

660. A Conductivity Method for the Accurate Determination of Carbon in Low-carbon Steels.

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A modified conductivity method for the determination of carbon in low-carbon steels (0.1%) with an accuracy of $\pm 1\%$ on samples of approx. 0.3 g. is described.

DURING the investigation of the decarburisation of steel by wet hydrogen, it became necessary to determine carbon concentrations in steels containing less than 0.1% of carbon to an accuracy of $\pm 1\%$ on quantities of metal which contained approximately 100 μg . of carbon. Standard methods, other than the low-pressure method, do not give the required accuracy, but Cain and Maxwell's conductivity method¹ provides the basis for a more accurate technique. They used a standard combustion train and absorbed the carbon dioxide by alkali, the change in resistance of which provided an estimate of the carbon.

Kalina and Joseph² described an absorber with a simple liquid circuit. The oxygen, carrying the carbon dioxide, was injected at the base of a vertical capillary tube causing the liquid to rise; the liquid returned by a tube from the top of the capillary to below the injection point. Ericsson³ improved this system by employing a capillary tube (blown into bulbs for more efficient absorption) leading upwards to a chamber containing a dip-type conductivity cell, while the return circuit was a glass spiral of which the temperature was controlled by thermostat. More recent methods^{4,5} have been directed towards compactness, secured by using a spiral absorption column, the production of a robust apparatus suitable for heavy usage, and greater accuracy.

General Considerations of Apparatus Design.—Size of sample. It was essential that the method should employ as small a sample (0.1—0.5 g.) as possible; the conditions chosen were those most suitable, evaporation losses and the time of determination being borne in mind, for the work in hand and permitting the use of a 0.3-g. sample. Each determination required approximately one hour.

Cell and absorption system. It seemed that the conventional low-frequency, high-frequency, or direct current method could be adopted; the high-frequency method has the advantage that the electrodes are not immersed in the alkali, but requires the screening of the thermostat bath. Use of direct current^{6,7} permits simplification of the electrical circuit, but demands four immersed electrodes. For the low-frequency method, data⁸⁻¹⁰ are available on work carried out at a comparable frequency with potassium chloride, and continuous observation of the readings during the course of the determination can be made. The measurement of the electrical resistance requires to be extremely sensitive (*i.e.*, 1 part in 10,000) and accurate. There must be complete compensation for all reactive effects.

The most suitable frequency is 1—3 kc./sec., and Jones and Bollinger¹¹ have described a cell which has a reliable cell constant over fairly wide ranges of resistance. These authors overcome errors due to polarisation by platinisation of the electrodes by using a frequency greater than 1 kc./sec.; errors due to the Parker effect are minimised by employing as low a frequency as practicable, widest possible separation of electrodes and filling tubes, and a thermostat bath of low dielectric constant.

The cell and carbon dioxide absorber need to be a single unit to avoid errors due to transfer of alkali.

¹ Cain and Maxwell, *Ind. Eng. Chem.*, 1919, **11**, 852.

² Kalina and Joseph, *Heat Treatment and Forging*, 1939, **25**, 169.

³ Ericsson, *Jernkontorets Annaler*, 1944, **128**, 579.

⁴ Gardner, Rowland, and Thomas, *Analyst*, 1950, **75**, 173.

⁵ Still, Dauncey, and Chirnside, *ibid.*, 1954, **79**, 4.

⁶ Gunning and Gordon, *J. Chem. Phys.*, 1942, **10**, 126.

⁷ Brönsted and Nielsen, *Trans. Faraday Soc.*, 1935, **31**, 1478.

⁸ Kohlrausch, *Z. phys. Chem.*, 1888, **2**, 561.

⁹ Parker and Parker, *J. Amer. Chem. Soc.*, 1924, **46**, 312.

¹⁰ Jones and Bradshaw, *ibid.*, 1933, **55**, 1780.

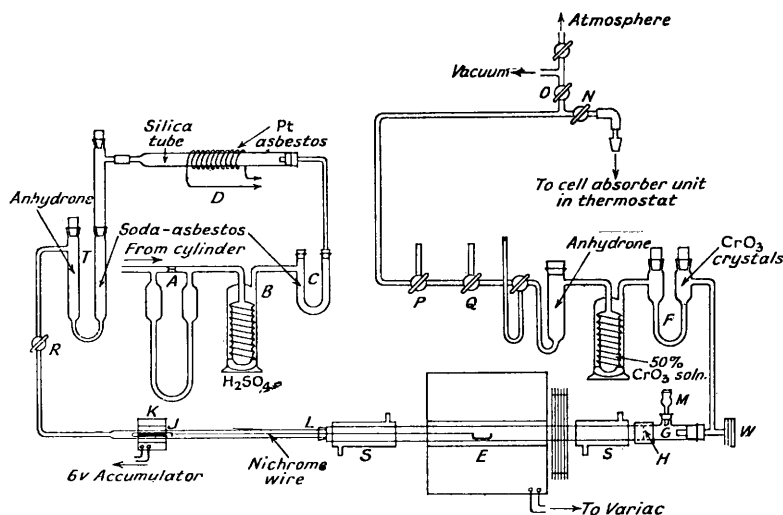
¹¹ Jones and Bollinger, *ibid.*, 1931, **53**, 411.

EXPERIMENTAL

Apparatus.—The train. Oxygen was supplied from a cylinder with a good-quality reducing valve leading to a venturi-type flowmeter *A* (Fig. 1) followed by a Friederich-type spiral bubbler *B* containing concentrated sulphuric acid. The dried gas, freed from carbon dioxide by soda asbestos contained in a U tube *C*, was passed into a platinised asbestos catalyst chamber *D* kept at 1000° to decompose any hydrocarbons and to cause reaction with any hydrogen. The oxygen then entered the furnace *E* through a drier of "Anhydron" and a carbon dioxide trap *T* of soda asbestos. Sulphur dioxide was removed from the gas leaving the furnace in two stages by (a) a U tube *F* packed with chromic anhydride and (b) a Friederich gas-absorption bottle containing a 50% aqueous solution of chromic anhydride. The gas then entered the conductivity cell-absorber unit either directly or *via* the calibration tube.

The furnace. The furnace was a 1" diameter Pythagoras tube 30 in. long, glazed inside. A loading chamber *G* of Pyrex tubing was attached flush to the output end of the furnace by a wide rubber sleeve. The input gases were introduced by means of a long glass tube *L*, which contained a soft-iron slug *J* sealed in a Pyrex envelope. Also sealed into one end of the latter was a semi-rigid nichrome wire which extended into the furnace and was loosely hooked to

FIG. 1.



the combustion boat. The position of the boat could be adjusted therefore by means of the solenoid *K* around the tube *L*, operating on the slug.

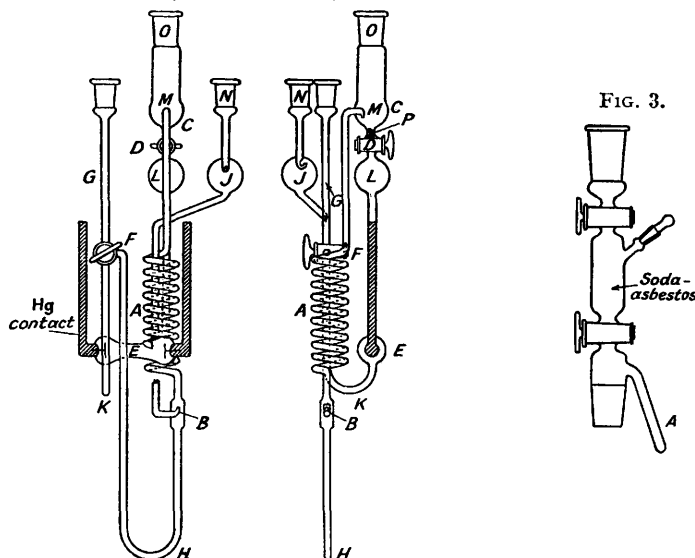
Both ends of the furnace were sealed with rubber joints which were protected from the heat of the furnace and the boat by copper cooling fins and water jackets *S,S*. An 18-gauge Kanthal spiral placed as near to the refractory tube as possible heated the furnace. The element was made by winding a suitable length of wire (75 ft.), without distortion or straining, on a clean $\frac{1}{4}$ in. mandril. Because the Kanthal hardens and embrittles during mechanical working, the spiral was extended slightly, roughly coiled round a 1 in. former, and annealed at 800° for 20 min. by passage of electricity. Six layers of paper were wrapped round the combustion tube, and the spiral was wound accurately in its final position and embedded in alundum cement. When this had hardened, a mullite tube, of 2 in. internal diameter, was cemented over the spiral, and after this cement had set, the inside refractory tube and paper were removed. The compact element was then embedded in tightly packed asbestos and encased in a magnesite brick housing. A "Variac" transformer controlled the temperature (1250–1300° which was found adequate to ignite all the steels). While the apparatus was not in use the furnace was kept at 1000° with a slow stream of oxygen passing through it in order to safeguard the element from damage and to ensure the best performance of the unit.

Thermostat bath. This was an oil-bath regulated by a Lowry-type acetone-mercury regulator and thyatron relay at $25^\circ \pm 0.01^\circ$.

The cell-absorber unit. The design of this unit (Fig. 2) ensured continuous circulation of the alkali. The solution travelled upwards through 90 cm. of 0.2 mm. capillary spiral *A* which had

been blown into 0.5 mm. bulbs at 2 cm. intervals. The liquid was propelled upwards by the oxygen bubbles injected at the jet *B*. The oxygen was released at the jet *M*, while the alkali proceeded downwards through cup *C* and two-way tap *D* into the cell *E* and back to the base of the spiral *A* via tube *K*, the three-way tap *F*, and tube *H*. The cell was filled independently of the absorber, a definite volume of liquid being enclosed between the two taps. There was no "dead" liquid which escaped circulation. *G* served as a filler to provide a head of liquid greater than that at tap *D* until tap *F* was closed to complete the liquid circuit. The extended connection *H* between *F* and *B* prevented passage of gas backwards (*i.e.*, from *B* to *F* and into the cell) owing to back pressure produced by the adsorption spiral. The lead into jet *B* from the train was via a B 14 socket *N* and included a trap *J* to contain the alkali in the event of a partial vacuum being produced as a result of too rapid combustion of the sample. The jet *M* curved back almost to the wall of cup *C* to prevent splashing. To make the unit more robust, Polythene bridges (not shown) were employed as braces. The guard tube (Fig. 3) connected into B 19 socket *O*. The dimensions of the cell were: Interelectrode separation, 5 cm.; electrode area, 1 sq. cm.; height of absorption spiral (10 turns), 13 cm.; external diameter of absorption spiral, 3.5 cm.; total volume of liquid enclosed, 18.45 ml.

FIG. 2. (Drawn to scale.)



Measurement of Cell Resistance.—The electrical circuits used in the cell resistance measurement can be conveniently divided into four parts.

(a) *The oscillator and preamplifier.* The oscillator was designed to provide a stable note of about 1 kc./sec. with the minimum of harmonic distortion. A phase-shift circuit was used containing resistance and capacitance only. This system gave a well-defined balance point with distortion of the order of 0.1% only. The amplifier following served primarily to isolate the oscillator from the bridge, but gave ten-fold distortionless amplification. By using small components a very compact arrangement was possible.

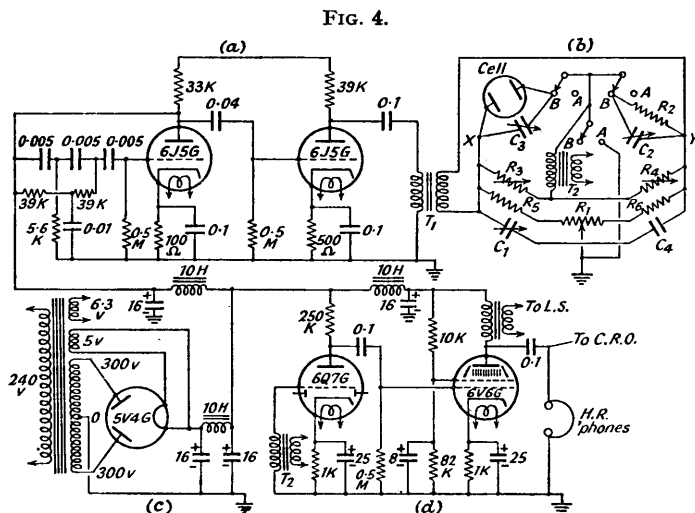
(b) *The bridge.* Owing to the wide separation of the electrodes and the dilute solutions employed, high resistance readings were often obtained. These were comparable to the impedances to earth of the various bridge sections and introduced errors. The Wagner earth was therefore incorporated to provide, with simple switches and adjustment of a potentiometer and variable condenser, that the ratio arms of the bridge were balanced to earth with respect to resistance and reactance. Switching the cell and variable arm into the bridge circuit then gave a true balance. Reference to Fig. 4 shows that the Wagner earth ensured that points *X* and *Y* had exactly the same impedance to earth, *i.e.*, by placing the switch contacts in position *A* and by adjusting R_1 and C_1 to the point of balance. Placing switch contacts in position *B* included the cell and a balancing decade box R_2 and condenser C_2 while the junction of the ratio-arms was disconnected from earth. The accuracy was then of the required degree.

(c) *The power pack and (d) post-bridge amplifier.* These are conventional circuits; indication

of the balance point was given by oscilloscope, loud speaker, or phones, as convenient. In practice ear phones gave a satisfactory balance point.

Manipulation.—Cleaning and drying the cell-absorber unit. Spent alkali was withdrawn with a water-pump and the unit was washed several times with distilled water. The interior of the apparatus was dried by rinsing with acetone followed by a current of air. Silicone stopcock grease was unsatisfactory since the above method of drying soon deposited a water-repelling layer on the interior of the unit which could only be removed by alcoholic potash. With use of a petroleum grease this problem was avoided and periodic cleaning with fuming nitric acid was satisfactory. The electrical connections were made with platinum wire through clean mercury. No amalgamation therefore occurred and the contact tubes remained clean.

Filling the cell-absorber unit. In order to reduce the volume of liquid to a minimum, the cell only was filled, independently of the absorption circuit HAC (Fig. 2). Tap *F* was turned to join *G* to the base of cell *E* through *K*. The top of cell *E* communicated directly to tap *D*.



R_1 , 250 ohms, wire wound rheostat.

R_2 , Muirhead non-inductive decade resistance box (1—10,000 ohms).

R_3 and R_4 , as R_2 , 1000—10,000 ohms.

C_1 , Variable condenser, 0—500 μF .

C_2 , Bank of condensers giving multiples of 100 μF up to 0.01 μF with a variable condenser of 0—500 μF .

C_3 , Bank of condensers, 100 μF —0.001 μF .

C_4 , 200 μF .

T_1 , Wharfedale multi-ratio loudspeaker transformer.

T_2 , Transformer, ratio primary : secondary = 1 : 10.

Conductivity water was added through *G* until it exactly reached tap *D*, which was then turned off, care being taken to exclude air bubbles. Tap *F* was turned to a neutral position while the surplus liquid was removed from *G*, which was then stoppered. This gave an exact volume of liquid in the cell. Tap *D* was opened, and tap *F* turned to connect tube *K* with tube *H* and spiral *A*, which filled with liquid while the level fell in bulb *L*.

Preparation of solution. About 1 g. of sodium amalgam (17% Na, w/w) was placed on a glass-wool pad *P*, by means of a glass spatula, and the carbon dioxide guard tube (Fig. 3) replaced. The water was circulated, and its resistance continually checked until a suitable value was given. The gas flow was then stopped, the liquid allowed to drain away from *P*, and the amalgam tipped into the side-tube *A* to be removed later. The alkali was then circulated for 1 hr. to mix it thoroughly. Thus prepared, the alkali was almost carbonate- and silicate-free, but where many determinations were to be made over the same concentration range a stock solution was employed. This alkali was circulated for about 20 min. to ensure complete mixing.

Operating conditions. The head of liquid and the viscous drag encountered as it passed through the capillaries made an initial pressure of about 30 mm. of Hg necessary before circulation could commence. Back diffusion of atmospheric carbon dioxide was eliminated by the

guard tube. Final readings were made when the liquid had attained the bath temperature; normally 10 min. were necessary, and in summer much shorter times sufficed.

Determination of blank. The blank estimation was conducted under conditions exactly comparable with those in an actual estimation; *i.e.*, the boat (Pythagoras unglazed, size h4 or h5) was placed in the hot zone of the furnace, the speed of gas flow (500 ml./hr.) and temperature of the furnace being identical.

Combustion of a steel sample. The optimum quantity of sample was weighed into a special weighing tube fitted with a B 14 cone. The boat was withdrawn slowly from the furnace (Fig. 1), being allowed to cool before it passed over the rubber joint *H* into the loading chamber. A precautionary increase in gas flow ensured an outward movement of gas through the loading tube *M*, which was lowered to the boat as the sample was inserted. The tube was closed by means of a rubber bung and an excess pressure of 100—120 mm. generated in the apparatus before isolation of the furnace by closing taps *R*, *O*, and *N*. The manometer was observed to verify that leaks were absent, and the boat was towed into the furnace. The vigorous combustion of the steel which followed caused the excess pressure to be reduced, and *R* was opened before the pressure fell to atmospheric, causing a sudden inrush of gas into the furnace which swept the combustion products to the remote end of the train. When the operating pressure had been attained, tap *N* was opened to admit the oxygen and combustion products into the cell-absorber unit. Within 30 min. about 80% of the carbon dioxide had been absorbed and the same flow rate was continued for a further 30 min. The process was generally finished by this time, but the end of the operation was indicated by no further increase in resistance. Finally, the gas was diverted to the air and the liquid allowed to re-attain the bath temperature for the final reading. The metal combustion was observed through the window *W*. Satisfactory ignitions were accompanied by fusion, and several estimations were possible in the same boat. The double-boat procedure of Still *et al.*⁵ was at first employed but abandoned when no cases of fusion to the tube occurred.

Measurement of Change of Resistance.—The cell resistance was rapidly determined by means of an A.C. bridge. The values of the ratio arms were first selected to be of the same order as the cell resistance, followed by adjustment of the Wagner earth. The cell and variable arms were then included, enabling the bridge to operate under the most accurate conditions. The end of the absorption was clearly indicated by the resistance of the cell remaining constant while the alkali was still circulating. The final reading was taken when the cell had attained the bath temperature.

Calculation of Result.—The carbon content could be readily calculated by reference to calibration curves constructed by burning quantities of sucrose containing *ca.* 100 $\mu\text{g.}$ of carbon in the oxygen stream. The change in cell resistance was plotted against the mean resistance of the cell; the calibration curve is illustrated in Fig. 5.

Carbon content is calculated from the following expression :

$$C(\%) = (R_1 - R_2)/(10 \times \Delta r \times \text{wt. of sample})$$

where R_1 = initial resistance of cell, R_2 = final resistance of cell after deduction of blank, Δr = change of resistance in cell when the carbon dioxide from 100 $\mu\text{g.}$ of carbon is passed through the cell-absorber unit while the mean resistance of the cell = $\frac{1}{2}(R_1 + R_2)$. Δr is obtained from the calibration graph (Fig. 5).

Time required for a Determination.—About 70 min. were required for a determination after the blank was known. Undoubtedly, this is long compared with other methods of comparable accuracy, but the investigation to which this method was applied provided only very small samples.

Calibration.—One method^{4,5} is to evaporate known volumes of sugar solution contained in platinum boats over phosphoric oxide in a desiccator, and then to burn off the sugar in the furnace. It was considered more convenient to avoid using the furnace and the following method was adopted.

A sucrose solution containing 100 $\mu\text{g.}$ of carbon in 0.1 ml. of solution was prepared. Small known volumes of this were placed almost half way down the horizontal Pyrex tube *A* (Fig. 6) by means of an "Agl" micrometer syringe, fitted with a 2" needle. The rubber stopper was quickly replaced, and the air withdrawn from the tube through a trap *B* containing phosphoric oxide. The water was removed by gentle heating (inaccurate results were obtained when the water was not removed). Pure oxygen from the train was allowed to enter the tube until the necessary working pressure had been attained to operate the absorber, into which the gases were passed after the trap *B* was removed from their path. The gas flow was continued for 15 min.

in order to sweep all the carbon dioxide out of the calibration tube. The cell liquid was permitted to come to rest and reach the thermostat temperature before the cell resistance was determined. The oxygen flow was restarted, and the tube heated by Bunsen burners at (1) and (2). The heating at (2) was carried out gently, approaching the sugar, so that about 5 min. were needed to burn it off, giving a suitable dilution of the carbon dioxide in the oxygen stream. The heating at (1) was strong and steady and served to burn any volatilised but undecomposed sugar. The final resistance reading was made as described previously. The calibration curve was constructed by plotting the change in cell resistance against the average resistance during the combustion of 100 μg . of carbon. (The values found were reproducible to within $\pm 1\%$.) Recalibration was only carried out when the cell was cleaned and after every month of continuous daily operation.

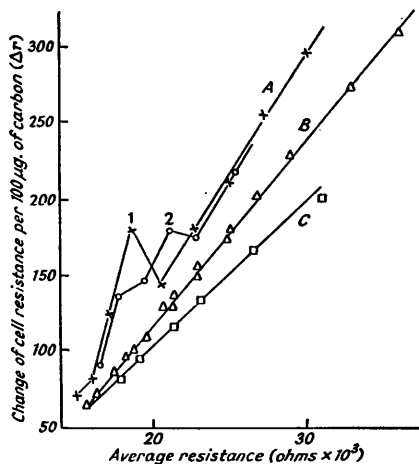


FIG. 5. Solutions, approximately 0.01N of A, $\text{Ba}(\text{OH})_2$ (X, soln. 1; O, soln. 2); B, NaOH; C, LiOH.

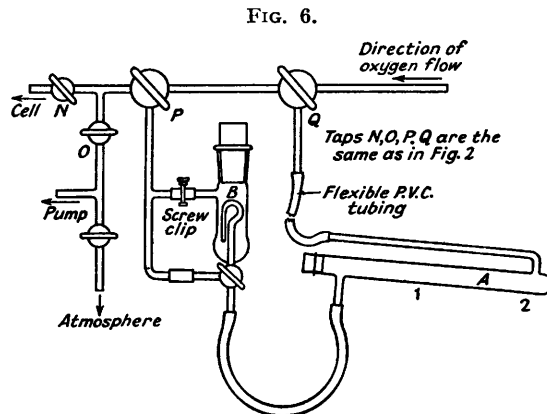


FIG. 6.

DISCUSSION AND RESULTS

Factors influencing Accuracy.—Cell constant. Measurements using a preliminary cell absorber unit indicated that the cell constant did not vary by more than 0.05% [$(24.76 \pm 0.11) \times 10^{-4}$] when using solutions of potassium chloride over the concentration range 0.002–0.1N, which corresponded to the required working ranges.

Change in equivalent conductance of the solution. In absorbing the carbon dioxide from 100 μg . of carbon the 0.01N-alkali underwent an overall change in concentration of 4.5%. At this dilution the change in equivalent conductivity was only 0.04%. Since this apparatus was calibrated directly against carbon these errors were eliminated.

Choice of alkali. Sodium and lithium hydroxides were employed successfully in the cell-absorption unit, giving calibration curves as indicated in Fig. 5. It was found that up to about 40% of the strength of these alkalis could react with the carbon dioxide before hydrolysis of the carbonate became appreciable, causing the specific change in resistance per 100 μg . of carbon to depart from the calibration curve. Carbon dioxide equivalent to 600 μg . of carbon could be absorbed in the 0.01N-alkali before such hydrolysis occurred. Sodium hydroxide was selected since the use of lithium hydroxide held no advantages. Barium hydroxide often gave erratic results, sometimes much higher than expected, with no apparent connection between the deviations. The results for this alkali are also given in Fig. 5. Similar behaviour was observed by Still *et al.*⁵ It was not corrected even when the precipitated carbonate was filtered out of the cell by means of the glass-wool plug P.

Evaporation. Still *et al.*⁵ found that the evaporation losses were approximately 0.1% of the original volume for a 40-min. determination and it was found possible to carry out two successive determinations in the same alkali solution without adverse effect. In the present investigation evaporation losses for a 60-min. determination amounted to only 0.062% of the volume of the solution. At least four determinations therefore were possible

without refilling. In practice, only two or three were carried out, since the unit could be washed out and refilled very quickly.

In more accurate work it is possible to determine the weight of solution lost, by absorbing in drying tubes and then replacing the lost water by means of an "Aglä" micrometer syringe. The present investigation did not merit this degree of accuracy.

Conditions for efficient absorption. The circulation of alkali had to be steady, *i.e.*, it had to move upwards through the spiral at constant speed with regular spacing of bubbles. A flow rate of 500 ml./hr. just permitted this, and greater speeds, *e.g.*, 1 l./hr., were possible without serious loss of accuracy. Lissapol, used by many other workers, caused considerable irregularity in the alkali circulation, and low results were obtained.

Method of making measurement. The most accurate conditions under which a simple bridge circuit can operate is to have the ratio arms equal, and of the same general order as the unknown and variable arms. The use of equal ratio arms also simplified the Wagner earth circuit which comprised two fixed carbon resistors with a central wire-wound potentiometer from which balance was made.

The blank. Since the present investigation was not concerned with alloy steels, the problem of oxidising stable carbides was absent, and also therefore the need for fluxes and igniters which would contribute to a much larger blank. The boat and tube only were responsible for the blank, and it was found that new tubes gave very high figures, *i.e.*, more than 30 μg . for 200 ml. of gas, and new boats often gave 5 μg . Continuous heating of the tube at 1250° for 72 hr. and of the boat for 12 hr. sufficed to reduce the combined blank to below 1 μg . for the duration of a complete run, *i.e.*, 45–60 min. There was no evidence of the gas blank reported by other workers.⁵

Absorption of silicate. This amounts to the equivalent of about 10 μg . of carbon in 24 hr. This error is also accounted for in the blank.

Optimum size of sample. Low results were invariably obtained when the steel sample was too small. Hence the optimum sample size was determined for each range of carbon contents. The major factor appeared to be that enough heat should be generated during combustion to evolve all the carbon dioxide. This determined the minimum size; the maximum was limited by the capacity of the alkali. Generally, 0.3 g. of steel was adequate over the range chosen.

Results.—The precision of the method was satisfactory, since the results given in the Table are reproducible to 1% in general. In order to examine the accuracy of the method,

No.	B.C.S.		Conductivity method			
	Range	Average	Values			Average
237	0.080—0.086	0.083	0.0840, 0.0845, 0.0847			0.0843 \pm 0.0004
152/1	0.067—0.076	0.072	0.0742, 0.0741, 0.0742			0.0740 \pm 0.0004
265	0.043—0.050	0.047	0.0472, 0.0471, 0.0470, 0.0479			0.0473 \pm 0.0006
264	0.033—0.040	0.037	0.0375, 0.0379, 0.0373, 0.0375			0.0375 \pm 0.0004
149	0.002—0.005	0.004	0.0041, 0.0038, 0.0036, 0.0042			0.0039 \pm 0.0003
152	(old sample)	0.1140	0.1130, 0.1125, 0.1128, 0.1122			0.1126 \pm 0.0004

determinations of the carbon content of standard low-carbon steels, issued by the Bureau of Analysed Samples, Ltd., were made. The Table shows the average values and the range of the values found by the individual analysts. Comparison of the carbon content found by this conductivity method shows that the average values in all cases lie within the range of the B.C.S. values, but in general appear to be 1–2% above the B.C.S. average. The analysts providing the figures for the B.C.S. values usually employed sample weights of 2–10 g. to give greater accuracy. The low-pressure method (using 0.5-g. sample) appears to yield values 1–3% lower than the B.C.S. average; the earlier conductivity method⁵ requires the use of 0.5–2 g. samples for the same order of accuracy. It therefore appears that the method described here gives an order of accuracy comparable with other standard methods, with the advantage that only 0.3–0.5 g. of sample is needed for a determination.