the discrepancies are well within the limits of experimental error. In other words, the respiration calorimeter, although complicated and of such size and construction that a man may remain in it with comfort for a number of days or weeks, will measure carbon dioxide, water, and heat given off in the respiration chamber as accurately as these factors are measured by the usual laboratory methods. The accuracy obtained is much greater than with any similar apparatus with which we are familiar.

Improvements in details are constantly being made. In general, it may be fairly said that the object sought has been accomplished; that is, that the balance of income and outgo of matter and energy of the human subject may be accurately measured during comparatively long periods of time.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

ELECTROLYTIC DETERMINATION OF TIN IN TIN ORES.

BY E. D. CAMPBELL AND E. C. CHAMPION.

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IN the methods at present in use for the determination of tin in tin ores, the decomposition is effected by fusion with sodium carbonate and sulphur, in order to form sodium sulphostannate, from which the tin is obtained either by precipitation as sulphide with subsequent ignition to the oxide or by electrolytic deposition from the ammonium sulphide or oxalate solution. Some of the objections to the Rose method of precipitation as stannic sulphide and subsequent weighing as stannic oxide are the difficulties of washing the sulphide free from sodium salts, the ignition to stannic oxide without loss of stannic sulphide, and the contamination of stannic oxide with silica.

Electrolytic deposition of tin from the ammonium sulphide solution does not seem to give entirely satisfactory results, for although the tin may be completely precipitated, it is very difficult to obtain complete deposition without at the same time precipitating some sulphur. On the other hand, under proper conditions tin may be very satisfactorily deposited electrolytically from the double oxalate solution; and in the method herewith proposed the principal modification is in the method of converting the tin from the sulphostannate into the double oxalate. In the method as given by Classen for the conversion of sodium sulphostannate into the double ammonium oxalate, the solution of the sulphostannate is first acidified with sulphuric acid and the tin then oxidized to metastannic acid by means of hydrogen peroxide. The metastannic acid so formed has to be filtered, washed, and dissolved by means of ammonium acid oxalate and oxalic acid, in order to convert it into the double oxalate ready for electrolysis. It was in order to avoid any necessity of precipitating the tin and filtering it out, after it had been once obtained in solution as sodium sulphostannate, that the method given below was perfected. The method in detail, which has given us very satisfactory results on ores tested, is as follows:

Mix one gram of finely ground ore intimately with five to six grams of a fusing mixture made up of equal weights of dry sodium carbonate and sulphur. Place the ore so mixed in a covered porcelain crucible which in turn should be in a larger covered porcelain crucible. This arrangement of double crucibles will prevent oxidation of stannic sulphide during the ignition. Place the crucible upon a triangle and cover with a large Hessian or clay crucible, from which the bottom has been removed, in such a way that the heat from the burner used in the ignition will be kept in, so that the whole of the porcelain crucible will be evenly heated. Raise the temperature of the porcelain crucibles by means of a good burner, such as the Detroit or Fletcher style, to a full red heat, and maintain the temperature for one hour. After allowing it to cool, place the inner crucible in a beaker or casserole and dissolve out the sodium sulphostannate by heating with forty or fifty cc. of water. After complete disintegration of the fused mass, remove the porcelain crucible from the solution and filter out the insoluble oxides and sulphides from the solution, which will contain almost all the tin as sodium sulphostannate. Wash the insoluble residue with hot water. This insoluble residue will usually carry a small amount of tin and must therefore be ignited in the crucible, in which the fusion was performed and after ignition be re-fused as in the first case, with fresh sodium carbonate and sulphur. After fusing the insoluble residue from the first fusion and dissolving out the tin, unite the solutions of sodium sulphostannate. Add to the united solutions of sodium sulphostannate hydrochloric acid, until the solution is slightly acid and the tin has been precipitated as stannic sulphide. Boil down rapidly, until the excess of hydrogen sulphide has been boiled off and the bulk of the solution has been reduced to seventy-five or eighty cc. Add to the hot solution ten cc. of hydrochloric acid (sp. gr. 1.20). Then stir in, a little at a time, sodium peroxide, until the stannic sulphide has been completely oxidized to stannic chloride and the solution has become clear, except for a little sulphur which collects easily on boiling for two or three minutes and can be easily removed by filtering.

The oxidation of stannic sulphide to stannic chloride is very easily effected, requiring usually from two to three grams of sodium peroxide. After oxidizing the stannic sulphide to stannic chloride, boil two or three minutes until the separated sulphur is collected, then filter into a large platinum dish, and wash thoroughly with a little hot water. Add to the solution ammonia until a slight permanent precipitate is obtained, then fifty cc. of a ten per cent. solution of acid ammonium oxalate. This will give a clear solution from which the tin is easily deposited.

Electrolyze over night with a current $N. D._{100} = 0.10$ ampere with an electromotive force of four volts. This current can be obtained from two storage cells using suitable resistance. In the morning the tin will be found to be completely precipitated as a pure white, firmly adherent metal upon the platinum dish. When eight volts E. M. F. were used the deposit was found to be more strongly crystalline and less firmly adherent than when lower voltage was employed. When the tin is completely deposited, disconnect and wash the tin first with water, then with alcohol. Drain off the latter as completely as possible and dry between 80° and 90° C. If the deposited tin is found to have small crystals of ammonium oxalate adhering to it, they may be easily removed by washing with a little warm water before the final washing with alcohol. After weighing the platinum dish containing the precipitated tin, the latter is dissolved off by heating with a little hydrochloric acid and the weight of the platinum dish obtained after washing and drying as before.

In electrolytic determination of metal where they are deposited in platinum dishes, the results will be found to be much more satisfactory, if duplicate determinations are made in platinum dishes of practically the same size, and the dishes are washed, dried, cooled, and weighed under the same conditions, each dish serving as a counterpoise for the other. By using dishes in this way, variations of weight due to atmospheric changes may be reduced to a minimum and the results made more accurate than when a dish is weighed alone.

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ON THE INFLUENCE OF SILICON UPON THE HEAT OF SOLUTION OF COKE CAST IRONS.

BY E. D. CAMPBELL AND WM. E. HARTMAN.

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THE principal object of the following research was to determine if any thermochemical evidence could be obtained indicating a change in the condition in which silicon exists in cast iron, this change being due to differences of the temperature at which the iron is made. It is well known that when the temperature in a blast-furnace passes a certain point, namely, that at which No. 1 foundry iron is made, the color of the cast iron produced changes somewhat as the temperature of the furnace rises. This change continues until it reaches the temperature at which silvery or glazed iron is made, when there is a very abrupt change in the appearance and properties of the iron. It was thought that the appearance peculiar to silvery iron might be due to a change of form in which the silicon exists, and that this change might be indicated thermochemically.

The cast irons used in this work, with the exception of the two ferrosilicons, were all made in the same blast-furnace from approximately the same stock. They were selected from among a large number of samples with a view to obtaining a regularly increasing per cent. of silicon as the temperature at which the iron was produced increased, this temperature being judged by the grade of the iron.

The chemical analyses upon these irons included the deter-