25 ohms, which is gradually lowered to about 7 ohms, so as to keep the current constant at 6 ampères. In this apparatus a piece of copper, weighing 10 to 15 grams, is completely fused in three to five minutes. As the furnace cools in about ten minutes, successive determinations of oxygen in copper are easily carried out in twenty-five minutes each—a considerable saving in time as compared with older methods of heating. One such tube has now been in use for about eight months, has not needed any repairs in that time, and is still in good condition. Recently, from experience gained by this earlier procedure, a second furnace was constructed, in which foil composed of 5 per cent. iridium-platinum alloy was used, with leads of platinum foil, 5 mm. wide by 0·03 mm. thick,

soldered outside the fireclay cylinder to small silver forks. The iridium-platinum alloy withstands heating better than does platinum; the new form of lead represents a considerable saving in precious metal. This second form of furnace will probably last even longer than the first. In passing, it may be mentioned that the hydrogen generator used is of the form described by Browne and Brown (*Journ. Amer. Chem. Soc.*, 1907, **29**, 859; ANALYST, 1907, **32**, 344). This generator gives a constant stream of hydrogen for many hours, though, curiously enough, it works badly when used for generating hydrogen sulphide. It should be stated that a furnace similar to the above has been described by Professor S. A. Tucker (*Journ. Amer. Chem. Soc.*, 1907, **29**, 1442; ANALYST, 1907, **32**, 435) for low voltage currents.

Determination of Carbon in Steel.—It has been shown previously (B. Blount, ANALYST, 1900, **25**, 141) that even stout fragments of steel are completely oxidised when burnt in a stream of oxygen, provided only that the temperature used is high enough, and *prima facie* a furnace of the type described seems suitable for the direct combustion of carbon in steel. The problem presented here is, however, essentially different from the last—viz., the determination of oxygen in copper. Metals kept free from oxide by hydrogen do not attack silica, however high the temperature. The very nature of the process of combustion of steel involves the presence of metallic oxides, which, at the temperature used, instantly and thoroughly destroy quartz tubes. Steel, when burning in oxygen at high temperature, gives off sparks of incandescent material, which are projected with considerable force for some distance. If air only is used, a very large quantity of gases must be passed through the purifying and absorbing apparatus, and the time required by the process is correspondingly increased. Heating must be continued for a considerable time at a high temperature, thus subjecting the platinum resistance to a severe strain. During the burning of the steel a large quantity of oxygen is suddenly absorbed, necessitating, unless special arrangements are made, anxious manipulation of the oxygen supply to prevent entry of air at the wrong end of the tube. To meet these difficulties the apparatus shown in the figure and photograph (p. 91) was evolved, after preliminary experiments had shown that the foil used in Heræus furnaces is too thin to withstand the prolonged heating repeatedly; that platinised quartz does not completely oxidise the carbon monoxide evolved unless supplementary oxgen is supplied to it; and that combustion in air alone lengthens the process unduly. The apparatus described has now been in use for some time, and is used as a matter of routine to check the results obtained by the solution process.

Referring to the figure, combustion is carried out in a tube of clear silica, E, 525 mm. long and 22 mm. in bore, joined at one end to a clear silica tube 75 mm. long and 5 mm. in bore. At the drawn-out end of the wide tube a narrow silica tube is sealed into it, which terminates inside the wide tube at a point 175 mm. from this end, and projects for 75 mm. outside the tube, being joined by a rubber connection to a glass tube, I. Two sections of the wide tube, each 150 mm. long, 25 mm. apart, and placed close to the drawn-out end of the tube, are separately wound with iridium-platinum foil, the portion nearest the open end, G, being wound with foil 3 to 3·5 mm. wide and 0·015 mm. thick, whilst the other section, H, is wound with foil 4 mm. wide and of about the same thickness. The leads are made of stouter





platinum foil soldered to silver forks screwed to the three terminals. The sections are wired so that the main current of 200 volts can be sent, through an adjustable outside resistance, either through the farther section, H, only, or through the two sections in series with each other. The relative resistance of the two windings is calculated so that when they are placed in series, using a current of 5·5 ampères, section H is heated to a dull red heat, and section G to a temperature of at least 1,050° C. Each section is enclosed in two fireclay semicylinders, R, S, which fit tightly on the quartz tube, and which are further protected by wrappings of asbestos cloth secured by copper wire. The section G serves for the actual heating of the boat containing the steel; injury to the tube from sparks is prevented by surrounding the boat with a piece of iridium-platinum foil, 150 mm. long, 80 mm. wide, and 0·03 mm. thick, which is rolled into the form of a tube and inserted together with the boat. The latter itself is protected from the action of the burning steel by placing a layer of well-ignited alumina in the bottom. One boat usually lasts two or three times. The farther section H is packed with a mixture of platinised quartz and platinum scrap, so as to form a sort of contact chamber; oxidation of the carbon monoxide evolved is effected here by means of a stream of supplementary oxygen introduced through the narrow tube, I. Most of the small quantity of ferric oxide projected from the boat collects harmlessly in the short, comparatively cool space between the two sections. The "contact mass" is emptied out occasionally, and cleaned by boiling with hydrochloric acid. A piece of silver foil, F, placed close to the boat section protects the rubber stopper from the intense radiation characteristic of quartz tubes. The spy-hole, D, is placed in alignment with a hole in the silver shield, and enables the combustion to be watched to some extent. The supplementary oxygen is purified by the potash bulbs, K, and soda-lime tube, L. The main stream of oxygen and the air used to sweep out the weighed bulbs are purified by a second set of bulbs, B, and soda-lime tube, C. The oxygen passes to the bulbs through two arms of a Y-tube, T, the third arm being joined to a trap, A, leading to the air outside the laboratory. The gases leaving the quartz tube are dried by passing through two sulphuric acid tubes, M and N. They then pass through the weighed potash bulbs, O, and sulphuric acid tube, P, to a sulphuric acid guard-tube connected to a water-pump.

Coming to the actual process of combustion, 5 grams of steel are placed in the boat, the latter is pushed into its iridium-platinum envelope, and the whole inserted in the quartz tube by means of a rubber-tipped rod pressed against the foil. A current of about 7 ampères is sent through section H for about five minutes. The pump is started, a slow current of supplementary oxygen is passed into the tube through I, and the main current of oxygen supplied at such a rate that, whilst about four bubbles pass through the potash bulbs, B, for every one through the bulbs, K, about the same quantity of oxygen goes to waste through the trap, A. The quantity of gases passing through the weighed potash bulbs is constant throughout the whole combustion, being regulated only by the suction of the pump. As soon as the platinised quartz has attained a dull red heat, the current is sent through both windings, being kept at 5·5 to 6 ampères by means of the adjustable outside resistance. After about one minute this resistance is taken out. At this point the

boat section, G, is at a bright red heat, and almost immediately after the steel begins to burn. As a large quantity of oxygen is required for the oxidation of the steel, the oxygen which was bubbling to waste during the preliminary operations is sucked into the tube. After a short time air also enters through the trap A; combustion slackens until most of the nitrogen has been sucked out of the tube and an atmosphere of oxygen restored. Violent oxidation then begins again, and is again checked as before. As a rule there are three well-marked periods of energetic oxidation in each combustion, lasting altogether five to ten minutes. The time during which the steel is heated in oxygen is twenty minutes for ordinary drillings or planings, and thirty to forty minutes for stout fragments. At the end of this time, both supplies of oxygen and the electric current are shut off, and air is sucked into the combustion tube through the trap, A, for another twenty minutes, after which the bulbs are placed on the balance for twenty minutes. It will be seen that for ordinary samples of steel successive combustions require sixty-five minutes, and that, as the oxygen supply regulates itself automatically, the operator need give attention to the combustion at four periods only for a few minutes at a time. The device of passing oxygen into a combustion tube from a Y-tube, and applying suction at the other end of the tube, has been in use for the combustion of volatile liquids for several years, and there also works well.

In the table on p. 94 the results obtained on typical steels and pig-irons are compared with those obtained by the solution method, a neutral solution of the double chlorides of copper and potassium being used.

The results for steels differ by less than 0·02 per cent. from those given by the solution method, and agree well with each other. Blanks also, and combustion of diamond, are satisfactory, the blanks varying from 0·004 to 0·008 per cent., expressed as carbon on 5 grams of steel, as against 0·005 to 0·009 per cent. for the solution method. The blanks are *complete* in each case, only the steel being omitted. The direct method compares favourably with the solution method as regards length of time required and work involved. Drillings of any ordinary thickness may be handled; thin drillings, as required for the direct combustion methods of Johnson (*Journ. Amer. Chem. Soc.*, 1908, **30**, 773; ANALYST, 1908, **33**, 288) and Rosenhain (*Journ. Iron and Steel Institute*, 1908, No. I., 96), are unnecessary. Stout drillings of steel are completely burnt if the time is moderately extended. Regarding sources of error, that due to the possible formation of sulphur dioxide is the most apparent. This gas would pass through the sulphuric acid tubes, be absorbed in the potash bulbs, and weighed as carbon dioxide. Chromic acid might be placed in one of the sulphuric acid tubes to stop this sulphur dioxide; but, as a matter of fact, it has been shown, by repeatedly passing the gases from burning steel and pig-iron through a dilute solution of potassium permanganate acidified with nitric acid, or through a solution of barium hydroxide, immediately after leaving the combustion tube, that neither sulphur trioxide nor dioxide leaves the tube. Incidentally it was found that a large proportion of the sulphur present is evolved from the burning metal, and condenses in the form of minute drops of sulphuric acid inside the wide quartz tube at the point where it is joined to the narrow tube.

The drawbacks of the method are these. Care is required not to spill the steel

Sample.	Solution Method. Per Cent. Carbon.	Direct Method. Per Cent. Carbon.	Difference.
Diamond, 0·0537 gram corresponding to 1·074 per cent. of carbon when 5 grams of steel are taken	—	1·089	+0·015
Tram-rail	0·553	0·535	−0·017
,, ...	—	0·537	
,, plus 0·504 per cent. diamond	—	1·034	−0·023
Carriage-tyre, 1	0·571	0·573	+0·002
,, 2	0·585	0·575	+0·002
,, 2	0·559	0·572	
Carriage-axle, 1	0·425	0·432	+0·007
,, 2	0·439	0·407	−0·021
,, 2	0·425	0·415	
,, 3	0·393	0·409	+0·016
,, 4	0·357	0·385	+0·016
,, 4	0·359	0·366	
,, 4	—	0·372	
,, 4, resampled ...	0·359	0·372	+0·013
,, 5	0·340	0·345	−0·006
,, 5	0·341	0·331	
,, 5	0·343	0·330	
,, 5	0·335	0·328	
,, 5	0·339	—	—
,, 6	0·315	0·322	+0·007
,, 7	0·334	0·328	−0·006
,, 8	0·344	0·331	−0·013
Boiler-plate, 1	0·168	0·164	−0·004
,, 2	0·141	0·138	−0·003
,, 3	0·100	0·107	+0·007
Pig-iron, 1	3·987	4·058	+0·071
,, 2	3·802	3·758	−0·044
Complete blank	0·005	0·008	—
,, ,, ...	0·009	0·004	
,, ,, ...	—	0·007	

in inserting the boat, as this infallibly leads to speedy destruction of the quartz tube. The winding of the boat section, although of iridium-platinum foil twice as stout as that used for the furnace for the determination of oxygen described in this paper, fails after about thirty combustions. Although a broken winding is easily patched, since the foil welds very easily, yet after patching a few times, failure becomes so frequent that it is best to remove the winding entirely and replace it by a new one. This operation takes about an hour. Apparently the high temperature used injures the foil in some way. The quartz tube itself lasts a long time if care is used, but gradually becomes devitrified.

For the solution method, also, the porcelain tubes used for the combustion of the separated carbon have been replaced by quartz tubes, in this case of the "vitreous" or translucent variety. The tube is drawn out at the farther end, thus doing away with the cap or stopper formerly used. Copper oxide is used as auxiliary oxidant; to protect the tube, the copper oxide is enclosed in a sheet of iridium-platinum foil 0·03 mm. thick, rolled into the form of a tube closely fitting the quartz tube. The column of copper oxide is kept in place by fragments of quartz placed at both ends. Combustion takes considerably less time than formerly, as the burners may be at once turned up to their full extent. The plugs must, however, be washed free from copper chloride; if this is not done, copper oxide may be deposited inside the quartz tube and will destroy it. The quartz tubes last much longer than porcelain tubes, and stand rougher treatment.

Marsh-Berzelius Test for Arsenic.—Some years ago we constructed a small electric furnace, at Dr. Bernard Dyer's request, for heating the glass tubes used in the Marsh-Berzelius test for arsenic. Although quartz does not enter into its construction, this furnace may be described here. The problem of how to dispose of 200 volts in the short length available was finally solved by winding fine platinum wire (B.W.G., No. 40) forty times around a fireclay tube 37 mm. long and 27 mm. in external diameter, packing this tube into a second fireclay tube of the same length, and with an external diameter of 35 mm., with kaolin, and winding another twelve turns of the same platinum wire around the outer tube in series with the inner winding. The whole was then packed into a third fireclay tube 75 mm. in diameter, and held in place by uralite discs bound with copper wire, the leads consisting of somewhat stouter platinum wire. The glass tube to be heated was supported by perforated sheets of mica placed at each end. As external resistance a 32 candle-power 100-volt incandescent lamp was used, which was cut out when the furnace became hot. The current used was 1 ampère. The furnace worked well, and is still in existence, but has not yet superseded the Bunsen burner.

Our thanks are due to Mr. H. E. Course for valuable help rendered in connection with the electrical part of the work.

Discussion.

Mr. Blount desired to add that the difficulties encountered in working out the details of this operation were considerable, and had been entirely sustained by Mr. Levy. The regulation of the temperature in the oxidising part of the operation was the fundamental difficulty, and when that was overcome by a difference in winding, the difficulty presented itself of supplying the supplementary oxygen, and supplying it at the proper rate, as well as supplying oxygen for the combustion. It might not, perhaps, be generally realised that one of the chief difficulties was that oxygen must be supplied for the steel as well as for the carbon, and when oxygen was passed in in the ordinary way it was taken up so quickly that no gas passed on, and therefore the present method of supplying supplementary air or oxygen was elaborated. The solution of these practical questions converted a process which

was not very difficult to design in principle into a working success, and this fortunate result was due to Mr. Levy.

Mr. ARCHBUTT said that, while he congratulated the authors on the evolution of this piece of apparatus, he was rather surprised (regarding more particularly the part relating to the determination of carbon in steel) at the ingenuity which seemed to have been expended in making the apparatus complicated. The apparatus which he used for the direct combustion process seemed to him to be very much simpler. In Mr. Blount's paper some years ago the necessity for a very high temperature was pointed out, and at that time he (Mr. Archbutt) only used the direct method for checking purposes. Since then, however, he had found out how to make these direct determinations in an ordinary combustion furnace, and now used no other method except for checking. The necessary temperature could not be obtained in the ordinary Erlenmeyer furnace, but the Griffin furnace, with a single radial burner, answered excellently, giving a temperature of 1,000° C., which was essential. He had begun by doing as some other workers had done—namely, mixing the steel with small pieces of fireclay—but this was found later to be unnecessary, it being sufficient to burn the steel without any admixture of red lead, pieces of fireclay, or anything else. The steel was introduced into small boats of what was known as "asbestos paper," shaped in wooden moulds. These were found to be more suitable than porcelain boats, because they held the steel better and spread it out better, being narrower and longer. The gases passing out of the furnace were very hot, which at first made it impossible to maintain the potash bulbs (which were Geissler bulbs, not like those used by the authors) at constant weight, moisture being driven off from them. This was prevented by attaching to the end of the combustion tube a narrow glass tube, which was bent in the form of a U and placed in water, with the result that the gases were cooled as they passed through the tube. With this arrangement, a current of oxygen could be passed through the apparatus for four hours at the same speed at which the combustions were carried out, without any gain or loss in the weight of the potash bulbs. A difficulty at first experienced was the liability of the ordinary porcelain tubes to breakage. This led him to try the Huxley furnace, supplied by Messrs. Griffin, in which the porcelain tube was surrounded by a fireclay tube, so that the gas-flame impinged on the fireclay tube, the porcelain tube being heated by radiation. Used in that way, the porcelain tubes lasted from twelve to fifteen months. About 3½ inches of copper oxide was placed in the tube just inside the furnace, and 2 inches of lead chromate in the thickness of the wall and just beyond it, as it was not desirable to heat the chromate of lead too much; 2·727 grams of the steel were placed in the asbestos boat (which had been previously ignited in a muffle and cooled in a desiccator), and passed into the tube, which had been already fully heated in the previous combustion. When carbon was being burnt, it could not be run into a fully heated tube, because the carbon would take fire and CO_2 might be lost; but steel could be quite safely run into a red-hot tube. With the asbestos boat there was no risk of cracking the tube by undue chilling. As soon as the steel began to burn, it was simply necessary for someone to stand by the apparatus and feed the oxygen as fast as the steel would take it consistently with its being properly purified. This lasted only a few minutes,

and caused no difficulty; and when that stage was passed, the speed of the current was reduced, and the combustion continued. He had never experienced any difficulty through the potash in the bulbs sucking back. Before the steel was put in, the potash bulbs were weighed full of oxygen at intervals of ten minutes until constant, and when the combustion was finished they were weighed again at similar intervals until constant. The whole process was completed in from three-quarters of an hour to an hour. The results were much the same as the authors', but the tendency seemed for the direct method to give slightly higher results than the solution method, owing, he believed, to the carbon being given a little more accurately. The difference, however, was generally only in the third decimal place. He had not been so successful as the authors in burning pig-iron, owing to fusion taking place, but he was continuing his experiments in this direction. Another advantage of the Huxley furnace might be mentioned—namely, that it would accommodate as many as four tubes at once. This, of course, would be possible with the authors' apparatus, though at the expense, probably, of some further complication.

Dr. Dyer expressed his thanks to Mr. Levy for his care and ingenuity in making for him the small furnace for heating the tubes when testing for arsenic by the Marsh-Berzelius process. The furnace worked excellently—much better than the Bunsen burner. In the electric furnace the heat could be well regulated, but the great point was that it did away with the flicker of the Bunsen burner caused by draughts, and with the consequent frequent annoyance caused by shifting or displacement of mirrors before the deposition was complete.

The President remarked that he had been surprised lately to learn that quartz could be used for vessels of comparatively large size—*e.g.*, basins up to 18 inches in diameter, which could be used for concentrating sulphuric acid. He had never been able to understand why silica glass (*i.e.*, the transparent material) should be so much more expensive than the opaque fused quartz.

Mr. Levy, in reply, said that, although they were aware that composite tubes were being sold, they had had no experience of them as yet, having obtained a stock of the others before composite tubes were put on the market. The composite tubes would probably last very well, though they had the disadvantage that one could not see so well what was going on, or how far the tubes were attacked. It might be mentioned that the electrical direct combustion process could be quite comfortably carried on in an ordinary room without any special ventilating devices, which would certainly not be the case if a Griffin or Huxley furnace, standing on an ordinary laboratory bench, were used. He had made a good many determinations by direct combustion in a gas-furnace, and had always experienced difficulty in supplying sufficient oxygen to the burning steel without getting air in at the other end, unless some sort of trap were used. If four tubes were used in one furnace, it would probably be worth while for an operator to give his whole attention to it; but the process they had described only required attention for a very short time—about four times during the combustion, and then only for about a minute each time. Otherwise it was as nearly automatic as one could make it. With four tubes in one furnace they would probably try cutting out the supplementary oxygen and platinised quartz, and putting in

copper oxide protected by platinum, as in the indirect method; but with one tube only, when the number of determinations was not very large, this probably would not be so convenient as the present arrangement. The difference in cost between the vitreous quartz and the porcelain tubes was not great, and probably Mr. Archbutt would find the superior lasting power of the quartz tubes to be an advantage even when using a gas-furnace for determining carbon in steel. The chief advantage of the electrical heating was that there was no inconvenience from fumes. They had generally found the direct method to give slightly lower results than the indirect The largest piece of quartz apparatus they had tried was a muffle of vitreous quartz