

# FUEL, WATER AND GAS ANALYSIS

FOR STEAM USERS,

By

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With 50 Illustrations.

LONDON.

ARCHIBALD CONSTABLE & CO. LTD.

1907.

**BUTLER & TANNER,  
THE SELWOOD PRINTING WORKS,  
FROME, AND LONDON.**

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## PREFACE.

**S**TEAM-USERS have shown a tendency in the past to neglect the boiler-house for the engine-room, and have concentrated their efforts for the improvement of the efficiency of the plant almost exclusively upon the latter. A study of the losses incurred during the conversion of the thermal energy stored in coal into the thermal energy of steam, will show that it is in the boiler-house that the greater preventable losses are occurring, and that the ratio may be expressed by the numbers 25 and 5.

It is however, now beginning to be recognized that a scientifically managed boiler-house is a *sine qua non* for the economic generation of steam power, and considerable attention is being given by steam-engineers to this portion of their power generating plant.

The chemical examination of the fuel, water, and of the waste gases has been found to be of great service in attaining the highest efficiency from the boiler plant ; but no work has hitherto been published, at once scientific and practical, covering the ground required by the boiler-house engineer.

The author, in the following pages, has therefore attempted to meet a real want, and has brought together descriptions of apparatus and information as to methods of analysis, which it is hoped may prove of value to all engaged in the management of steam boilers.

The descriptions and information are based, as far as possible, upon practical experience with the apparatus and

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methods of work described. Especial attention may be directed to the three chapters in which the practical applications of the test results are illustrated; since, often when tests have been made, there is failure to make use of the information obtained, for improvement of the efficiency of the plant.

It is hoped that a book which is thus based upon science and practice may prove of considerable service to all engineers who are anxious to obtain the highest possible efficiency from their steam generating plant.

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*January 31, 1907.*

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**PART I: FUEL.**

**I**

**B**



## CHAPTER I.

### Natural and Artificial Fuels :—Their Origin, Composition and Methods of Sampling.

THE form in which fuel may be used under steam boilers, in order to produce the heat energy which it is desired to utilize in the form of steam, is exceedingly diverse. Natural fuels are either solid or liquid, but both varieties, by aid of suitable apparatus and plant, may be converted into gaseous fuel. A natural gas which may be used as fuel is also found in certain localities in Europe and America. In the latter country it is largely used for lighting and heating purposes. At the present time there is a decided tendency to employ fuel-gas in place of solid fuel for many purposes in the arts and industries. The control of the combustion process is much more easily carried out when employing fuel-gas than when using solid fuel ; and the loss of heat which occurs in the gas-producing plant is to some extent balanced by the value of the ammonia and tar products, obtained by suitable treatment of the producer gases. The sulphur impurities of the coal may also be removed, and obtained as valuable by-products. Although gaseous-fuel has not been applied on any considerable scale to the firing of steam boilers in this country, this method of steam raising will receive increased attention and application in the future ; and, in the writer's opinion, the increased use of fuel-gas is likely to prove one solution for the smoke problem which now confronts manufacturers using solid fuels for heating purposes in large cities.

Carbon and hydrogen are the essential heat-producing elements in all natural or artificial fuels. The amount of heat produced by the complete combustion of one pound of fuel depends upon the percentage of these two elements present in the free or combined state. Combustion is in reality an oxidation process. The products of the complete combustion of fuel are carbon dioxide gas ( $\text{CO}_2$ ) and aqueous vapour ( $\text{H}_2\text{O}$ ). The incomplete combustion of

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fuel produces a number of secondary products, chief of which are carbon monoxide gas (CO) and various hydrocarbon gases (methane, ethylene and acetylene); these latter being either present as such in the fuel, or formed by combination of the carbon and hydrogen of the fuel when it is first heated. On further heating, in presence of an adequate supply of air, these gases burn with evolution of heat and production of carbon dioxide gas and aqueous vapour. The further chemistry of the combustion process will be dealt with in Chapter IX. It may, however, be stated here that the exact nature of the physical and chemical changes which occur when coal is heated is still unknown. Chemists have not yet discovered whether the hydrogen present in solid fuels exists in the free or combined state. Boernstein has recently published an investigation bearing on this subject (see *J. Soc. Chem. Ind.*, March 15, 1906, p. 213).

Natural solid fuels may be classified in the following order: wood, peat, lignite, bituminous coal, semi-anthracite and anthracite; while petroleum and its by-products stand as the representatives of liquid fuels; and coal-gas, coke, peat-coke and briquette fuels represent the artificial derivatives of the above natural fuels.

All naturally occurring solid fuels are held to be modifications of wood and woody fibre, absence of air, heat and pressure being the agencies which bring about decay and fossilization of the vegetable matter.

Geologists assert that anthracite is the oldest of the natural solid fuels. Cellulose, the chief constituent of wood and woody fibre, is represented by the formula— $C_6H_{10}O_5$ , and contains 44 per cent. only of carbon; while anthracite contains 90 per cent. The process of conversion of wood into coal is thus accompanied by a gradual escape of portion of the oxygen and hydrogen, which make up 56 per cent. of the weight of cellulose, and a gradual increase in the density and hardness of the product of this change. Lignite, soft or bituminous coal, and hard or steam coal, are the successive stages in the conversion of wood into anthracite. Peat is a similar product from the plant life which grows in bogs, of less age and therefore of less fossilized character, than coal. In peat, the percentage of volatile matter which is given off on heating is often as high as 65 per cent., and the solid carbon is thus less than

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one-third of the total weight of the peat. Time, heat, and pressure would no doubt convert peat into a fuel resembling coal.

Petroleum and natural gas are fuels that have been produced by another series of changes in the strata of the earth's crust ; but limits of space will not permit of any discussion of the various theories relating to the formation of these products.

## WOOD.

Although wood is not used to any great extent as a fuel in countries with extensive and available supplies of coal, yet as the original material from which our coal supplies have been derived by natural processes, its composition and characteristics deserve some mention here. Wood in its natural state is composed of thickened plant cells, which on microscopic examination reveal three constituents—the woody fibre or cellulose, the sap, and the mineral salts taken up from the soil.

The sap consists chiefly of water, with the organic salts, required for nourishment of the tree or plant, in solution. In freshly felled timber the water present in the sap may amount to 45 per cent. of the total weight of the wood ; by air drying this can be reduced to from 10 to 20 per cent. according to the nature of the wood and density of its fibres. The woody-fibre contains from 40 to 44 per cent. of carbon, and is the real heat-producing element of wood. Owing to the large amount of hydrogen and oxygen present in cellulose ( $C_6H_{10}O_6$ ) in the molecular proportions of aqueous vapour, the thermal value of wood as a fuel is not high. Direct tests have shown that 1 lb. of air-dried wood on the average will only evaporate 4 to 5 lbs. of water. Owing to the low percentage (under 1 per cent.) of mineral matter present in wood, however, after dry distillation has removed the water and other volatile constituents, it is one of the purest forms of carbon, and *wood-charcoal*, as the product is called, has an evaporating efficiency more than double that of the wood from which it is derived. The cost is, however, prohibitive of its use as a fuel on a large scale.

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## PEAT.

Peat is formed from plants and shrubs which find their habitat in swampy districts, under conditions which produce decay in the absence of oxygen or air—i.e., under water.

Owing to the peculiar conditions under which peat is formed, the amount of water and ash which it contains is always high, and these two constituents on an average amount to more than three-fourths of its composition by weight. The following are approximate analyses of typical samples of peat :—

	Irish Peat. Air-dried.	English Peat. Air-dried.
	Per cent.	Per cent.
Moisture . . . . .	21.60	20.36
Ash . . . . .	2.90	1.30
Coke . . . . .	27.90	35.00
Volatile matter . . . . .	72.10	65.00
Fixed carbon . . . . .	25.00	33.70

Air-dried peat still retains from 20 per cent. to 30 per cent. of water, and on this account its value as a fuel is very low. By mechanical and chemical treatment this water can be reduced by one half, and peat in this state then becomes a fuel comparable in appearance and evaporative value to bituminous fuel.

It is probable that as the coal-fields of this and other countries become exhausted, the immense reserves of peat which exist in nearly all countries will be drawn upon, and that by modifications of processes now in use, supplies of peat-coke and peat-fuel will be made available for industrial and household use.

## LIGNITE OR BROWN COAL.

Lignite is a natural fuel intermediate between peat and bituminous coal in age and appearance.

Lignite is formed by the gradual decay of shrubs and trees under conditions which have excluded air and oxidation, but have differed materially from those which have obtained in the formation of peat. The percentage of water present in freshly won lignite is however high—vary-



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ing from 40 per cent. to 50 per cent.—and even after air-drying, 20 per cent. of water is still present in the fuel. The ash contents vary from 5 per cent. to 10 per cent, while the carbon present ranges from 70 per cent. to 80 per cent. Though lignite is not used to any great extent as a fuel in this country, its evaporative value is fairly high. When the deposits of lignite lie close to the works where they can be used, and the cost of cutting and transport are low, this fuel can compete in price and efficiency with the more generally used bituminous coal, and there are many works in Germany using lignite alone for steam-raising purposes.

### BITUMINOUS COAL.

This is the type of fuel employed most generally on land for firing boilers, since it is much cheaper than the anthracite and semi-anthracite fuels, and when burned under scientific conditions, can be used so as to produce high efficiency and little smoke. The following are analyses<sup>1</sup> of a typical bituminous fuel from the Lancashire district ; but all fuels containing over 20 per cent. of volatile matter come under this classification.

#### APPROXIMATE ANALYSIS OF DRY FUEL.

	Per cent.	Moisture.
Volatile matter . . . . .	29.10	3.05
Fixed carbon . . . . .	58.04	
Ash . . . . .	12.86	
	70.90 per cent coke.	
	100.00	

#### ELEMENTARY ANALYSIS.

	Per cent.
Carbon . . . . .	72.60
Hydrogen . . . . .	4.79
Oxygen . . . . .	7.28
Sulphur . . . . .	1.64
Nitrogen . . . . .	0.71
Ash . . . . .	12.86
	99.88

The calculated calorific value of this fuel was in round numbers 7,000 lb.-centigrade thermal units, equivalent to

<sup>1</sup> From tests made by Dr. Hethrington.

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12,600 British thermal units. It is interesting to note that it contained 3·89 per cent. of hydrogen over and above that required to combine with the 7·28 per cent. of free oxygen present in the coal; while 14·56 per cent. of the carbon was present in some form which yielded volatile hydro-carbons on heating. Although much has been written upon the subject of coal, the exact constitution and state of the various chemical elements before heating are still unknown; and it is an undecided point as to whether the oxygen and hydrogen and volatile portions of the carbon are present in coal in the free or combined state.

Approximate analyses of other bituminous fuels, with their calculated calorific values in lb.-centigrade units, are given below:—

No.	Ash.	Volatile Matter.	Coke.	Calculated Calorific Value.
	Per cent.	Per cent.	Per cent.	
1	12·45	27·90	72·10	7,565
2	13·80	31·00	69·00	7,347
3	6·20	33·30	66·70	8·041
4	7·75	34·00	66·00	7·764
5	6·50	36·50	63·50	7·703

All the above tests were made on samples dried at 230° F., and the low percentages of ash contained in samples Nos. 3, 4 and 5, were due to these being washed slacks of exceptional cleanliness.

When the percentage of volatile matter, yielded by a fuel on heating, rises above 35 per cent., the fuel is exceedingly difficult to burn without smoke production. The percentage of volatile matter given off by a fuel is in reality a measure of the difficulty of burning it under the boilers, with perfect combustion of its component parts. Bituminous coals containing over 36 per cent. of volatile matter are known as “*cannel*” coals, and are used chiefly for gas-making purposes. All bituminous fuels require careful management and large brick-lined combustion chambers, if they are to be burned without smoke.

The length of flame produced by bituminous coals depends upon the percentage of volatile matter, and this in its turn depends upon the amount of hydrogen they contain over and above that required to form water with the oxygen present in the coal.

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This surplus hydrogen combines with the carbon to form methane ( $\text{CH}_4$ ), ethylene ( $\text{C}_2\text{H}_4$ ), and acetylene ( $\text{C}_2\text{H}_2$ )—three hydro-carbon gases which yield carbon dioxide and aqueous vapour when burned under perfect conditions of combustion. When the air supply or the temperature is insufficient, partial oxidation only occurs, and a portion of the carbon of these gases separates in the form of soot. The percentage of surplus hydrogen is, therefore, another measure of the difficulty of burning bituminous fuel. This difficulty increases with the ease and rapidity with which these hydro-carbon gases are evolved by the fuel on heating.

Nearly all bituminous fuels contain sulphur in the form of iron sulphide ( $\text{FeS}_2$ ) as an impurity. The percentage of iron sulphide, or "brasses," varies greatly in different classes of this fuel. On heating, half of the sulphur is liberated and burns with evolution of heat to form sulphurous acid gas ( $\text{SO}_2$ ), which sooner or later condenses in the form of sulphuric acid ( $\text{H}_2\text{SO}_4$ ). It is this compound, and not the carbon or soot, which produces the larger part of the destruction of vegetation and of buildings in the neighbourhood of industrial districts and of large cities. Recent calculations<sup>1</sup> have been made to show that in London over 500,000 tons of sulphuric acid are produced annually by the sulphur impurity contained in the coal burned in the metropolitan area. A similar calculation for the coal burned annually in the whole of the United Kingdom gives 5,000,000 to 7,500,000 tons of acid. The use of lime has been advised for fixation of this sulphur in the form of calcium sulphate in the ash of the fuel, but a far more certain and safer method would be to pass the products of combustion through scrubbing towers filled with flints. The sulphur contained in the exit-gas could then be recovered in the form of a valuable by-product, namely hypo-sulphite of lime or soda. As already stated, it is the sulphur, and not the more visible soot and smoke, which is the chief cause of the damage effected by smoke. The carbon blackens; but the sulphur corrodes metal, destroys brick and stone, and kills vegetation. Any practical method which would remove the sulphur from coal, or its products from the waste gases, deserves, therefore,

<sup>1</sup> Dr. Rideal at London Smoke Abatement Conference, Dec. 1905.

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most careful consideration by steam-users. Until such method has been generally adopted the sulphur contents of coal ought always to be kept as low as possible, by careful picking of the fuel and removal of the veins of pyrites or "coal brasses." In large purchases of fuel by contract, a clause ought to be added with respect to the amount of this impurity, and no coal should be accepted containing over one and a quarter per cent. of sulphur.

### SEMI-ANTHRACITE OR STEAM-COAL.

Fuels which when heated yield from 10 per cent. to 20 per cent. of volatile matter are known as semi-anthracites or steam-coals. They are very largely used for steam-raising purposes in the Royal Navy, and by factories located in cities where smoke prosecutions are frequent. Approximate analyses of typical semi-anthracites are given below :—

No.	Ash.	Volatile Matter.	Coke.	Calculated Caloric Value in Centigrade Units.
	Per cent.	Per cent.	Per cent.	
1	14.95	10.00	90.00	7,405
2	15.25	11.80	88.20	7,398
3	10.00	12.50	87.50	7,855
4	10.75	13.60	86.40	7,783
5	8.85	15.50	84.50	7,950

Fuels of this type can be burned without smoke production in most types of boiler-furnace, and they do not require large combustion chambers or very skilled management in order to obtain perfect combustion. As shown by the approximate analyses, the greater portion of the fuel remains as an incandescent mass of coke after the preliminary heating upon the fire-bars of the furnace, and radiation transfers the heat from this mass of glowing fuel to the water in the boiler.

### ANTHRACITE.

Anthracite is the nearest approach to coke in chemical constitution which is found naturally, but it differs from coke in its physical properties, being very dense and of shining appearance. Anthracite gives off only from 3 to

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10 per cent. of volatile matter when heated, and consists chiefly of fixed carbon, with little oxygen or hydrogen.

The following is an approximate analysis of a typical South Wales anthracite fuel :—

Ash.	Volatile matter.	Coke.	Calorific value.
1·70 per cent.	3·64 per cent.	96·36 per cent.	8,305

Anthracites are difficult to ignite, owing to their density and low percentage of volatile matter ; but under proper conditions this type of fuel can be burned completely, and yields a very intense but localized heat. Anthracite is chiefly used in metallurgical operations, and is not employed to any great extent for steam-raising purposes ; but when so employed no combustion chamber is required, and the boiler surface may be placed close to the mass of burning fuel.

### PETROLEUM AND ITS BY-PRODUCTS.

Although liquid fuels have little application in the United Kingdom, owing to the limited supply available for industrial purposes, in Russia and the United States they are largely used for heating and steam-raising purposes. Crude petroleum contains a large number of liquid hydro-carbons of the general formula  $C_nH_{2n+2}$ , and it is the crude oil or the residues obtained in refining it, that is used for steam-raising purposes. In Russia especially, the residue from the first distillation of the crude oil, called "*astatki*," is utilized also most entirely in this way.

The following tests<sup>1</sup> show the difference in composition and heating value of the Russian and American oils :—

	Per cent. Carbon.	Per cent. Hydrogen.	Per cent. Oxygen.	Calorific Value. B.Th. Units.
Russian crude light . .	86·3	13·60	·10	22,628
"    "    heavy. . .	86·5	12·3	1·1	19,440
" <i>astatki</i> . . .	87·1	11·7	1·2	19,260
Pennsylvania crude . .	84·9	13·7	1·4	19,224
West Virginia crude . .	86·6	12·9	·5	21,240

When burnt in suitable furnaces with proper provision for the supply of the oil in the form of a spray, petroleum is superior to ordinary coal as a fuel, and has 33 per cent.

<sup>1</sup> *The Calorific Power of Fuels*, H. Poole.

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higher evaporative value than anthracite. Actual tests have given an evaporation of 20·8 lbs. of water per lb. of petroleum. Liquid fuel is easily transported and stored; yields no ashes on combustion; and were the supply of crude oil sufficient, there is little doubt that it would be very largely used for steam-raising purposes in this and other countries. Under present conditions, however, the price of petroleum is too high to enable it to compete with coal as a fuel.

### ARTIFICIAL FUELS.

*Gas-Coke and Coke-oven Coke.*—These two forms of fuel are obtained by submitting bituminous fuels to dry-distillation—that is by heating in closed retorts or ovens in the absence of air. The moisture and volatile constituents of the coal are driven off, and only the carbon, ash, and impurities remain as a solid residue in the retorts or ovens. Gas-coke is the residue obtained in the manufacture of coal-gas, and here the quality of the coke is of secondary importance to that of the gas. The coke produced from coke-ovens on the other hand, is the chief product of the coking process, being designed for use in the iron smelting industry, and in many cases the gases from coke ovens are allowed to escape into the atmosphere.

The use of coke for steam-raising purposes is very limited, since its price is comparatively high; but it is sometimes purchased and mixed with bituminous fuel, to lessen the trouble from smoke in very heavily worked boiler plants. Coke can be burned completely without any combustion chamber.

The following is an approximate analysis of a typical coke :—

Ash.	Volatile matter.	Coke.	Calorific value.
18·85 per cent.	1·90 per cent.	98·10 per cent.	6,972

Owing to the loss of the volatile constituents of the fuel, the percentage of ash in coke is always higher than that of the original fuel.

Coke contains as a rule from 2·0 per cent. up to 6·0 per cent. of moisture, owing to its absorbent properties and to the fact that on drawing from the retorts or ovens it is often quenched with water.

Coke retains also a large portion of the sulphur impurity

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of the original fuel, and it is not therefore a very suitable fuel for use in towns or cities for the reasons already given under *Bituminous Fuel*.

*Peat-Coke*.—This artificial fuel is obtained by the dry-distillation of peat in retorts of special design, after a large portion of the original water contents of the peat have been removed by mechanical methods. The following is an analysis of a peat-coke prepared by an electrical method :—

	Per cent.	
Moisture . . . . .	17·50	}
Ash . . . . .	18·00	
Volatile matter . . . . .	57·60	
Coke . . . . .	42·40	
Fixed Carbon . . . . .	24·40	
		on the dried sample.

This test must not be taken as representative of peat-coke generally however, as it is possible by scientific methods to obtain a much lower percentage of moisture and of volatile matter in the finished product. The ash-test in this case has also been increased by the unwise addition of chemicals to promote electrical conductivity.

A sample of peat-coke from Argyleshire contained only 6·50 per cent. moisture and 2·70 per cent. ash ; while Norwegian peat-coke contained 4·82 per cent. moisture and 3·00 per cent. ash.

Although peat-coke has not so far been manufactured upon a large scale, it is now being produced at several small works in Norway, Canada, Ireland, Germany, and other peat-producing countries. When the coal-fields of Europe and America are exhausted, peat-coke is likely to play an important rôle in the maintenance of the world's industries. Owing to its low percentage of volatile matter, and freedom from sulphur, peat-coke is a far more perfect fuel for household and industrial use than ordinary coal.

*Briquette-Fuels*.—Briquette-fuels are made chiefly from semi-anthracite and anthracite coal, by mixing the dust and fine coal obtained in the course of mining and screening, with tar or other binding materials, and by moulding the mixture into bricks, in specially designed presses. The resulting briquettes burn slowly with evolution of little smoke, and find a large use in Germany and other European countries for domestic purposes. The following shows the composition of such a briquette-fuel made from German peat :—

## FUEL, WATER AND GAS ANALYSIS

	Per cent.
Moisture . . . . .	10.78
Ash . . . . .	7.35
Coke . . . . .	36.50
Volatile matter . . . . .	63.50
Fixed Carbon . . . . .	29.15

} on dry sample.

As the cost of briquette-fuel delivered in manufacturing districts is higher than that of coal, it is little used for industrial and steam-raising purposes.

*Gaseous-Fuel.*—There are many engineers who believe that the power and heat required by our industries in the future will be obtained from gaseous-fuel. Some of the advantages of this form of fuel have already been mentioned. Others are, that with slight modifications in the gas-producing apparatus, the gas obtained can be used either for heating or for power purposes. Large gas-engines—driven by producer gas (obtained from ordinary bituminous slack costing only 6s. per ton d.d.) have now been running satisfactorily for some years in Germany, in America, and in the United Kingdom; and as one h.p. can be obtained from one lb. of coal by this method, the advantage over the present methods of power-generation are undoubted. Even with the existing power plants—consisting of steam-boilers and reciprocating or turbine-engines—there is much to be said for heating by gas; and in many works the installation of a large gas-producer plant would lead to fuel economy, and incidentally also solve the smoke problem.

Producer-gas varies in composition with the type of producer used, the method of working, and with the composition of the fuel consumed. When steam is used in the working of producers, a mixture of ordinary producer-gas and water-gas is obtained. Carbon monoxide and hydrogen are the essential heating constituents of producer-gas, and upon the percentage of these constituents present in the gas, its thermal value depends.

The earlier forms of gas-producers could only be worked satisfactorily with semi-anthracite and anthracite fuel. Modern producers and methods of working permit the cheapest forms of bituminous slack to be employed with satisfactory results. The ammonia recovered in the form of sulphate as a by-product is also of considerable value. The following is the composition of gas from a typical Mond-gas plant, using cheap fuel:—



## FUEL

	No. 1.	No. 2.
	Per cent.	Per cent.
CO <sub>2</sub> (Carbon dioxide) . . . . .	16·3	16·0
CO (Carbon monoxide) . . . . .	10·2	11·0
CH <sub>4</sub> (Methane) . . . . .	2·5	2·0
H (Hydrogen) . . . . .	26·4	29·0
N (Nitrogen) . . . . .	44·6	42·0
	100·0	100·0

No. 2 gas has a heating value of 140 B.Th. Units per cubic foot, and contains 84 per cent. of the thermal value of the original fuel. In the writer's opinion the transition from steam-engines to gas-engines for power-generation, will be marked by an intermediate stage, in which gaseous fuel will be employed for steam-raising purposes.

### SAMPLING FUELS.

The sampling of fuel has not in the past received from engineers the attention it requires. It is perfectly useless having elaborate chemical and calorific tests made of fuel, if the sample be a non-representative one. The sampling operation is, in fact, one demanding as much care and attention as the later chemical examination; and the idea that a few pounds of coal selected haphazard from any part of a wagon-load or heap of fuel can form a representative sample, is utterly absurd.

The sampling of slack and small fuel is simpler than the sampling of mixed large and small coal; but in each case a truly representative sample of coal can only be obtained by strict adherence to the rules for sampling given in the Appendix to this volume. The sampling of liquid fuels is simplest of all, since here the contents of a barrel or tank can be well mixed by blowing air through or, in the case of tar, by using a plunger for a few minutes before taking the sample. The only difficulty then is the selection of the number of barrels from which to take samples, and the usual proportion in sampling work is every third or fifth—excepting when the total number is small—when every barrel may be sampled with little extra expenditure of time.

## FUEL, WATER AND GAS ANALYSIS

The sampling of peat and briquette fuels is best carried out by taking borings out of a large number of selected blocks, and reducing these to powder by rubbing between serrated iron plates. A proper sampling plate and suitable hammer—(see Fig. 1)—are required for the preparation

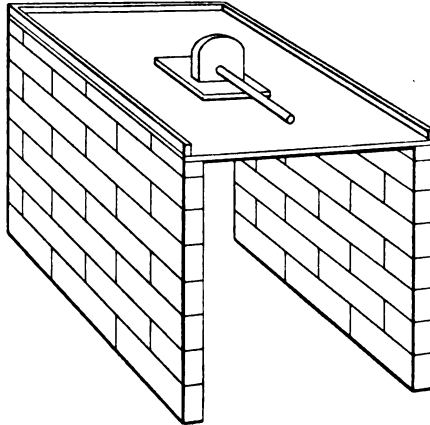


FIG. 1.—SAMPLING PLATE AND HAMMER.

of fuel samples when this work is often carried out; and in large works where fuel sampling is a regular portion of the scientific management of the plant, a small mortar-mill, or large crushing and grinding mill, are essential for the speedy performance of the work.

The ordinary type of coffee mill is useful for crushing samples of fuel in the final stage of their preparation for laboratory examination.

## CHAPTER II.

### The Approximate Analysis of Fuel.

#### PREPARING THE SAMPLE.

21  
**T**HE sample of fuel after the operation of sampling as described in Chapter I should amount to about one pound, with no particles that exceed  $\frac{1}{4}$ -inch in diameter. This should now be passed through a brass wire sieve (A)—(Fig. 2) of 1-12 inch mesh, and the portion which will not pass through should be finely crushed by grinding in a No. 3 Kenrick mill. Fig. 2 (B) shows a small mill adapted for

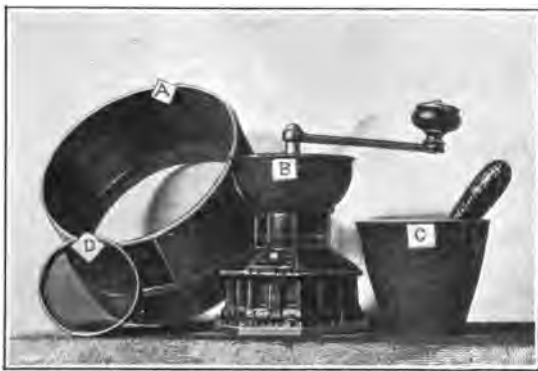


FIG. 2.—GRINDING MILL, MORTAR AND SIEVES.

the preparation of laboratory samples of fuel. If the fuel be very wet, or if the sample contain any very hard lumps of shale, this method of preparing the sample requires modification.

The excessive moisture can be removed by spreading out the whole of the fuel sample on a piece of paper, and by leaving it exposed to the air—for two or three hours, in a warm place in the laboratory—before sieving and grinding. The difficulty caused by very hard lumps of shale can be dealt with by picking these out of the sample and by crushing them separately in the steel mortar (C) shown in

## FUEL, WATER AND GAS ANALYSIS

Fig. 2. Care must be taken that none of the shale is lost in this operation, for shale possesses little heating value, and the proportion of it in a sample of fuel has great influence upon the tests for ash and calorific value. Shale and dirt are, in fact, the chief causes of the differences in value of bituminous fuels, and when the thermal results are worked out upon pure coal or combustible matter only, the variations are small and are chiefly those due to differences in the chemical constitution of the coal. For this reason it is wise to cover the mortar and the grinding mill with a card or towel when crushing shale, since bits have a decided tendency to jump out and to get lost during this operation. After crushing in the mortar, the whole of the shale must be passed through the grinding mill, and the ground material returned to the general mass of the sample, which will now occupy double the former volume, and resemble in appearance a heap of coarse gunpowder.

The sample is then reduced by repeated mixing and quartering—as described in the Appendix—until only about 120 grams ( $\frac{1}{4}$  lb.) remain. This is divided into two equal portions, one of these being used for the following tests, and the other being reserved in a stoppered bottle for use in case of any mishap in carrying out the tests with the first portion.

The remaining portions of the sample are likewise not thrown away, but are retained in the 1 lb. tin in case of accident or dispute. Each sample tin should bear a label giving full particulars of the date of sampling, the origin of the fuel, and any other information regarding it that may be necessary for proper identification of the sample and test. In cases where a large number of samples are being dealt with at one and the same time, considerable care is necessary to prevent confusion of the samples, and the use of written labels is all the more urgent. For testing purposes the samples may be simply marked A, B, C., etc.—if the original sample tins bear corresponding letters—in addition to the full details of the fuel and date of sampling.

### TESTING THE FUEL.

The approximate analysis of fuel covers the estimation of the following constituents:—(1) moisture, (2) ash, (3) volatile matter, (4) coke, (5) fixed carbon and (6) sulphur. These will now be dealt with in the order named:—

## FUEL

1. *Moisture*.—Ten grams of the fuel sample prepared as already directed are weighed out upon a chemical balance reading to 1 milligram, and are heated for two hours at 230° F. (110° C.) in a copper or aluminium air-bath. The loss of weight multiplied by ten gives the percentage of moisture in the original sample. A desiccator must be employed for cooling the sample before weighing, as perfectly dry fuel absorbs moisture from the air and gains in weight, even while being weighed on the balance. It saves time, however, if the crucible be allowed to go nearly cold in the air with the lid on, before being placed in the desiccator.



FIG. 3.—BALANCE AND WEIGHTS.

On no account must the crucible be placed on the balance pan and weighed while still hot, as this will give increased weighings.

The crucible must be covered during heating in the air-bath and the lid only removed when weighing

The balance shown in Fig. 3 is most suitable for fuel testing work ; it carries a load up to 50 grams and reads correctly to one milligram. The weights should always be

## FUEL, WATER AND GAS ANALYSIS

placed in the left hand pan, the fuel in the right. The sample of fuel should not be weighed out directly upon the pan, but in a tared porcelain crucible. (A No. 1 Berlin crucible holds 10 grams of most fuels.) A lead counterpoise can be made of sheet lead with little trouble, and the operation of weighing out ten grams of the fuel sample with this crucible is then very rapidly performed, since the lead counterpoise undergoes little change in weight, and only rarely requires fresh adjustment. The lead counterpoise should be bent into the form of the letter L, to facilitate removing on and off the pan of the balance. The second weighing of the fuel sample, after heating two hours at 230° F. can be most quickly performed by placing the lead counterpoise and the ten gram weight on the left hand pan of the balance, and by adding the fractional parts of 1 gram to the right hand pan upon which the crucible is placed, until equilibrium is obtained. The final adjustment should always be made by means of the rider—(the little platinum weight which rides across the beam and records decimal fractions of one centigram)—with the front of the balance case closed; in order to avoid any disturbance by draughts.

The total of the weights placed on the right hand pan to restore equilibrium after heating, then represents directly the loss of moisture, and multiplied by ten gives the percentage of moisture in the original sample.

The air-bath most suitable for heating fuel is shown in Fig. 4. It is made of copper, and is provided with a thermometer reading up to 300° F., and with an automatic gas regulator which keeps the temperature within 5° F. of that desired. That shown in Fig. 4 is the Reichardt Muencke type of regulator. The burner is a Bunsen gas burner, with a rose top, and this must be placed quite close to the bottom of the oven. Unless a gas regulator be used, the air-bath requires constant attention, for the gas-pressure varies greatly at different hours of the day. The only precaution necessary with a gas-regulator is to see that there is no danger of lighting back when the main gas current is entirely cut off, and only the by-pass supply is in use.

A water-bath is less troublesome than an air-bath, but the temperature attained in these cannot rise above 212° F., and therefore they are of no use for determining the moisture in fuels, the last traces of which can only be got rid of by heating above 212° F.

## FUEL

Should it be necessary to determine the total moisture in very wet fuels, or in the fuel as delivered, it is necessary to determine the loss which occurs during the grinding and sampling operation.

For this purpose, the whole of the sample contained in

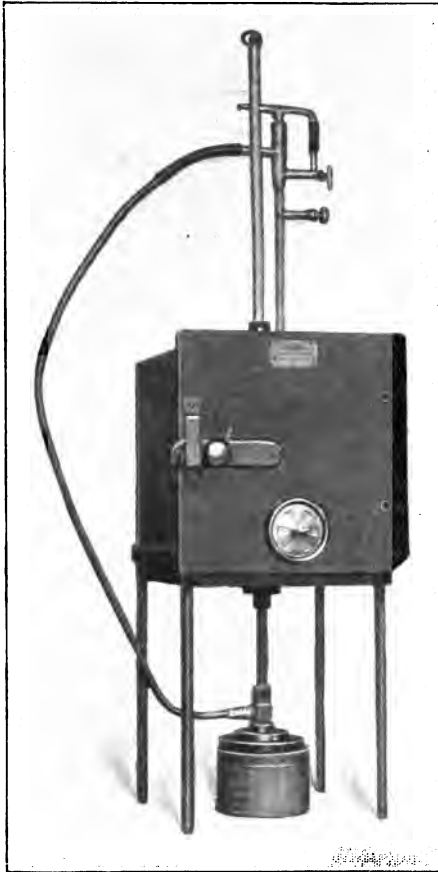


FIG. 4.—COPPER AIR-BATH WITH THERMOMETER AND GAS-REGULATOR.

the sample tin is placed on a porous plate and is weighed as accurately as possible on a pair of ordinary scales. The plate with its contents is then placed in the sun, or in a warm place on the boilers for two hours, and the fuel is twice turned over during this period. A second weighing of the

## FUEL, WATER AND GAS ANALYSIS

plate is made when cold. The loss of weight during this preliminary drying is then worked out as a percentage on the original weight of fuel, and must be allowed for in the final calculation of the moisture, as ascertained by the second and more accurate drying operation.

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The remaining tests are all carried out with the 10 gram sample of fuel, after drying in the air-bath at 230° F. (110° C). This sample must, however, be still further reduced in fineness before commencing these further tests. The sieve (*D*) and steel mortar and pestle (*C*) shown in Fig. 2 are employed for this work. The former is of very fine brass wire, 1-60 inch mesh, equal to 3,600 holes to the square inch; the latter is of cast steel and is 4 inches in diameter. The whole of the 10 grams sample must be passed through this sieve. It will be found that this is most quickly carried out by repeated sievings, and return of the larger particles free from the finer portion, to the mortar. With semi-anthracite and shaly fuels, this final grinding operation is troublesome, but it is essential that it be carried out carefully, and that the whole of the ten grams be passed through the 1-60 inch mesh sieve, if correct results are to be attained. The final particles of very hard coal or scale which resist crushing to the last, must on no account be rejected. As already stated in Chapter I, correct sampling is the basis of correct testing, and it is too often slovenly and carelessly performed. If left to untrained persons, it is certain to be badly carried out, and the whole of the test results are then worthless.

The finely ground sample is now carefully mixed on a sheet of glazed paper, and is then transferred to a No. 00 (2 $\frac{3}{4}$  inch diameter) porcelain basin, which is covered with a clock glass, and is placed in the air-bath for one hour's re-heating at 230° F.

This is necessary to remove the moisture taken up during the final grinding of the sample. The sample is now ready for the remaining tests, and must be transferred to a stoppered glass weighing tube, or kept covered in the porcelain basin in the desiccator. Should the tests be delayed some hours, a re-heating of the sample in the air-bath for an hour will be necessary, as coal in this fine state of subdivision is very hygroscopic.



## FUEL

2. *Ash*.—Two grams of the finely ground and perfectly dry sample are weighed out in the pan of the balance,<sup>1</sup> and are transferred to a No. 00 size Berlin porcelain basin. This is placed upon an asbestos board having a hole cut in its centre for the reception of the basin (*see* Fig. 6), and is heated

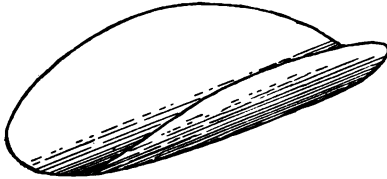


FIG. 5.—COPPER FOIL FOR WEIGHING PURPOSES.

until all the carbonaceous matter of the fuel is volatilized or burnt. The heating of the basin is best carried out over a No. 1 Bunsen burner, the asbestos board being supported by a tripod stand tilted at an angle as shown in Fig. 7,

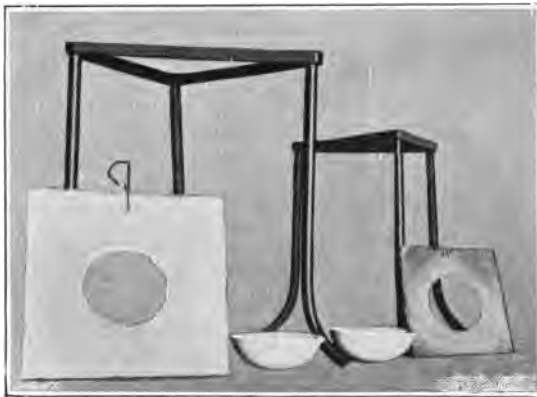


FIG. 6.—PORCELAIN BASINS AND SUPPORTS FOR ASH TESTS.

so that the products of combustion may pass away behind, and a current of heated air flow over the fuel from the front.

Bituminous fuels require very gentle heating at first, in order that the volatile matter may escape gradually, without carrying off any particles of solid fuel, and that the residue

<sup>1</sup> If the balance be unprovided with removable pans, a piece of copper foil  $2\frac{1}{2} \times 2$  inches can be cut to the shape shown in Fig. 5, and bent into the form of a small scoop. A lead counterpoise must then be made to balance exactly this piece of foil.

## FUEL, WATER AND GAS ANALYSIS

may not bake itself into a very hard mass of coke. The fuel should be turned over repeatedly with a platinum wire or spatula, during this stage of the heating process, to facilitate the escape of the hydrocarbon gases, and to prevent sintering together of the mass. After the hydrocarbon gases have escaped, the heat of the flame can be gradually increased, until the bottom of the basin where the



FIG. 7.—ARRANGEMENT OF APPARATUS FOR ASH TEST.

fuel rests is at a dull red heat. The fuel as the fixed carbon burns away gradually becomes lighter in colour, but it is somewhat difficult to get rid of the last few per cent. of carbon. In order to effect this, the basin should be removed from the flame, allowed to cool on a piece of asbestos board, and the ash carefully crushed with a small agate or glass pestle. The ash adhering to this is then brushed back into the basin with a small camel's hair brush, the fine carbon dust which collects round the edges of the basin is brushed down into the centre, and the whole is again raised to a red heat temperature, commencing with a small flame to avoid cracking the porcelain basin.

## FUEL

The first heating of the fuel to remove the hydrocarbon gases and to burn off the greater part of the fixed carbon of the coke requires generally from 30 to 60 minutes ; and a further 10 to 20 minutes heating are required to remove the last traces of carbon.

From  $1\frac{1}{2}$  to 2 hours are therefore required for carrying out the ash test, and any attempt to reduce this time with bituminous coal will produce incorrect results. The ash should be light in colour and quite free from black specks, which denote unburned carbon. The basin after removal from the flame is allowed to nearly cool in the air, and is then placed in the desiccator and its contents weighed when cold. The ash is carefully brushed out of the basin on to the pan of the balance or on to the copper foil for weighing, and the spatula or wire used for mixing the fuel must also be carefully brushed free from any particles of ash adhering to it. The weight of ash multiplied by 50 gives the percentage of ash in the dry fuel.

Ash which is red in colour denotes the presence of iron impurities in the fuel, probably as "coal brasses" (pyrites).

The behaviour of bituminous fuels on heating is quite different from that of semi-anthracite and anthracite fuels ; and after a little experience in testing coals from various sources, much information can be obtained as to the character and quality of the fuel, by careful observation during the ash test.

When a large number of ash tests have to be performed daily, it saves time to use a muffle heated to redness in a gas-muffle furnace, the fuel samples being contained in shallow trays made from platinum foil. These must be numbered from 1 to 6 or 12 by notches cut with scissors in their edges, and great care must be given to avoid confusion of the samples, and to the question of a proper current of air over the samples. If the heating be too rapid, or if the draught be too great, some of the finer particles of fuel or ash may be carried away with the exit gases. For this reason the porcelain basin method is the safest for ash determinations, especially for those non-conversant with muffle-furnace management. The ash obtained from each fuel test should be placed in a small paper bag and kept in the tin with the original fuel sample, for reference in case of trouble with the fuel or of dispute.

## FUEL, WATER AND GAS ANALYSIS

3, 4, and 5. *Volatile Matter, Coke and Fixed Carbon.*— These three constituents of fuel are all determined by the one test which consists in heating one gram of the finely crushed and dry sample of fuel in a covered platinum crucible until all the hydro-carbon gases are expelled. The crucible and its contents are then again weighed. The loss in weight multiplied by 100 gives the percentage of volatile matter, and the residue multiplied by 100 gives the percentage of coke. On deducting the percentage of ash as



FIG. 8.—PLATINUM CRUCIBLE AND SUPPORT FOR COKE TEST.

ascertained in test 2 from the percentage of coke, one obtains the percentage of fixed carbon.

Very careful manipulation is required in carrying out this test in order to obtain correct results, and the following conditions must be strictly adhered to. The apparatus is shown in Fig. 8. The platinum crucible should measure 1.40 × 1.10 inch diameter and should be provided with a very closely fitting lid. If the crucible has been bent out of shape, causing the lid to fit badly, it can be restored to its original circular form by rolling on a hard surface while hot, with pressure applied by a rounded stick or glass rod in its

## FUEL

interior. The crucible and lid should be thoroughly cleaned after each test, by burning off the adhering graphite and soot, and by polishing inside and out, with wet sea-sand. The grey deposit formed by the burner flame on the bottom of the crucible —(due to formation of a carbide of platinum) —should also be removed by sea-sand after each test, as a platinum crucible rapidly corrodes and deteriorates when dirty and dented.

A platinum wire triangle is made for holding this crucible by twisting together three pieces of thick platinum wire, and by mounting these in the centre of an ordinary pipe-stem triangle, as shown in Fig. 8. No other method of supporting the crucible in the flame is admissible for coke tests, since it is absolutely essential that the crucible and its lid should be *entirely surrounded by flame* during the test. The Bunsen burner must be of No. 1 size, and should give a steady colourless flame at least 7 inches high. The tripod stand should be 8 inches in height, and must be so arranged that the bottom of the crucible, when supported by the platinum wire triangle, is not more than  $1\frac{1}{2}$  inches from the top of the burner. If the place where the test is carried out is at all subject to side draughts, cardboard screens must be arranged round the tripod and burner to prevent access of air to the crucible while the heating is in progress.

A lead counterpoise should be made for the crucible and its lid to facilitate the weighing operation. This counterpoise will require adjustment at short intervals of time, since the platinum crucible will lose gradually in weight by the frequent cleanings. The one gram of fuel must be very carefully weighed into the crucible, with a possible error of not more than one milligram.

The crucible is then covered, inserted in the triangle, and placed upon the tripod stand in the centre of the gas flame, which has been previously ignited and surrounded with any draught-protecting device that may be necessary. The hydrocarbon gases commence to escape from under the lid as soon as the crucible attains a red heat, and these burn with a yellow and smoky flame for a period which depends upon the percentage of volatile matter in the fuel.

As a rule the gas evolution lasts from 1 to  $1\frac{1}{2}$  minutes with bituminous fuels, and its duration and volume enables one, with a fair degree of accuracy, to judge the character and nature of the fuel. As soon as the last luminous "candle"

## FUEL, WATER AND GAS ANALYSIS

has disappeared from the Bunsen flame above the crucible lid, the crucible is removed from the flame very carefully, by lifting away the tripod which supports it without disturbing the lid, and is allowed to go nearly cold in the air, before placing in the desiccator. When quite cold it is then weighed with the lid still on, and from the loss in weight, the percentage of volatile matter, coke and fixed carbon are calculated as already described. The final weighing must be within one milligram. The deposit of soot found upon the inner surface of the lid, and the deposit of graphite upon the inner walls of the crucible are ignored in the final weighing, since although they appear to be of considerable volume and importance, they weigh only from 3 to 5 milligrams.

The coke left in the crucible after the expulsion of the hydrocarbon gases is very hygroscopic, and on this account it should not be exposed to the air before weighing. The appearance and character of the coke differs greatly with different coals, and it may be obtained either as a powdery non-adhering residue or as a solid cake. With the South Wales steam-coals, which cake together on heating, a slight explosion often occurs during the coke test, and some of the fuel is generally thrown out of the crucible. This effect appears to be due to the formation of an impermeable crust of coke around the fuel, before all the volatile matter has escaped.

The best way to obtain correct coke tests with this and other fuels which produce detonations, is to use only .70 or .50 gram for the test in place of 1 gram.

6. *Sulphur*.—The determination of sulphur in fuel involves the performance of an ordinary gravimetric analysis, and some practice in quantitative analysis will be necessary before accurate results can be obtained. It is therefore useless to attempt this test without some training in the methods and apparatus used by chemists in analytical work. The directions for carrying out this determination are consequently only given in condensed form.

If a bomb calorimeter be used for finding the calorific value of the fuel, the determination of the sulphur is simplified, for the liquid obtained by rinsing out the bomb after the explosion contains all the sulphur in the form of sulphate. The whole of the rinsings are transferred to a porcelain basin, and are evaporated to dryness with addition of 5 c.c.

## FUEL

of pure hydrochloric acid (1.18 sp. gr.) upon a water-bath, in order to remove the nitric acid formed by oxidation of the nitrogenous constituents of the coal. The residue is dissolved in 100 c.c. of water, 2 c.c. of pure hydrochloric acid are added, and the solution is filtered before precipitating the sulphur with barium chloride. Boiling the solution for five minutes after the addition of the barium chloride renders the precipitate more dense, and less likely to pass through the filter paper.

The remainder of the determination is carried out in the usual way. The weight of barium sulphate finally obtained multiplied by .1375 gives the corresponding weight of sulphur, and this multiplied by 100 and divided by the weight of fuel used in the calorimeter gives the percentage of sulphur present in the coal.

Should a bomb calorimeter not be available, the sulphur in the fuel must be oxidized by means of lime or magnesia and sodium carbonate, according to the method described by Garrett & Lomax.<sup>1</sup> One gram of the fuel is placed in a small platinum crucible and is intimately mixed with 4 grams of a mixture of four parts of pure lime to one of anhydrous sodium carbonate. The crucible is completely filled with this lime-soda mixture, and a larger platinum crucible is then placed over the smaller one, mouth downwards. The two crucibles are now inverted, and the space between the two is filled with the same lime-soda mixture. The mouth of the larger crucible is then covered with a small square of thick asbestos board, and the whole is placed in a muffle-furnace heated to bright redness. Distillation of the volatile portion of the coal occurs in about two minutes, and as soon as a flame appears round the asbestos board, this may be removed. To ensure complete oxidation of the carbon, the heating must be continued for two hours. The contents of the crucibles are then allowed to cool, brought into water, and the sulphides oxidized to sulphates by means of bromine. The solution is then made acid with hydrochloric acid, filtered, and the sulphur determined in the filtrate by precipitation with barium chloride in the usual way. The calculation of the percentage of sulphur in the fuel is made as before.

<sup>1</sup> *Journal Society Chemical Industry.* December 15, 1905, p. 1,213.

## CHAPTER III.

### The Calorific Valuation of Fuels.

**T**HE laboratory calorific valuation of fuels is carried out by burning a weighed quantity of the dry fuel in a confined space surrounded by a known volume or weight of water, and by noting the increase in temperature of the latter due to the combustion of the fuel. A very large number of calorimeters have been designed and employed in the laboratory for carrying out this test, but all of these may be brought into three classes, according to the character and method of supplying the necessary oxygen.

Either the oxygen is brought to the fuel in the form of a chemical compound or in the free state; and calorimeters using gaseous oxygen for combustion of the fuel are differentiated by the pressure at which this oxygen gas is supplied, the Fischer & Mahler bomb calorimeters being the leading representatives of these two different types. In the following pages one calorimeter only of each class will be described, and the method of use will be explained in considerable detail.

Of class 1 the Lewis Thompson calorimeter has been selected. Although the results obtained by this calorimeter have been often discredited, when used with the modifications suggested by the author, it yields concordant results with certain classes of fuel.<sup>1</sup>

Of calorimeters using oxygen gas at normal pressure, the "Darling" Calorimeter has been described; while of class 3, the Mahler Donkin bomb calorimeter has been dealt with.

In each case the descriptions and details are based upon lengthy trials in the author's own laboratory.

#### GENERAL REGULATIONS FOR CALORIMETRIC WORK.

Wherever possible a room heated by hot water pipes or by hot air, and kept at the same temperature day and night,

<sup>1</sup> Scheurer Kestner's tests with this form of calorimeter confirm this opinion.



## FUEL

should be used for calorimetric work. Rooms heated by open fires vary greatly in temperature at different times of the day, and this difference in temperature of the air causes difficulties in the calorimetric work. The whole of the calorimetric apparatus should be kept under cover in the same room, and it should be thoroughly cleaned and dried after each test. The water used in the tests should be drawn at least twenty-four hours before required, and stored in large bottles in the calorimetric room, so that both the apparatus and water may be at the air temperature of the room when required for use. Direct sunlight must not be allowed to fall on the apparatus during the tests; and when choice is possible a room with a north or east aspect is preferable to one facing south or west. Temperatures should be taken with standardized mercury thermometers read off with a magnifying glass. All temperatures taken during the tests should be noted down on paper with the time at which they were recorded; omission to form this habit will generally lead to spoiled tests at some later date.

In the winter months in laboratories heated by open grates the tap water, if the other supply has failed, is often many degrees colder than the air of the laboratory. In such cases it will be found that the large volume of water required for filling the calorimeter can be speedily raised in temperature by the radiated heat from a coal fire. The water is placed in large pale green glass bottles eighteen inches from the bars of the grate, and the bottles are turned round at intervals of fifteen minutes. This method is less troublesome and less likely to lead to breakage, than heating over the fire in a kettle or over the lamp in beakers.

When working with only half a gram of fuel, radiation losses can be ignored, and water at the laboratory temperature may always be employed.

### THE LEWIS THOMPSON CALORIMETER.

Fig. 9 shows the separate portions of the Lewis Thompson Calorimeter, as usually employed. *A* is a large glass cylinder holding 2,000 c.c. of water when filled to the mark; *B* is a copper cylinder open below and closed above by the copper pipe and tap through which the final gases of the combustion are allowed to escape; *C* is a small copper cylinder in which the combustion of the fuel actually

## FUEL, WATER AND GAS ANALYSIS

occurs ; *D* is the holder for the same ; and *E* is a mercury thermometer graduated in tenths, and reading from  $0^{\circ}$  to  $45^{\circ}$  C.

The method of use is as follows :—Two grams of the finely powdered and dried sample of coal, prepared as described in Chapter II, are weighed out and intimately mixed with twenty-two grams of the oxygen mixture.<sup>1</sup> This mixing is best carried out upon a sheet of glazed white paper and



FIG. 9.—LEWIS THOMPSON CALORIMETER (ORIGINAL FORM).

must be continued until no black specks are visible, and the mixture is of a uniform grey colour. The mixture is now transferred to the copper cylinder *C*, with the aid of a dry funnel having its leg cut off, and is pressed down by means of a glass rod having a flattened glass button on its end.<sup>2</sup> When the whole of the mixture has been transferred to *C*, this is placed in the holder *D*, a few strands of fuse are embedded in the top of the mixture, the projecting free ends are ignited, and after quickly covering with the copper cylinder *B*, the whole is placed in the vessel *A*, containing 2,000 grams of water, the temperature of which has been most carefully noted. If the ignition and combustion are

<sup>1</sup> This mixture contains three parts of potassium nitrate to one of potassium chlorate, and must be quite dry.

<sup>2</sup> This is easily made by heating the end of a glass rod to redness and by pressing the hot end on a flat surface of cold iron.

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successful, the test is now nearly completed, for after the whole of the combustion gases have bubbled up through the water in *A*, it is only requisite to open the tap at the top end of *B*, allow the water access to the cylinder *C*, and to thoroughly mix the water in *A*, by plunging the cylinder up and down in it, to obtain the final reading of the ther-



FIG. 10.—LEWIS THOMPSON CALORIMETER (MODIFIED FORM).

mometer, which gives the increase in heat due to the combustion of the two grams of fuel.

The calculation which yields the calorific value of the fuel is then simply obtained by use of the equation

$$C = \frac{(2,000 + x) t}{2}$$

in which *C* = calorific value; *x* = the water equivalent of the apparatus in Centigrade units; and *t* = the gain in temperature. The value of *x* for this apparatus, and in fact for all forms of calorimeter is best

## FUEL, WATER AND GAS ANALYSIS

obtained by testing a standard sample of fuel or pure cellulose of known calorific value, and by using  $x$  as the unknown in the above quotation in place of  $c$ , the value of which can then be inserted.

The improvements in the Lewis Thompson calorimeter and method of use devised by the author are as follows:—

1. The weight of water used for each test is increased to 3,000 grams, by use of a larger vessel (*see* Fig. 10).

A thin Jena glass beaker replaces the thick vessel shown in Fig. 9. This change lessens the rise in temperature and thus diminishes radiation losses.

2. Radiation losses are further minimized by use of the tin cylindrical shield  $B$  in Fig. 10, which surrounds the beaker, and provides a non-conducting air jacket between the water and the outside air.

3. A copper gauze is provided to fit on to the copper cylinder and nearly touch the beaker at all points. This breaks up the bubbles that pass through the water on making a test, and causes the waste gases to be better cooled.

4. The usual thermometer is replaced by one which allows the temperature to be read to 1-100th of a degree Centigrade. This improvement in reading off the increase in temperature must of course be accompanied by increased care in the weighing, mixing and measuring operations. A one-litre flask is used for measuring the water used for the test.

5. The oxygen mixture is dried before use (one hour at 110° C. for each test), and the amount to be employed is calculated from the combustible actually present in the fuel.

The formula used for this calculation is  $W = \frac{100 - x}{4}$ ,

in which  $W$  = the weight of oxygen mixture required for 2 grams of the fuel, and  $x$  = the percentage of ash in the dry sample.

6. The mixing of the oxygen compound with the 2 grams of fuel and charging of the copper cylinder with the same are most carefully carried out, and no loss of fuel is allowed to occur in this operation. The cylinders are numbered according to their capacity as measured by water contents, and as far as possible it is planned that the fuel and oxygen mixture shall fill the cylinder to within  $\frac{3}{4}$  inch of the top. The precise degree of pressure it is necessary to employ in filling the cylinder with this mixture can only be learned by experience; if too loosely packed the combustion is too

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rapid ; if too tightly packed the charge will probably become extinguished before all is burnt. A combustion should last 1 minute.

7. The ignition fuse is made of four strands of lamp wick, one inch in length, dipped in potassium nitrate solution and dried. The four strands are twisted together, and one quarter inch of the ends are then spread out in the form of feet, and the little igniter is placed upon the top of the charged cylinder with the ends lightly embedded in the mixture, which must be left loose and porous at this place.

8. The water equivalent of the apparatus is determined by actual trial with a standard fuel as already described.

9. The copper vessels, *B*, *C* and *D* in Fig. 9 are placed in the calorimeter after *C* is charged, and the temperature is read when equilibrium is established. The tap of *B* must, of course, be closed during this period. The charge is then ignited by withdrawing and disconnecting *B*, *C* and *D* for a very brief period of time.

Operating as described in 6 and 7, the author is seldom troubled with failures to ignite or with incomplete combustions.

Using this modified form and method of working with the Lewis Thompson calorimeter, the author has obtained results which are within 2 per cent. of the calculated values of the fuel, when testing bituminous fuels containing over 25 per cent. of volatile matter. The conditions under which the test is made must, however, be kept as far as possible the same as those under which the water equivalent is determined, and any wide variation in these conditions will lead to discrepancy in the results. With semi-bituminous and anthracite coals the Lewis Thompson form of calorimeter yields, however, unsatisfactory results, owing to the amount of unconsumed carbon. Coke and peat also cannot be burned in the calorimeter, so that its field of usefulness is somewhat narrow and restricted.

For correct calorific tests of all these classes of fuel, either of the calorimeters about to be described must be used.

### THE DARLING CALORIMETER.

The Darling Calorimeter is based upon the principle of combustion in a current of oxygen gas at normal pressure,

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and the apparatus is a modified and improved form of the well-known William Thomson Calorimeter. Fig. 11 shows the essential parts of the Darling calorimeter. A small nickel or platinum crucible,  $1\frac{1}{2}$  inches high by 1 inch in dia-



FIG. 11.—DARLING CALORIMETER (ORIGINAL FORM).

meter, is held by brass arms in the centre of the perforated brass base-plate of the apparatus. A flanged glass bell-jar provided with a rubber cork, carrying a brass oxygen supply pipe, and two copper conducting wires is clamped to the base-plate by means of rubber rings and by a brass ring plate held in position by screws and nuts. It is advisable to use a rubber ring above and below the glass flange on the

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bell-jar to avoid breaking this when tightening the milled head screws. A brass gauze ring is shown in position on the bell-jar in Fig. 11, but this is an addition to the original apparatus. Fig. 12 shows another form of the apparatus



FIG. 12.—DARLING CALORIMETER (MODIFIED FORM).

in which the brass oxygen supply tube is replaced by a tube of hard potash glass widened out to form a cup at its lower end, and connected above to the oxygen cylinder or gas-holder by a glass T piece. In the first form of the Darling apparatus ignition of the charge occurs by means of a fine platinum wire fixed between the lower ends of the two copper conducting wires, which are themselves connected to four bichromate cells or to some other source of electrical energy. Fig. 13 shows a convenient Bichromate Battery made up of four pint cells. In the second form of apparatus, ignition occurs by means of a small piece of glowing charcoal ( $\cdot 01$  to  $\cdot 02$  gram) this being dropped

## FUEL, WATER AND GAS ANALYSIS

down the oxygen supply tube by removing the small cork which closes the vertical end of the glass T piece. This method of ignition is preferable to that recommended by Darling, as the use of sulphur for igniting the charge has many disadvantages. In both forms, a sheet tin cylinder surrounding the glass vessel diminishes the radiation losses and is a useful addition to the original apparatus.



FIG. 13.—BICHROMATE BATTERY OF FOUR CELLS.

The method of carrying out a determination with the Darling calorimeter is as follows :—

1,400 grams of water are measured carefully into the glass vessel shown in Fig 12, using a one-litre flask and graduated cylinder for this purpose. From half to one gram of the dry sample of fuel is weighed out into the crucible, this is placed in its holder, and the apparatus is clamped together as shown in Figs. 11 and 12. If electric ignition is to be employed the ends of the two copper conducting wires



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are joined by a short piece of very fine platinum wire, the loop of which is made to dip under the surface of the fuel contained in the crucible. It is wise to try the effect of the current on this wire before clamping up the apparatus for each test, since at times the bichromate battery requires cleaning and re-charging. The oxygen supply tube is connected to the gas-holder or cylinder containing oxygen, and a slow but steady current of oxygen is passed through the apparatus, which is now ready for immersion in the glass vessel containing the water.

When immersed the water should reach up to the neck rim of the bell-jar, but not above it, and the air which is being displaced from the interior of the apparatus by oxygen should bubble up through the water in *small bubbles* from *all portions* of the perforated brass-plate. The temperature of the water is next taken at two minutes' intervals, and when the mercury in the thermometer has become stationary, the stream of oxygen is made much more rapid, and the coal is ignited. If charcoal be used for ignition, the small weighted particle is held over a lighted match until it commences to glow, when it is dropped down the oxygen tube. When the coal contains much volatile matter, there is some danger of explosion during the early part of the combustion, and considerable skill and experience in the management of the apparatus are necessary to attain perfect combustion. It is advisable, therefore, to start with the lower end of the oxygen supply pipe high up in the bell-jar, and to have a very rapid current of oxygen when the coal (as shown by the approximate analysis) contains over 30 per cent. of volatile matter.

When the greater portion of the volatile matter has been distilled and burnt, only coke remains in the crucible, and the oxygen tube can be pushed down gradually until it is below the crucible rim. The combustion can be finished with the lower end of the oxygen supply tube nearly touching the glowing residue in the crucible. When the tube shown in Fig. 11 is employed for supplying the oxygen to the fuel, it is necessary to work this from side to side, in order to spread the stream of oxygen over the whole of the fuel and residue.

The combustion is finished when the residue in the crucible ceases to glow, but the crucible itself should become red-hot during the combustion, and in order to avoid pre-

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mature loss of heat it is advisable to support the crucible upon an asbestos tray. The current of oxygen gas through the apparatus is then slackened, and the temperature of the water is noted every half minute until a fall occurs. According to the inventor,  $4\frac{1}{2}$  minutes should suffice to burn one gram of fuel, but the author has never succeeded in carrying out a test in this time. The calculation is made as before by use of the equation  $C = \frac{(1,400 + x) t}{w}$ ,

in which  $C$  equals the calorific value of the fuel,  $t$  equals the gain in temperature of the water,  $w$  is the weight of fuel used, and  $x$  is the water equivalent of the apparatus. Although a value for  $x$  is given with each apparatus sold, it is far better and safer to determine it by use of a standard combustible such as cellulose or pure carbon, as described in the previous section of this chapter.

The Darling calorimeter only yields entirely satisfactory results with fuels low in ash and in volatile matter. When fuels containing a high percentage of volatile matter are burned in the Darling apparatus there is a tendency for some of the volatile hydro-carbons to escape unconsumed; and when fuels high in ash are tested, there is a tendency for portion of the fixed carbon to remain unburned in the crucible. In the case of coke this unconsumed carbon may amount to 10 per cent. of the total combustible matter.

The first of these difficulties may be overcome by mixing one-third of its weight of china clay with the fuel before burning in the calorimeter. This remedy, however, is only partial, for it increases the amount of ash remaining in the crucible, and therefore the risk of some of the fixed carbon remaining unconsumed.

The second difficulty can only be overcome by making small pellets or briquettes of the fuel sample, and using these for combustion in the calorimeter in place of the finely powdered sample. Fig. 14 shows the pellet mould used by the writer for this purpose. Two grams of the finely powdered sample are mixed in a small agate or glass mortar with one c.c. of a 1 per cent. solution of pure gum-arabic in water. Very bituminous fuels can be moulded without adding gum-arabic. This paste is then pressed into three cylinders in the mould shown. Each of these is cut while still moist into two halves with a sharp knife, and the six little pellets of fuel obtained in this way are then dried at

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230° C. for one hour in the air-bath. Two, three or four of these pellets, according to the weight required, are then used for the calorimetric test, which is carried out as already described.

When fuels containing less than 10 per cent. of volatile matter are tested in the Darling calorimeter some difficulty will be met with in the absence of an electric current in causing them to ignite, for neither charcoal nor sulphur will always suffice to start the combustion. The best plan in such cases is to use a small weighted portion of some pre-

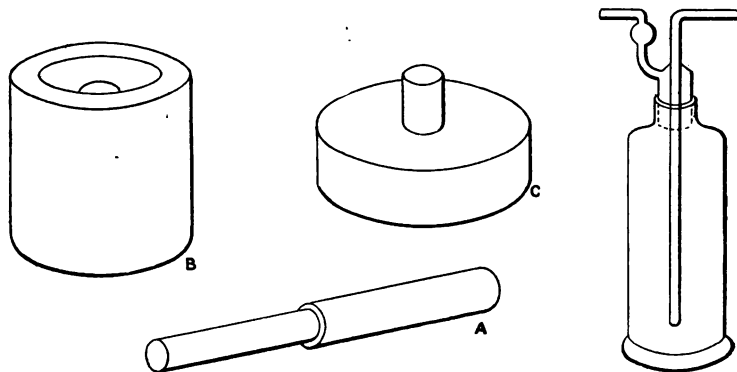


FIG. 14.—BRIQUETTE MOULD.

FIG. 15.—WASH BOTTLE FOR REGULATING OXYGEN SUPPLY.

viously tested bituminous coal, either making a mixed pellet of the two coals or using both in the powdered form and sprinkling a little of the standard bituminous fuel on the surface of the other in the platinum crucible. The different calorific value of the added fuel must of course be allowed for in calculating the result of the test.

By using only half a gram of fuel and a thermometer reading to 1-100th of a degree Centigrade, the time required for burning the fuel and the gain in temperature can be reduced one-half, and the errors due to radiation losses correspondingly diminished. When working with this small amount of fuel, very careful and accurate weighing and measurements are required to obtain reliable results.

The combustion of the fuel can be effected much more quickly when the fuel is in briquette form, since the current of oxygen gas can be increased greatly without danger of blowing the fuel out of the crucible.

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The oxygen used in working the Darling apparatus should either be stored in a gas-holder over water, or should be passed through a glass tower filled with pumice soaked in water, in order that it may take up before use all the water it can carry at the temperature of the laboratory.



FIG. 16.—MAHLER-DONKIN BOMB CALORIMETER.

It is also useful to have a wash-bottle through which the oxygen bubbles, inserted between the gas-holder or cylinder and the calorimeter, as in this way the speed of the current can be more easily noted and controlled. Fig. 15 shows a suitable form of wash-bottle.

When used with the precautions described above, the Darling calorimeter can be made to yield accurate results

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with all classes of fuel. But as usually employed, the combustion is in many cases imperfect, and unless allowance be made for the unburned hydro-carbon gases and fixed carbon, the calorific values obtained are too low.

### THE MAHLER-DONKIN BOMB CALORIMETER.

Figs. 16 to 19 show the component parts of the Mahler-Donkin bomb calorimeter. The combustion of the fuel in this calorimeter is carried out in oxygen gas at from 200 to 400 pounds pressure. Fig. 16 shows the most important



FIG. 17.—WATER VESSEL AND MIXING PADDLES.

portion of the apparatus—namely the bomb. This is a heavy gun metal cylinder (*A*), provided with three screwed stud pins for bolting down the cover (*D*), and lined inside with gold to protect the metal from corrosion by the acids formed during combustion of the fuel. The cover is provided with a milled head screw valve (*B*) for regulating the inlet of oxygen gas, with an insulated conducting wire (*C*), which runs through the cover and terminates below, and with three heavy nuts for bolting down the cover on to the cylinder. Thin lead wire is used to make the joint between the cylinder and cover, and the bomb is tested up to 1,500 pounds pressure before leaving the makers' works. Fig. 17

## FUEL, WATER AND GAS ANALYSIS

shows the rest of the apparatus, namely a water container and paddles for quickly obtaining a uniform temperature. A water-jacket and also an air-space surround the inner vessel containing the measured volume of water and the bomb, and the mixing paddles fit round the latter. These paddles can be worked up and down, or in a circular manner, by the wooden nob which projects six inches above the



FIG. 18.—BOMB COVER WITH PLATINUM DISH AND IGNITION WIRE.

water container, when all the apparatus is fitted together. The ignition of the fuel occurs by electric heating, a fine platinum wire being used as bridge between the lower ends of the two electrodes fixed on to the bomb cover. Fig. 18 shows the cover alone supported on a tripod stand, with the small platinum dish and the platinum wire ignition loop. It is well to make a trial test of the electrical connections in this position, since if the platinum wire does not heat to redness it is comparatively easy to find out the cause, whereas later on, when the cover is bolted on to the cylinder and the bomb is immersed in the water, a failure

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to ignite causes much trouble. Platinum wire must be used for ignition purposes. The author uses the finest made, of which twelve inches weighs 2 grains. Iron wire cannot be used, for it produces fused iron oxide on ignition and this speedily corrodes the gold plating of the bomb at those places where it falls. A small platinum dish 1 inch in diameter and  $\frac{3}{8}$  inch deep is preferable to a crucible for



FIG. 19.—BOMB WITH OXYGEN SUPPLY CONNECTIONS AND PRESSURE-GAUGE.

holding the fuel, since it is easier in this case to arrange that the platinum loop shall dip in the fuel. For this purpose the wire is wound seven or eight times round the straight electrode, and the loop is lengthened as required by pulling one or more of these coils down with a pair of small forceps. The weight of fuel used for carrying out a test with the bomb calorimeter varies from .40 to 1.0 gram. The smaller the quantity of fuel used, the smaller is the rise in temperature of the water, and the less is the time required for completing a test, both of which reduce the error due to radiation

## FUEL, WATER AND GAS ANALYSIS

losses. On the other hand this method of working demands great care in all weighing and measuring operations; and some degree of skill in manipulating the apparatus is necessary, before correct results can be obtained when working with .5 gram of fuel.

After weighing out the fuel roughly into the platinum dish,



FIG. 20.—OXYGEN CYLINDER WITH REDUCING VALVE AND PRESSURE GAUGE.

it is advisable to heat the same for one half-hour in the air-bath at  $230^{\circ}$  C., and to re-weigh carefully before making the test with it. The dish is then transferred to the holder under the cover, the platinum wire ignition loop is lowered carefully until its lowest section just dips into the fuel, and the cover is placed on the bomb and bolted down. Ten c.c.



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of distilled water, to absorb the acid gases produced by the combustion, have been previously measured into the bomb. Great care must be taken not to jerk or jar the bomb while bolting on the cover, since this may cause a displacement of the ignition wire and a failure to ignite later on. A wooden block-holder is provided with the Mahler-Donkin bomb, which can be screwed to the laboratory working bench. This greatly facilitates the screwing tight of the cover.



FIG. 21.—BOMB IMMERSSED AND READY FOR IGNITION OF THE FUEL.

The next step is to fill the bomb with oxygen, and the necessary connexions to the oxygen cylinder are shown in Fig. 19. A pressure gauge recording up to 400 pounds is provided between the oxygen cylinder and the bomb, and a thick walled copper tube provided with flanged ends and nuts is employed to connect this with the cylinder and bomb. Small lead washers assist in making these joints

## FUEL, WATER AND GAS ANALYSIS

gas-tight. It is well to have a fine screw regulating valve and a pressure gauge reading up to 120 At. attached to the oxygen cylinder as shown in Fig. 20. Otherwise it is difficult to control properly the flow of gas into the bomb, and too rapid a rush of oxygen may cause some of the finely-powdered fuel to be blown out of the platinum dish. The gas must be admitted to the bomb slowly. The amount required, as indicated by the pressure, varies with the amount of fuel used. For half a gram of fuel a pressure of 220 pounds suffices, for one gram of fuel 400 pounds is necessary. With this higher pressure there will be some difficulty in keeping all the joints tight, but slight leaks may be ignored. In the Mahler-Donkin bomb as originally designed, a considerable loss of pressure and of gas occurred also on closing the milled head screw valve on the top of the bomb, since to close this it was necessary to loosen the screw nut connecting the oxygen supply pipe above it. The author has therefore had a small back pressure valve inserted in his bomb in the portion of the cover marked *B* (Fig. 16), and this comes into action and closes the exit-pipe as soon as the exterior pressure is relieved. This is a most useful addition to the earlier design.

The milled head screw valve is now closed, the bomb disconnected from the supply, and the opening in the top of the bomb is closed by the screw nut shown in the foreground in Fig. 16. The bomb is now carefully transferred to the water vessel which has been previously filled with 2,500 c.c. of water at the laboratory temperature, the mixing paddles are placed in position, and the conducting wires from a bichromate battery of four cells, or from some other source of electrical energy (two ampères at 12 volts are required) are connected to the terminals on the bomb. Fig. 21 shows the general arrangement of the apparatus when ready for firing the charge of fuel. The screw nut projecting above the water in the calorimeter vessel is used as the second terminal on the bomb. The mixing paddles are now worked gently until the thermometer dipping in the water of the inner vessel ceases to rise or fall, and the fuel is then fired by depressing for three seconds the last of the zinc plates of the bichromate battery. Within half a minute, if the ignition has occurred properly, the thermometer will begin to rise, and the mixing paddles are now worked steadily until the mercury again becomes stationary.

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The final temperature is then recorded, and the test is finished.

For work with this calorimeter, the author uses two specially made mercury thermometers 24 inches in length, graduated in 50ths and ranging from 0° C. to 25° C. With the aid of a magnifying glass, 1-100th of a degree can easily be read on these thermometers.

The calculation is carried out as before by aid of the equation  $C = \frac{(2,500 + x) t}{w}$  in which  $C$  represents the calorific value,  $x$  the water equivalent of the apparatus,  $t$  = the gain in temperature, and  $w$  = the weight of fuel used in grams. The value of  $x$  is best determined as before by making a test with pure cellulose, naphthalene or carbon, and by inserting  $x$  as the unknown value in the above equation. Pure naphthalene has a calorific value of 9,692 calories, pure cellulose of 4,200 calories, and pure amorphous carbon of 8,137 calories.

The Mahler-Donkin bomb yields accurate results with all classes of fuels, and when once fitted up with all the necessary accessories, tests can be made with it in from one half to one hour. The whole of the apparatus should be dismantled and cleaned after each test, especial attention being given to the bomb, cylinder and cover, as the gold plating of these requires very careful cleaning and drying, if it is to last any length of time. Portion of the thin platinum wire used for ignition is generally fused during the combustion, but the heat absorbed by this is included in the value of  $x$  used for the water equivalent of the apparatus.

When testing anthracite or coke, the platinum wire ignition sometimes fails to ignite the charge, and to overcome this difficulty .10 gram of a standard bituminous fuel may be used on top of the weighed portion of coke or anthracite, as ignition charge. The thermal value of this addition must be allowed for, in calculating the results of the test.

## CHAPTER IV.

### The Practical Applications of the Test Results.

**E**NGINEERS who have never made use of the results obtained by laboratory tests of fuel, either in relation to their supplies of fuel or in the working of their boilers, are disposed to be somewhat scornful as to the value of fuel testing to the practical engineer. In their view the results obtained from steam-raising trials are alone worth depending upon. That this view is superficial and incorrect is proved by the fact that engineers who have adopted fuel testing as an aid in the work of boiler management rarely relinquish it, and as their knowledge of its usefulness extends, they place more and more reliance upon the laboratory test results, and less upon the steam-raising trials, in forming their comparative judgments of different fuels. When one remembers that the essential conditions obtaining during steam raising tests are never exactly the same; that all fuels are treated alike although different fuels demand different methods of firing and different treatment as regards draft to obtain their maximum evaporative effect; and that the fireman or engineer who is in charge of the boilers may very probably be receiving a bonus or present from one of the fuel supply firms, this loss of confidence is not surprising. The value of comparative steam-raising tests as a guide in the placing of fuel contracts, or in the control of the fuel supplies is, in fact, greatly over-rated, and the larger number of these tests, as they are at present carried out, are not worth the time and expense entailed in obtaining them.

In the following pages the author will deal with three practical and scientific applications of the test results as obtained in the laboratory examination of fuels, and will show how these can be utilized in—

1. Placing fuel contracts.
2. Controlling the fuel supplies.
3. Checking the evaporative efficiency of the boilers.

# FUEL

## I. PLACING FUEL CONTRACTS.

Contracts for the delivery of large quantities of fuel involving the expenditure of many hundreds of pounds, ought always to be based upon the laboratory test results for the reasons already given. The sampling and testing of each sample load of fuel should be conducted as described in Chapters II and III, both approximate and calorific tests being carried out.

If possible, a bomb calorimeter should be employed for the latter tests, since in this case the results obtained are reliable for all classes of fuel. Steam-raising tests can of course be made at the same time ; but the author has given reasons for doubting the value of these unless much more scientifically carried out than is usual at present. The laboratory test results of the various sample loads of fuel are then grouped as shown in Table I (see Appendix). If the contract is to be based solely on cheapness, the decision is easily made by comparison of the figures given in column 10. These figures are obtained by dividing the calorific value multiplied by 2,240, by the price per ton in pence of the fuel delivered in the bunkers. As a rule, however, the percentages of ash and of volatile matter will have some influence upon the choice of fuel. Having eliminated from the list those which are unsuitable owing to high ash contents, or to too high a percentage of volatile matter, the selection from those remaining in the list, of the fuel which yields the greatest number of calories per penny of cost is an easy matter. Provided that correct conditions of stoking and draft are employed in burning the fuel under the boilers, the fuel which gives the greatest number of calories per penny of cost will prove the most economical in actual use.

That wide variations exist in the value of different fuels when judged by this method is proved by the following figures, based on actual tests and prices :—

South Wales	{No. 1.	68,544	calories per penny of cost.
steam coals	{No. 2.	89,600	” ” ”
	{No. 3.	128,128	” ” ”
Lancashire	{No. 4.	119,168	” ” ”
bituminous	{No. 5.	148,512	” ” ”
coals	{No. 6.	193,088	” ” ”

The calorie used in this table is the pound Centigrade unit, and the above figures must be multiplied by 1·8 to

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obtain the corresponding value in British Th. Units. If burnt under "correct conditions" to obtain the maximum efficiency, it is therefore evident that the coal marked No. 6 in the above list would prove the most economical in actual use, for it yields double the heat units of Nos. 1 or 2 per penny of actual cost. If burnt in furnaces designed for South Wales steam coal, with a small combustion area, it is, however, possible that this No. 6 coal would not show this superiority, and the author must once again emphasize the necessity for adapting the furnace design, dimensions and methods of firing, to the type of coal which is to be burned, if good results are to be obtained. The discrepancies which occur between the laboratory test results and those obtained in actual practice are chiefly due to the neglect to observe this essential condition for obtaining good results under the boilers. The subject of furnace design and control of the combustion process, however, is somewhat outside the scope of this work, and readers must refer to the book named below for an adequate discussion of it.<sup>1</sup>

Having selected a fuel from the small or large number of which sample waggons have been submitted for trial, it is advisable that the contract should be based upon the results of the laboratory tests, and that some kind of a sliding scale relation between calorific value and price should be arranged. The exact details of this will vary in the individual cases; but the specification reproduced below is an example from actual practice of a fuel contract based on laboratory tests, with a sliding scale arrangement between calorific value and contract price of the fuel. The fuel in this case was a South Wales steam coal, delivered at 9s. 7d. per ton.

### SUPPLY OF LARGE WELSH SMOKELESS STEAM COAL. SPECIFICATION AND CONDITIONS.

1. **Quality.** To be Large Welsh Smokeless Steam Coal, free from dust, to contain not more than 15 per cent. of small, and to have a minimum calorific value of 13,300 (thirteen thousand three hundred) British Thermal Units per pound of coal, as measured by a calorimeter approved by the Borough Electrical Engineer.

<sup>1</sup> *Smoke Prevention and Fuel Economy*, by Booth & Kershaw. Constable, 1905.

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2. **Tests.** During the continuance of the contract, tests will be made once every week from samples delivered during that week, and if the mean of four tests during any month show that the calorific value is below the standard, the rate per ton paid to the contractor for the whole of the coal delivered during that month, shall be less than the contract price as set forth in the "Price Schedule" attached hereto.

3. **Right to reject inferior coal.** Notwithstanding Condition No. 2 the Council reserve to themselves the right to reject any portion of the coal delivered, the tests of which show that the calorific value is less than 13,300 British Thermal Units per pound of coal.

4. **Engineer's decision to be final.** Should any dispute arise as to the accuracy of tests, weights, quantity of dust or small, quality, or other matters whatsoever, the decision of the Borough Electrical Engineer shall be final and binding.

### PRICE SCHEDULE.

Scale of reduction in price for lower calorific value than 13,300 British Thermal Units.

Per Pound.	At Pit's Mouth.	Delivered.
For a minimum of 13,300 B.T.U. the contract price . . . . .	—	<i>s. d.</i> 9 7
Below 13,300 but not less than 13,200 a reduction of 5 <i>d.</i> per ton . . . . .	—	9 2
Below 13,200 but not less than 13,100 a reduction of 10 <i>d.</i> per ton . . . . .	—	8 9
Below 13,100 but not less than 13,000 a reduction of 1 <i>s. 3d.</i> per ton . . . . .	—	8 4

Clause 4 of this contract is obviously unfair to the Colliery Company, since an independent chemist or fuel expert ought to be appointed as referee in case of disputes. But otherwise the specification has much to recommend it.

Another method of working out the price variation for differences in calorific value, has been recently adopted by the city of Chicago in the purchase of 200,000 tons of coal. The standard price in this case was \$2.30 per ton of 2,000 lbs. for a coal testing 13,000 B. Th. Units in the undried state. Allowing for the moisture and cost of removing the

## FUEL, WATER AND GAS ANALYSIS

ash, this worked out to 100,000 B. Th. Units for one cent. If the B. Th. Unit per cent. came out above or below this limit, the price of the coal varied accordingly ; the principle underlying the contract being that in all cases one cent. should purchase 100,000 B. Th. Units of heating value in the fuel. Thus at times the seller, and at times the buyer, was favoured by the price variation, and the price asked and paid for the fuel was an absolutely fair one.

The author believes that in time this last described method of buying fuel will apply to all large fuel contracts. The present method is grossly unscientific and unfair alike to the buyer and seller, and the sooner it is replaced by another the better it will be for all concerned.

In drawing up fuel contracts it would also be well to stipulate that the moisture and sulphur contents shall be kept well within the percentage shown by the test of the sample waggon. Owing to various causes the percentage of moisture and sulphur in coal and slack may at times rise to a very high figure, and apart from the foolishness of paying from 7s. to 10s. per ton for this water and sulphur, there is the question of the heat which will be carried off to the chimney when the water is converted into steam in the furnace of the boiler. As regards ash contents, it would also be well to reserve the right to reject deliveries of fuel showing a percentage much above that embodied in the contract. But the increase in ash will always be accompanied by a corresponding diminution in thermal value, and the variation in ash contents is therefore covered by the sliding scale arrangement based on the result of the calorific tests.

Though the freedom to reject coal below the stipulated thermal value may be reserved to the buyer as in Clause 3 of the contract printed above, in most cases it is least troublesome to accept delivery, and to claim the deduction in price under the sliding scale arrangement. Otherwise much trouble and expense may be entailed in connexion with re-loading and railway charges.

### II. CONTROLLING THE FUEL SUPPLIES.

The laboratory testing of fuel can be employed most usefully to check the quality of the supplies of fuel from day to day and from week to week. When the contract has been based upon calorific value, this testing is of course essential.



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If the contract has not been based upon the results of the laboratory test of the sample waggon, no automatic reduction in price can follow should this laboratory examination of the daily and weekly samples yield bad results. But the fact that the deliveries of fuel are being regularly sampled and tested will be known to the Colliery Company supplying the fuel, and will cause them to be more careful in the selection and sorting of the fuel sent. Complaints also based on the results of laboratory tests, will receive more attention than those based merely on firemen's complaints, or upon a manager's inspection of the fuel. As already stated there is good reason to suppose that the firemen and sometimes the engineer in charge, have a financial interest in keeping the fuel contract to one particular firm. Therefore neither their silence nor their complaints can be accepted with any degree of security. Most engineers in charge of boiler plants, when attempting to make changes in their fuel have experienced the apparent stupidity or obstinacy of their firemen; and have had reason to suspect their impartiality as regards the fuels with which they are conducting trials. Even in the absence of contracts based on calorific value it is therefore well to have this independent check upon the character of the fuel supply, for a fireman receiving doles or presents from the Colliery Company is not likely to become very active in complaining of this fuel, when the deliveries fall off in quality. As a check therefore upon the supplies, the author advises daily sampling of the fuel either in the waggons and trucks, or during discharge into the storage bins.

When sampling fuel in trucks or waggons, it is necessary to make allowance for the fact that the jolting of railway or road transit causes all the fine coal and dust to fall to the bottom of the mass. To obtain a fair sample of coal from a railway truck is therefore a matter of some difficulty, and in most cases it will be easiest to sample the fuel during discharge. Coal conveyed in canal barges or by river to the works, does not undergo a similar mechanical separation into large and smalls, and in such cases the load of fuel can be sampled if necessary in the barge.

In all cases, however, the fairest sample can be obtained during discharge, and where conveyors and automatic weighing plant are in use, it is a comparatively simple

## FUEL, WATER AND GAS ANALYSIS

matter to arrange that every fifth, tenth or twentieth bucket shall be tipped into a sample storage bin. If fuel from more than one colliery is being delivered and used at one time in the works, it will of course be necessary to have an equal number of sample storage bins.

At the end of each day the fuel in these bins is crushed and sampled in accordance with the instructions given in the Appendix, and the one pound samples are sent to the laboratory or to the fuel expert for examination and test. It will not, as a rule, be necessary to carry through a complete approximate analysis and calorific test as described in Chapters II and III, with each of these daily samples; the determination of the moisture and ash in each being sufficient to enable one to check roughly the quality of the coal being supplied under the contract. The daily samples are, however, retained each in their own sample tin, and once a week or oftener, an average sample is made up from these by weighing out 50 or 100 grams of each, and by thoroughly mixing the same on the sampling plate, or on a sheet of glazed paper. A complete approximate analysis and calorific valuation is then carried out with this sample. Upon the results of these weekly tests complaints to the Colliery Company as to the quality of the supplies and the variations in price of the fuel delivered under the contract are based.

A book should be kept for entering up both the daily and weekly fuel tests. The results obtained during the delivery of coal under any one contract will prove of great value in fixing the terms for the next contract.

Special samples of single waggons or trucks of fuel that appear to be of bad quality should be taken occasionally, for at times the Colliery Company may become negligent in their supervision of the sorting and cleaning of the coal brought up from the pit, and, as already pointed out, much dirt and shale can be sometimes sold as fuel. The author has tested fuels containing only 6 per cent. of ash, from the same pit that produced slack testing up to 25 per cent. of ash, and some years ago he was asked to report upon a sample of so-called coal which contained no less than 37.70 per cent. of ash.

These figures prove the fallacy of the opinion held by many engineers that coal from one pit or from one seam is of fixed and unvarying composition when delivered into

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the trucks, and that it is alone necessary in drawing up fuel contracts to specify the pit or seam from which the supplies are to be drawn.

Fuel, in fact, appears at present to be the only raw material used in large quantities, the sale and delivery of which is still, in the majority of instances, conducted by rule of thumb methods. It is satisfactory to note, however, that in this matter also, the methods of the past are being replaced gradually by the more scientific and exact methods of procedure, outlined in this Chapter.

### III. CHECKING THE EVAPORATIVE EFFICIENCY OF THE BOILERS.

With the aid of the figures obtained by the calorific test of the average weekly sample of fuel, as described in Section II of this Chapter, it is possible to make out a balance sheet for the working of the boiler plant, and to calculate the evaporative efficiency of the same with a high degree of exactitude.

By evaporative efficiency is signified the percentage ratio between the total heat value of the fuel, and that utilized in the conversion of water into steam.

The other tests required for ascertaining this efficiency by calculation, are those showing the composition and temperature of the exit-gases. The methods of obtaining these will be dealt with in Chapters IX to XII, and in this Chapter the method of applying the results will alone be dealt with.

There are four directions in which the heat produced by combustion of fuel is dissipated in the furnace of a boiler.

In the first place, a certain definite and fixed loss occurs by radiation from the exposed surface of the boiler and of the surrounding brickwork. This loss can be roughly ascertained by drawing the boiler fires, closing the steam valve and feed water valve, *entirely* cutting off the draft, and by noting the time required for a fall of 10 or 20 lbs. in the pressure of the steam. As a rule, radiation losses account for from 7.5 per cent. to 10 per cent. of the heat present in the fuel. The figure when once ascertained for any one boiler may be used as a constant in all the future heat balance calculations.

The second direction in which heat is dissipated or lost in boiler working is with the waste gases passing away from the boiler flues to the chimney. The method of ascertain-

## FUEL, WATER AND GAS ANALYSIS

ing and calculating this loss will be described in Chapter XII. This loss may amount to from 10 per cent. to 30 per cent. of the heat value of the fuel burned.

The third direction of heat loss is by the ashes and cinders. The loss here is twofold, being partly due to the heat carried by the ashes and partly that due to the unburned carbon in the cinders. Once a week the ashes may be sampled and the unburned carbon determined by the method used for estimating the amount of ash in the fuel. (*See Chapter II*).

The total heat loss in the ashes and cinders should not exceed 5 per cent., but it may rise much higher with chain grate stokers when badly worked, or with untrained firemen and hand-fired boilers.

The fourth direction in which heat is dissipated is through the boiler plates. It is this portion of the heat alone which is the active agent in water evaporation and gives the evaporative efficiency of the boiler. It is ascertained by adding the three items of loss named above together and by subtracting the total from the thermal value of the fuel, as determined by the laboratory examination of the same.

The following is an example of this method of calculating the working efficiency of boiler installations:—

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Lancashire slack at 7s. 6d. per ton delivered in bunkers.  
Heat units produced per pound by calorimeter test, 13,500 B. Th. Units.

1. Losses by radiation, etc. (10 per cent.)	1,350
2. Losses with exit gases up the chimney (calculated) 10 per cent. CO <sub>2</sub> and gases at 465° F.	2,304
3. Losses by unburnt carbon in cinders and ashes, and heat carried away in same (5 per cent.)	675
4. Converted into steam in boilers (by difference)	9,171
	13,500

The efficiency of the plant, therefore, equals  $9,171/13,500$  or 67 per cent. Items 1 and 3 are based on estimates or upon previous test results, but these two items under ordinary working conditions should not vary more than 5 per cent.

Should the analysis of the exit gases show that carbonic oxide gas is present, a further entry will be necessary in

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the above heat balance to show the thermal units lost by this failure to burn all the carbon to carbon dioxide. Let us take, as an example of this additional calculation, exit gases containing 2 per cent. by volume of CO and 8 per cent. CO<sub>2</sub>. Since carbon, when burnt to carbon dioxide, yields the same volume of gas as when burnt only to carbon monoxide, the above percentages show that two-tenths or one-fifth of the carbon present in the fuel has escaped complete combustion. Now, as found by the approximate analysis, the percentage of fixed carbon present in the fuel was 60 per cent., and the thermal units liberated when carbon is burned to CO are 10,201 less than when carbon is burned to CO<sub>2</sub> (4,343 and 14,544 respectively).

The loss of heat due to incomplete combustion in the case under consideration is therefore :—

$0.60 \times \frac{1}{5} \times 10,201 = 1,224$  B. Th. Units, and the efficiency of the boiler is reduced to 58 per cent. in consequence of this incomplete combustion of a portion of the fuel.

This additional loss is a considerable amount (9 per cent.) of the total heat energy of the fuel, and the calculation shows the necessity for keeping a close check upon the presence of CO in the exit gases. Since the automatic recording instruments now in general use for checking the composition of the exit-gases from steam-boiler plants do not record the presence of this gas, it is evident that independent tests with an Orsat apparatus ought at times to be made, in order to check the presence or absence of CO. This gas is most likely to be present when attempts are being made to work with a minimum of air and thick fires, in order to attain a high percentage of CO<sub>2</sub> in the exit gases. Thus efforts to reduce the heat losses due to excess of air, unless under a chemist's control, may result in very considerable heat losses in another direction. The need for expert scientific control of the testing work is therefore apparent, and automatic testing apparatus, though useful, is not an efficient substitute for the trained chemist.

The subject of gas-testing will be dealt with at length in Chapters IX to XII, but it may be pointed out here that as fuel and gas analysis enable one with ease and a fair degree of accuracy to determine the thermal efficiency of the whole boiler installation, it is deserving of more attention than has yet been accorded to it by engineers in charge of boiler plants. In fact, these test results enable one, at a

## FUEL, WATER AND GAS ANALYSIS

moderate expense, to achieve daily or weekly what at present is only carried out at long intervals of time and with much disturbance to the usual routine, under conditions of working which cannot be regarded as normal. The money now expended upon special steam-raising and efficiency trials, if expended in the way suggested upon regular testing work, would lead, in the author's opinion, to far more valuable results, and to a far better average of efficiency than is attained under the present system.

## PART II : WATER.





## CHAPTER V.

### The Sources of Feed Water Supply and the Physical and Chemical Characteristics of the Same.

**T**HE water supply is only second in importance to that of fuel for the efficient working of steam-boilers, and an adequate supply of pure water is an essential condition of cheap steam-generation.

The dissolved impurities present in varying amounts in all natural waters separate as sludge or as a scale inside the boiler, and the greater the amount of these impurities the more often will cleaning and scaling of the boiler be necessary.

The water intended for use in boilers for steam-raising purposes cannot, therefore, be too free from impurity, and the generally held opinion that rain-water or condenser water is too pure is fallacious. The corrosive action observed with rain-water is due not to its purity but to the impurities, present in the form of dissolved gases. On heating the water these dissolved gases (oxygen and carbon dioxide) escape, and the pitting and corrosion found round the feed water supply pipe of boilers fed with rain-water is due to the chemical activity of these gases at the moment of their liberation. The best method of expelling these gases before the water enters the boiler will be dealt with in Chapter VII.

In addition to the gaseous impurities found in natural water, there are present varying amounts of dissolved salts, and in some cases suspended impurities. The carbonates and sulphates of lime and magnesia are the most common dissolved salts, but chlorides and nitrates are also found in some waters. The waters that are free from suspended impurities and appear the most clear and sparkling to the eye are not, as a rule, the most suitable for use in steam-boilers. Chemical examination is always necessary before we can be certain that it will be safe or advisable to use a

## FUEL, WATER AND GAS ANALYSIS

particular water for steam-raising purposes, without some preliminary treatment for removal of its impurities.

The source from which the water is drawn has much influence upon the character and amount of its impurity. Below, the general characteristics and composition of rain, river and well-waters are given, so far as these have any bearing upon the use of such waters for steam-raising purposes.

### RAIN-WATER.

This is the purest natural water, for it contains only the impurities taken up by the water during its passage from the clouds to the earth, namely oxygen, carbon dioxide, sulphur dioxide, soot and dust. In country districts rain-water is often entirely free from the three last-named impurities, and contains only comparatively small amounts of oxygen and carbonic acid gas. To obtain an adequate supply of such water for boiler feed purposes, however, involves the creation of large reservoirs fed by large catchment areas, and in most cases this is not possible for the ordinary works or factory, owing to the capital expenditure involved. Rain-water collected in towns or upon the outskirts of industrial districts is, on the other hand, so contaminated with sulphurous acid, soot, dust and other impurities, that filtration and chemical treatment are necessary before such water can be safely used in steam-boilers. For this reason rain-water is not often employed for feed water supply, except in those special cases where these two objections lose much of their force and weight. It is quite possible, however, that rain-water might be used much more extensively than at present is the case, for steam-raising purpose; and that some thought and ingenuity expended by engineers in arranging catchment areas and storage reservoirs would be well repaid in the greater freedom of the boilers from scale and corrosion due to the impurity of the feed water used. An average rain water will contain less than two parts of dissolved or suspended matter per 100,000 of water.

### SURFACE AND RIVER WATERS.

Rain-water after it has travelled any distance over the surface of the ground either in country or town districts becomes further contaminated with suspended and dissolved

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matter, and therefore less suitable for use in boilers without some purification treatment. Here again the appearance of the water may be wholly deceptive and chemical examination will alone reveal the nature and amount of the impurities present. In mountainous districts the amount of impurity taken up from the soil is small, and the surface water collected in the catchment area of Lake Vyrnwy, in North Wales, or in the catchment area of Thirlmere, in the Lake District, for supply of the cities of Liverpool and Manchester respectively, is remarkably pure and free from dissolved salts. As one comes down to lower levels and approaches the neighbourhood of towns, the amount of dissolved and suspended matter in the surface water increases considerably. The following tests of the Liverpool water supply are interesting in this respect :—

		Parts per 100,000 of water.	
Vyrnwy—Total solids in solution	4.46	Hardness	1.70
Rivington    "    "    "    "	10.36	"    "	3.90

Vyrnwy is a mountainous district in North Wales, while Rivington is the old catchment area near Bolton. The influence of the neighbourhood of towns upon the purity of the supply is shown by the increase of dissolved matter from 4.46 to 10.36 pts. per 100,000.

When the catchment area is formed by peaty land a large amount of organic matter finds its way into the water, due to the gradual decay of the plant life which forms the peat. In such cases the surface water will be coloured brown and may contain large amounts of organic acids. Surface waters coming from peat or moor-lands, even when colourless, should therefore always be examined by a competent chemist before use in steam-boilers, for these organic acids are not detected by the ordinary reagent, litmus.

Surface waters collected in chalky districts may contain large amounts of lime in solution, either as carbonate or sulphate. In some cases the dissolved impurities present in such surface waters may exceed in amount those found in well waters. The impurities present in surface waters, in fact, vary greatly in different districts, and the geological formation of the surrounding country has much influence upon the nature and amount of the impurities. As a general rule, surface waters collected in country districts are purer than river or well waters, and such waters may often be used in boilers without any preliminary purification.

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*River water*, on the other hand, is usually contaminated with the drainage and refuse of the villages and towns situated along its banks and the water, except when taken from near the river's source, is more impure than the surface drainage water which flows into it. The dissolved salts may in some exceptional cases be less, but the suspended impurities and organic matter are nearly always greater in amount.

As the river grows in width and volume the impurities, as a rule, increase in even greater ratio, and attain a maximum at the point where the river meets the tidal waters of the sea. Here sodium and magnesium chloride are added to the list of dissolved salts present in the water. It is therefore dangerous to use water from tidal rivers within five miles of their mouth for steam-raising purposes without daily sampling and testing for detection of these impurities; chlorides being most dangerous salts to have present inside a steam-boiler.

### SPRING AND WELL WATERS.

The water that has passed through any considerable thickness of the earth's crust is, as a general rule, highly charged with dissolved gases and salts. The greater the depth from which the water flows or is pumped, the larger will be the amount of these impurities. Carbonate of lime with the corresponding salt of magnesia is insoluble in pure water, but the presence of carbonic acid in the water renders these salts soluble. This acid is formed in the water by the carbon dioxide dissolved in its percolation through the upper soil and sub-soil of the earth's crust. Sulphate of lime on the other hand, is slightly soluble in pure water, and 1,000 grams of water can dissolve 2.72 grams of calcium-sulphate. Carbonates and sulphates of lime and magnesia exist in large masses in the earth's crust. The nature and amount of the dissolved impurities present in well and spring waters therefore varies in different districts, and water drawn from 300 feet below the surface in some districts will be much purer than water from a similar depth in other districts. Since the percolation through the soil removes all suspended impurities, and charges the water with dissolved gases, well and spring waters are generally clear and sparkling. Owing to the amount of gaseous and solid

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impurities they contain, these waters are, however, most unsuitable for boiler feed purposes, and they should never be employed if an alternative supply be available. When the local conditions are such that well or spring water must be used, a treatment by chemicals for removal of the greater portion of the impurities is essential to the economical working of the boiler plant.

All waters from whatever source, containing over fifteen parts of solid matter per 100,000 should, in fact, be submitted to chemical and mechanical purification treatment, and as far as possible the boiler should be fed with the purest water which can be obtained in this way. The formation of scale inside boilers leads to so many evils, and so diminishes the efficiency and life of the boiler, that in most cases the capital outlay upon and cost of working a softening plant is a wise expenditure of money, and is soon repaid by the savings in fuel and repairs.

The salts found in solution in natural waters may, in fact, be divided into two classes—*scale-forming* and *non-scale-forming*. To the first-named class belong calcium carbonate, magnesium carbonate, calcium sulphate and magnesium hydrate. To the second class belong the following salts: Calcium nitrate; magnesium sulphate, nitrate and chloride; sodium sulphate, nitrate and chloride.

The carbonates of lime and magnesia produce what is known as "*temporary hardness*" since it can be removed by boiling, while the sulphates and hydrates of lime and magnesia produce what is known as "*permanent hardness*."

It is important to note that the accumulation of the non-scale-forming salts in a boiler produces evils nearly as great as those caused by scale. Chlorides decompose at temperatures which may be attained in the boiler, and produce free chlorine, a most corrosive gas. The sulphates and nitrates, on the other hand, when present as concentrated solutions attack the brass and gun-metal fittings of the boiler and cause much trouble from leakage. When using feed water containing considerable amounts of these non-scale-forming salts, it is therefore necessary to blow off the boiler at frequent intervals. This, of course, means loss of heat and diminution of its working efficiency. For these reasons in nearly every large works it will be found that economy is promoted by the use of a purer water or by the erection of a water-softening plant.

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### SAMPLING BOILER FEED WATER.

The sampling of water does not present such difficulties as the sampling of fuel, but some thought and care must be expended upon the matter if fair and representative samples are to be obtained.

The water in large tanks or reservoirs can be adequately sampled by stopping the flow of water from the inlet pipe, using a wooden plunger to mix the water, and after waiting ten minutes, withdrawing one or more samples of the water in Winchester quart glass bottles, provided with well-fitting glass stoppers. These bottles are rinsed out twice with the water to be sampled, and are then held, until filled, in a vertical position with the mouth one inch below the surface of the water in the reservoir or tank. In large reservoirs it is advisable to take samples from more than one position filling an aliquot portion of the bottle from each selected point, and a boat is requisite in these cases for the work of sampling.

If the supply of natural water is known to be quite constant in character and composition, the sample may be taken either at the inlet or exit pipe of the tank or reservoir, but in most cases it is advisable at the same time to sample the whole body of water as described above and to compare the test results.

The sampling of water as it flows from the reservoir or tanks to the boilers can also be carried out by automatic apparatus, and below a description is given of an apparatus which is in use at Messrs. Joseph Crosfield & Son's Soap Works, Warrington, for this purpose.

Fig. 22 is a sectional elevation of portion of this sampling apparatus. *A* is an iron tank 24 inches in diameter by 36 inches in height, provided with a run-off tap at the bottom. Above this tank a  $\frac{3}{4}$ -inch wrought iron pipe branches from the main supply pipe to the boilers, and delivers the water into the tank *A*, by the  $\frac{1}{2}$ -inch diameter down-flow pipe marked *B*, and cock *C*. This cock is opened and closed by the lever *D*, formed of solid iron rod, and sufficiently heavy to fall into the position shown by the dotted line, when the support at the point *E* is withdrawn. *F* is a wooden float 8 inches in diameter and  $1\frac{1}{2}$  inches in thickness, which ordinarily rests on the support *H*, and by means of an elbow lever and pivoted joint at *G* provides a support

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for the cock lever at *E*. When the tank is quite filled with water the float *F* rises off its support, the lever *D* is released at *E* and drops into the position of the dotted lines, thus automatically closing the cock *C* and cutting off the supply of water to the tank *A*.

By arranging that the pressure of water in the  $\frac{3}{4}$ -inch pipe is not too great, and by providing a series of these

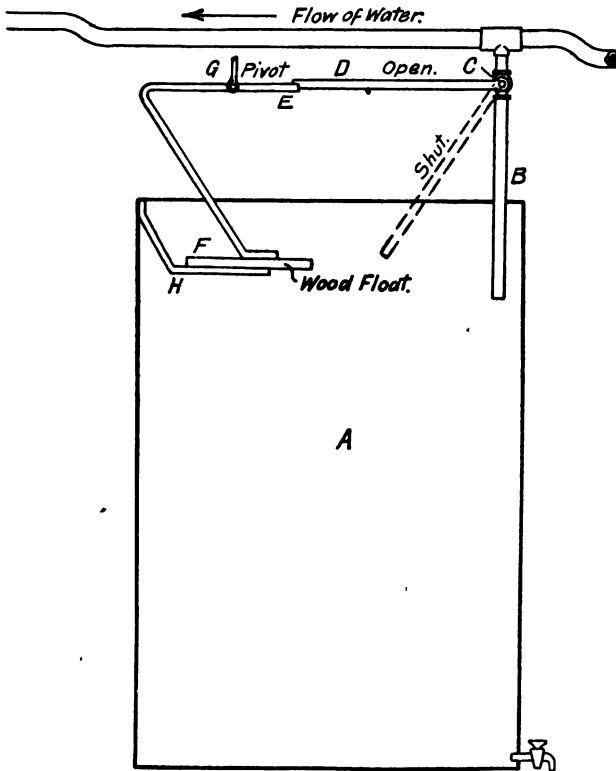


FIG. 22.—AUTOMATIC WATER SAMPLING APPARATUS.

tanks each with its float and cock, it is possible to collect any number of samples of water, each representing the flow from the softening apparatus or to the boilers for an equal period of time.

The supply pipe must be bent, as shown in Fig. 22, between each successive tank in order to make these fill in rotation,

## FUEL, WATER AND GAS ANALYSIS

and by aid of a cock on the  $\frac{3}{4}$ -inch pipe where it joins the main to the boilers, the flow of water can be regulated so that each of the tanks requires any pre-determined period of time for filling. A series of twelve tanks may thus be made to contain samples of twelve or twenty-four hours' work, and from these twelve tanks either a general sample may be prepared by putting twelve equal portions into a Winchester quart bottle and vigorously shaking, or any particular one may be sampled and tested as desired.

This apparatus is of especial use in checking the work of softening apparatus of the automatic and continuous type, since for the reasons given in the next chapter one can never be certain that the amount of softening chemicals is correct, unless regular and systematic sampling and testing are carried out.

The sampling of water from springs and artesian wells demands a different method, for here it is important that the water should lose none of its dissolved gases, before testing. In this case, therefore, the Winchester quart glass bottle is filled directly from the spring or well with as little delay as possible. Care must be taken also to select a bottle with a particularly close fitting stopper, which should be tied down after the sample is taken. Samples of well and spring water should not be exposed to sun-light and should not be violently shaken before testing, since either of these may influence considerably the amount of gaseous matter retained in solution in the water.



## CHAPTER VI.

### The Approximate Analysis of Feed Water.

**T**HE details given in the previous chapter relating to the sources of natural water supply, prove that all natural waters contain variable amount of suspended or dissolved impurity, and that in some cases these impurities may be present in very considerable quantity.

For the purposes of the boiler engineer it is of importance to know the total amount and the general characteristics of these impurities, although the exact determination of each individual chemical compound may be unnecessary. An approximate analysis of the feed water will supply the information required, since this may be carried out so as to yield the (1) Alkalinity or acidity; (2) total suspended solids, (3) total dissolved solids, (4) temporary hardness, (5) permanent hardness, (6) oils and fats: without the separate determination of the various salts that give the water these characteristics. An approximate analysis of a feed water, with strict attention to all the details of manipulation named below, may be carried out by an engineer after some little practice with the apparatus and methods described. A complete chemical examination, on the other hand, can only be carried out by a chemist skilled in water analysis, and no attempt is made in this chapter to deal with the methods by which the calcium and magnesium salts in water are separately determined. The engineer who attempts the approximate analysis of water is however advised to practise with samples of water that have been submitted to independent tests by a competent expert before venturing to place much dependence upon his own results, since, owing to the use of volumetric methods, the work is more difficult than the approximate analysis of fuels.

#### I. ALKALINITY OR ACIDITY.

Most natural waters are slightly alkaline, owing to the presence of dissolved carbonates of the alkaline earth metals.

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Such waters colour neutral litmus paper a slightly blue tint, and give a pronounced canary yellow tint to methyl orange, the indicator usually employed for this work. In order to estimate the total alkalinity of the water 200 c.c. of the sample taken as described in Chapter V are filtered, if suspended matter be present, and are measured in the flask shown in Fig. 23. This 200 c.c. are then emptied into a white porcelain basin of about 22 oz. capacity. The flask is rinsed out with distilled water, the washings are added to the liquid in the basin, and two drops of a con-

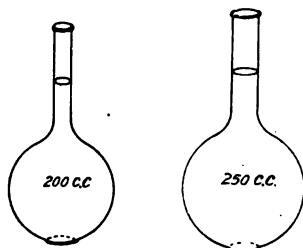


FIG. 23.—MEASURING FLASKS.

centrated solution of methyl orange are also added to the water. A standardized solution of hydrochloric acid of one-fifth normal strength<sup>1</sup> is now added from a burette, drop by drop, with constant stirring until the colour of the liquid in the basin changes from canary yellow to orange and finally to faint pink, this last change being taken as the end point of the reaction.

The number of c.c. of the hydrochloric acid solution used from the burette are then read off and the result is calculated as parts of calcium carbonate per 100,000 of water.

In the case of water from peaty lands it will often be found that these give a slightly acid reaction, due to the decomposition of the organic matter of the peat, but that these organic acids are not revealed either by litmus paper or by methyl orange. Such waters, in fact, appear to be alkaline with the last-named indicator. It is necessary in the case of these waters, therefore, to use an alcoholic solu-

<sup>1</sup> A normal solution contains the molecular weight of the chemical in grams, in 1,000 c.c. of water. A one-fifth normal solution yields a sharp end reaction in these tests, and is preferable to a weaker one, but the volume of solution used must be read off by aid of the Meniscus (see Fig. 27).

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tion of phenol-phthalein as indicator, and to heat the 200 c.c. of water after filtration and measuring, in the porcelain basin before titrating with the standard alkali solution—carbonate of soda.

Phenol-phthalein is colourless with acids, but yields a purple red tint with the slightest excess of alkali, and the standard solution of alkali is therefore dropped in from the burette with constant stirring of the liquid in the basin,



FIG. 24.—WATER-TESTING APPARATUS.

until a permanent purple red colour is obtained. The number of c.c. of the standard alkali solution used is then read off and from this the result is calculated, not as acid, but as the alkali equivalent of the acid present in the water.

Fig. 24 shows the apparatus used for making these tests. The burette holds 50 c.c., each c.c. divided in tenths, and is provided with a glass stop-cock. The standard solutions of acid and alkali employed are contained in the glass bottles shown on either side of the burette and titration basin.

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These standard solutions of acid and alkali are made as follows :—

21.5 grams of pure anhydrous carbonate of soda are weighed out and dissolved with the aid of heat in 250 c.c. of distilled water. This solution is then made up to nearly 1,000 c.c. in the large measuring flask shown in Fig. 25 and is cooled to 15° C. before finally diluting to the mark on the neck, and transferring to the stoppered glass bottle shown on the right in Fig. 24.

This solution is labelled *Standard Alkali*  $\frac{1}{10}$  N., the exact strength being placed on the label afterwards when the solution has been titrated with the  $\frac{1}{10}$  N. acid solution.

The latter is made by taking 40 c.c. of pure concentrated

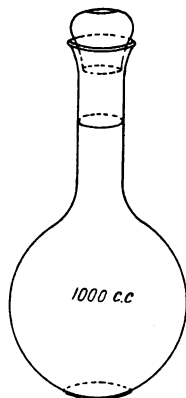


FIG. 25—ONE LITRE MEASURING FLASK.

hydrochloric acid and diluting this to 1,000 c.c. after cooling to 15° C.

This solution is now transferred to the other storage bottle shown in Fig. 24 and is labelled *Standard Acid*  $\frac{1}{10}$  N. It is checked by weighing out very carefully .40 gram of the pure carbonate of soda (after drying half an hour in the covered platinum crucible at a dull red heat) dissolving this in the porcelain basin in a small quantity of hot water, diluting with a large volume of cold water and titrating with the standard acid solution, using methyl orange as indicator. The change from canary yellow to faint pink—with orange as an intermediate stage—indicates the end of the reaction. It will be found that about 20.0 c.c. of

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the standard acid solution are required to neutralize the 40 gram of sodium carbonate, and the test is repeated for the sake of accuracy. Finally the standard alkali solution is itself checked, by measuring off 25 c.c. in the pipette



FIG. 26.  
TWENTY-FIVE C.C. PIPETTE.

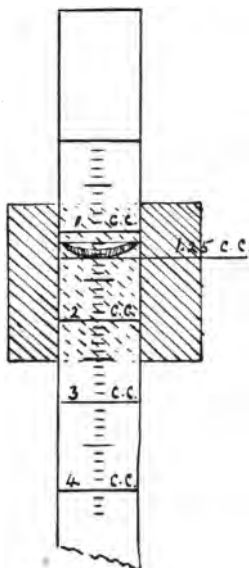


FIG. 27.  
MENISCUS READING OF BURETTE.

shown in Fig. 26 and by titrating this with the normal acid as before.

The following are examples of this method of checking the standard solutions :—

1.  $\frac{N}{5}$  *HCl* solution. 40 gm. of  $\text{Na}_2\text{CO}_3$  used for each test.<sup>1</sup>

No. 1 required	.	.	.	.	19.8 c.c.
No. 2 „	.	.	.	.	19.9 c.c.
Mean	.	.	.	.	19.85 c.c.

It was calculated from this that 100 c.c. of the  $\frac{N}{5}$  acid solution equalled 2.015 grms.  $\text{Na}_2\text{CO}_3$  or 1.900 grms.  $\text{CaCO}_3$ , and these figures were placed upon the label below the description.

2.  $\frac{N}{5}$   $\text{Na}_2\text{CO}_3$  solution. 25 c.c. used for each test.

<sup>1</sup> The chemical symbol for hydrochloric acid is  $\text{HCl}$ , for carbonate of soda,  $\text{Na}_2\text{CO}_3$ , and for carbonate of lime  $\text{CaCO}_3$ .

## FUEL, WATER AND GAS ANALYSIS

No. 1 required	.	.	24.0	c.c.	HCl. solution.
No. 2	,	.	24.1	c.c.	,
Mean	.	.	24.05	c.c.	

From this it was calculated that 100 c.c. of the  $\frac{n}{5}$  alkali solution equalled 96.2 c.c. of the  $\frac{n}{5}$  acid solution, or 1.937 grms.  $\text{Na}_2\text{CO}_3$ , or 1.827 grms.  $\text{CaCO}_3$ .

These values were therefore placed upon the label of the standard alkali solution.

In testing waters the basin and burette must be well washed and rinsed with distilled water before each test, and the burette must also be rinsed with the standard test solution before it is filled for the actual titration. The level of the solution is best read off by holding a black strip of paper behind the meniscus, and by reading from the lower curve of this, as shown in Fig. 27.

The following is an example of the calculation for water showing alkalinity:—

*Water used*, 200 c.c.

Standard acid solution required to neutralize it, 3.70 c.c.  

$$\frac{3.7 \times 100,000 \times .019^1}{200} = 35.15$$
 parts calcium carbonate per 100,000 of water.

An acid water from peaty land gave the following results:—

*Water used*, 200 c.c.

Standard alkali solution required to neutralize it, 1.10 c.c.  

$$\frac{1.1 \times 100,000 \times .01937}{200} = 10.653$$
 parts sodium carbonate per 100,000 of water.

### II. SUSPENDED SOLID MATTER.

Water from rivers and surface drainage generally, is often charged with suspended matter, and it is at times necessary to determine the amount of this. A 4-inch

<sup>1</sup> The factor 9.50 can be used in these calculations in place of  $\frac{100,000 \times .019}{200}$

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circle of specially prepared filter paper is folded in radiating rib fashion to promote quick filtrations, and is dried in the stoppered drying tube for one hour at  $230^{\circ}$  F. Fig. 4 shows the air-bath used, and Fig. 28 shows the tube employed for drying filters, the stopper being of course removed during the application of heat. The tube and filter are placed in the desiccator and are weighed together when cold, the stopper being inserted in the tube to prevent absorption of moisture by the filter while being weighed.

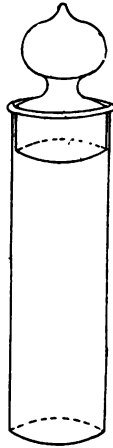


FIG. 28.—FILTER-DRYING TUBE.

The filter paper is now removed with small forceps from the tube, is placed in a funnel of suitable size with the least possible handling, or rubbing of the folds, and 200 c.c. of the water are measured and poured through it. The large sample of water must be well shaken before withdrawing 200 c.c. for this test. The filter with its contents is finally washed with cold distilled water, dried in the funnel as far as possible by suction, and is then removed carefully from the funnel and placed in the drying tube for the final heating at  $230^{\circ}$  F. The drying must be continued until a constant weight is obtained. The gain in weight multiplied by 500 gives the parts of suspended matter per 100,000 of water.

The following is an example of the figures obtained in this test :—

## FUEL, WATER AND GAS ANALYSIS

Drying tube and filter and residue . . .	12.122 grms.
"    "    "    alone . . .	12.067 "

Gain in weight . . . . . 0.055 grm.

$0.055 \times 500 = 27.50$  parts of solid suspended matter per 100,000 of water.

The colour of the dried residue upon the filter paper will give some indication of its composition, iron oxides being generally red, and clay or alumina compounds being slatey grey in colour.

### III. TOTAL SOLIDS.

If the suspended matter has been separately determined by the method just described, the filtered sample of water is used for this test. Should the suspended matter not have been separately determined, the *unfiltered water*, well shaken, is employed for the total solids determination. This is carried out by evaporating 250 c.c. of the water to dryness in a tared platinum basin. Fig. 29 shows the apparatus used for this test. The basin is 2.4 inches in diameter and holds 50 c.c. of water. The water bath is of copper,  $6\frac{1}{2}$  inches in diameter, holds 1,000 c.c., is provided with rings of various sizes, and is supported upon a piece of iron gauze resting on a large tripod stand.

A bamboo or glass triangle with a long leg fitted into a cork which slides upon the upright of a retort stand is employed as shown in Fig. 29 to carry a piece of glazed paper in order to protect the water in the platinum basin from dust or dirt. A large cork on the upper side of this dirt shield serves to hold it in its place. The platinum basin must not be allowed to touch the copper ring of the water bath, but must be supported by three squares of filter paper, folded to form thick wedges and inserted between the basin and the edge of the ring in such a way that an annular space is left for the escape of the steam from the water in the bath. The platinum basin must be thoroughly cleaned and dried by heating for five minutes in the air bath at  $230^{\circ}$  F. before weighing. About 40 c.c. of the sample of water measured in the 250 c.c. flask shown in Fig. 23 are then poured carefully into the basin, already placed in position on the ring of the water bath with the aid of the filter paper strips already referred to, and the evaporation is commenced.



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It is advisable never to fill the basin within  $\frac{1}{4}$  inch of the rim, since many salt solutions have a tendency to creep up and over the sides, when being evaporated to dryness. It is also advisable to keep the water bath in steady, but not violent, ebullition by regulation of the gas flame beneath it. As the evaporation proceeds the remainder of the 250 c.c. are gradually added, and finally the 250 c.c. flask



FIG. 29.—PLATINUM BASIN AND WATER-BATH.

is rinsed out with distilled water, and the washings are added to the liquid in the basin. The platinum basin is kept upon the water bath until the residue of salts is apparently quite dry. It is then removed, the bottom of the basin is carefully cleaned and wiped dry, any deposit being removed by aid of hydrochloric acid and a wet towel, and the basin and its contents are heated for three hours at  $300^{\circ}$  F. in the air bath. The desiccator must be employed during the last

## FUEL, WATER AND GAS ANALYSIS

stage of cooling, before weighing, as perfectly dry salts are always hygroscopic. The increase in weight of the basin, multiplied by 400 gives the parts of solid matter per 100,000 of water.

The following is an example of the figures obtained in the test :—

Platinum basin and residue from 250 c.c. of	
unfiltered water . . . . .	26·165 grms.
Platinum basin alone . . . . .	26·023 „
	26·142

Weight of residue    142 grm.

$\frac{142 \times 100,000}{250} = 56\cdot8$  parts of solid matter for 100,000 of water.

Should it be desired to find what proportion of this residue is present as organic matter, the basin and its contents are heated to redness for five minutes upon a platinum wire support over a large Bunsen burner, the change in colour being noticed during the further heating. Organic compounds darken and char under this treatment. The basin is then allowed to cool, the residue is moistened with a solution of ammonium carbonate in water to reconvert the oxides into carbonates, and the excess of ammonium carbonate and water is then driven off by application of a gentle heat. Care must be taken during this operation that the basin and its contents do not approach a red-heat, otherwise the calcium and magnesium carbonates will be again reconverted into oxides. Finally the basin is cooled in the desiccator and again weighed. The loss in weight by this treatment, multiplied by 400, gives the parts of organic matter per 100,000 of water.

The following is an example of the figures obtained in this test :—

Basin and residue after drying at 300° F. . . . .	26·142
Basin and residue after ignition and treatment with ammon. carb. . . . .	26·120
	022
Loss by ignition . . . . .	022

$\frac{022 \times 100,000}{250} = 8\cdot80$  parts of organic matter per 100,000 of water.

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### IV. AND V. TEMPORARY AND PERMANENT HARDNESS.

The temporary hardness of water is caused by the presence of carbonates of lime and of magnesia in solution; permanent hardness is due to the corresponding sulphates and oxides of these two elements. The Clark test for hardness is carried out by shaking the water before and after boiling with a standard soap solution, and by measuring the volume of this required to produce a permanent lather. The *Clark or English degree of Hardness* represents the grains of calcium carbonate in one gallon of water,<sup>1</sup> while the French degree of hardness represents the parts of calcium carbonate in 100,000 parts of water, and the German degree of hardness represents the parts of calcium oxide (CaO) in 100,000 parts of water. The Clark test for hardness is not very satisfactory, although still generally employed in this country. The results obtained vary within wide limits, and are much too dependent upon the personality of the tester. For this reason the Clark test with soap solution is now giving place to the more scientific ones described below, in which the weight of calcium and magnesium carbonates and of calcium and magnesium sulphates as determined by the approximate analysis are used for calculating the degrees of hardness of the water.

The alkalinity, test already described, yields the English degrees of hardness, if the parts of calcium carbonate per 100,000 of water as ascertained by the c.c. of standard acid solution used, be multiplied by .7.

The following is an example of the figures obtained in this test :—

200 c.c. of filtered water took 3.7 c.c. of standard acid solution, using methyl orange as indicator.

$$\frac{3.7 \times .019 \times 70,000}{200} = 24.61 \text{ English degrees of hardness.}$$

The expression  $\frac{.019 \times 70,000}{200}$  can be reduced to the factor—6.65—to simplify the calculation for temporary hardness. The c.c. of standard acid solution used, multiplied by 6.65, then gives the temporary hardness in English degrees.

<sup>1</sup> This figure was chosen by Clark because in his day the gallon was the standard of volume. There are 70,000 grains in one gallon.

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*The Permanent Hardness* of water can be approximately ascertained by aid of the results obtained in the tests for total solids, if the filtered water has been used for carrying out this test, and no organic matter be present to complicate the calculation.

The results of this test expressed in parts per 100,000, multiplied by  $\cdot 7$ , will then give the total hardness in English degrees, and the difference between the total hardness and the temporary hardness yields the permanent hardness. Taking the figures given in sections 1 and 3 of this chapter as an example we have :—

Total solids, 56·8 per 100,000 of water.

$56\cdot 8 \times \cdot 7 = 39\cdot 7$  parts  $\text{CaCO}_3$  per 70,000 of water, or total hardness in English degrees.

The temporary hardness of this water as found by test 1 was, however, 24·61 degrees and  $39\cdot 76$  less 24·61, gives 15·15 as the permanent hardness expressed in English degrees.

It is safer, however, to make a special test for the sulphates and oxides which produce permanent hardness. This is carried out as follows :—

100 c.c. of the filtered sample of water are taken and evaporated to dryness on the water bath in the platinum basin with an addition of 25 c.c. of the standard sodium carbonate solution. This treatment decomposes the sulphates and oxides and converts them into carbonates. The residue is dissolved in distilled water and is gently heated. The carbonates of lime and magnesia present in the residue are left insoluble, and are now removed by filtration. The filter and its contents are well washed with warm water to remove the excess of alkali. The filtrate and washings are collected in the porcelain basin shown in Fig. 24, and after cooling are titrated with the standard acid solution using methyl orange as indicator. The amount of acid solution required to neutralize the carbonate of soda remaining in the filtrate, enables one to calculate how much has been used for decomposing the sulphates and oxides.

The following is an example of the figures obtained in this test :—

100 c.c. of the filtered water were evaporated with 25 c.c. of standard alkali solution.

The filtrate and washings required 22·5 c.c. of standard acid solution to neutralize the excess of alkali.

Now as 100 c.c. of the alkali solution is equivalent to

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96.2 c.c. of the acid solution, 25 c.c. equals  $\frac{96.2}{4} = 24.05$  c.c., and  $24.05 - 22.5 = 1.55$  c.c. This is the volume of acid corresponding to the carbonate of soda which has disappeared in this test.

The calculation for the permanent hardness is therefore as follows :—

$$\frac{1.55 \times .019 \times 70,000}{100} = 20.60 \text{ parts CaCO}_3 \text{ per } 70,000 \text{ of water.}$$

The expression  $\frac{.019 \times 70,000}{100}$  can be reduced to the factor 13.3 to simplify calculation. The c.c. used, multiplied by 13.3, then yield the permanent hardness in English degrees.

It is possible to make the standard solutions of acid and alkali of such a strength, that the degrees of hardness can be read off directly from the c.c. of solutions used in making the test.

It is, however, somewhat troublesome to make a solution of hydrochloric acid, 100 c.c. of which shall equal exactly .143 gram of  $\text{CaCO}_3$ , and another of carbonate of soda, 1 c.c. of which shall exactly neutralize 1 c.c. of the standard acid solution. Moreover, such weak solutions yield very indefinite end reactions, and hydrochloric acid solution is liable to change in strength when above or below a definite limit of concentration. The writer has therefore thought it best to show how solutions of approximately fifth normal strength may be applied to water testing without alteration. As already pointed out, by the use of single factors for the fixed values of the calculation, the labour in calculating the temporary and permanent hardness of the water is reduced to a minimum.

In works where many water analyses are made in the course of a day it will, of course, be found advisable to make these solutions in large quantities at once and of such a strength that calculation is altogether avoided. In such cases when using 100 c.c. of water for the hardness tests the solutions should have the following values :—

100 c.c. standard acid solution = .143 gram  $\text{CaCO}_3$ .

100 c.c. standard alkali solution = 100 c.c. standard acid solution.

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No simple apparatus can be put into the hands of the fireman or boiler engineer which will enable him to determine for himself the degree of hardness of the feed water. The use of slips of neutral litmus paper (this is sold in books by chemical apparatus dealers) will afford some indication of the character and purity of the water supply, but exact chemical tests carried out as described, are necessary in order to obtain any information of real value to the boiler engineer.

Special testing sets provided with tabloid chemicals and printed directions which can be read and carried out by any fireman or stoker, are mere inventions of the unscrupulous for the delusion of those engineers who know little of the complex chemistry of the subject.

### VI. TESTS FOR OIL.

Oil is a most dangerous impurity in boiler feed water. When using water from condensers for boiler purposes it is



FIG. 30.—SEPARATING FUNNEL.

therefore always advisable to test the feed occasionally, in order to find if any oily or fatty matter be present.

The sample of water should be cooled before testing and then shaken vigorously with one-fifth of its volume of petrol or of ether in the type of separating-funnel shown in Fig. 30. The liquid is then allowed to stand fifteen minutes in the funnel supported in an upright position in a retort stand,

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the water is run off by the separating cock, and the petrol or ether solution which floated on the water and contained all the oil and fat, is run into the porcelain basin shown in Fig. 24. This is placed upon the water bath which is filled with hot water but has no lighted lamp beneath it, since petrol or ether vapour is a most inflammable gas and all lights must be extinguished in the room where it is present. The petrol or ether evaporates quickly and leaves the oily or fatty matter as a residue in the basin.

If desired this test can be made quantitative in character by using 250 c.c. of the water for the test, and by transferring the solution of the fat to the tared platinum basin towards the end of the evaporation. The large porcelain basin and the separating funnel must in this case be rinsed out with the same spirit, and the rinsings added to the solution in the platinum basin.

The oily residue in this, after heating for some time at  $212^{\circ}$  F., is finally weighed.

To distinguish between animal or vegetable and mineral oils the residue in the basin should be heated on the water bath with a strong solution of caustic potash. Animal and vegetable oils saponify (i.e. yield a soap) under such treatment, while mineral oils remain unaltered.

The presence of oily and fatty matter in boiler scale can be detected by heating the sample of scale to redness in the platinum basin. If charring occurs or if a disagreeable odour be noticed, some organic fatty compounds are probably present. Fats and oils of animal or vegetable origin are more dangerous lubricants for engines than hydrocarbon oils of the paraffin class, since the former contain oxygen, and yield organic acids when decomposed at the high temperature occurring in the boiler.

## CHAPTER VII.

### The Practical Applications of the Test Results.

#### I. FREQUENCY OF SAMPLING AND TESTING.

**T**HE feed-water from whatever source, used for the boilers ought to be sampled regularly, at shorter or longer intervals according to the nature of the supply, and these samples ought to be tested in accordance with the instructions given in Chapter VI.

In the case of surface and river waters the amount of impurities present in the water will be high during the dry season, and also after the first heavy rains at the end of such a season. At such times therefore the sampling and testing of the water should occur at least once weekly, or oftener if this be possible with the laboratory staff available for the work. During the winter and spring after the dry accumulations of the summer have been washed away, surface and river waters do not show such large amounts of dissolved and suspended matter, and at these periods of the year a monthly examination of the feed water will suffice.

Well waters, and waters drawn from large catchment areas in mountain districts and stored in artificial lakes, do not, on the other hand, show such marked variation in the amount of impurity at the various seasons of the year; and in the case of such waters, a monthly or quarterly examination of the water is sufficient.

#### II. OIL.

If any portion of the boiler feed be drawn from the condenser water this ought to be specially sampled daily, and tested for oil in the manner already described. In skilled hands the test will not require more than twenty minutes to carry out, and the results obtained may save very heavy expenditure upon boiler repairs at some later date. If oil be discovered in appreciable quantities the water should be



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rejected for making up the feed or should be put through a softening plant. In this case the calcium carbonate which is formed in the softening plant will enclose and carry down the oil particles; and the softening plant will, in fact, act as a chemical oil purifying plant, and save the cost of the latter.

Even when specially erected oil separating plants are in use it will be found advisable to pass the effluent from these through the ordinary softening plant as well, in order to remove the last traces of oil. The water as it enters the boilers should also be examined daily for oil, and every effort should be made to keep the feed entirely free from this most destructive impurity.

### III. ALKALINITY AND ACIDITY.

All waters containing carbonates of lime or magnesia in solution give an alkaline reaction with litmus paper and methyl orange, and as already stated the alkalinity test is a measure of the temporary hardness of the water. Waters showing more than five English degrees (5 parts  $\text{CaCO}_3$  per 70,000 of water) of temporary hardness ought to be submitted to the action of softening chemicals before admission to the boiler, otherwise these carbonates will separate inside the boiler in the form of scale and mud. Lime water is the chemical solution employed for removing temporary hardness. The chemistry and practice of the lime-softening process will be dealt with in the next chapter.

*Acidity* in feed waters generally arises from the presence of organic acids, and waters of this kind should not be used if any other source of supply be available. Should it be necessary to use such waters, the acidity must be neutralized with lime or with sodium carbonate, *before* the water is permitted to enter the boiler. The calculation of the amount of alkali required is easily made from the results of the test with standard alkali solution. The following is an example:—

250 c.c. of the water took 1.4 c.c. of the standard alkali solution (100 c.c. = 1.937 grms.  $\text{Na}_2\text{CO}_3$ ).

$$\frac{1.4 \times 1.937 \times 100,000}{250} = 10.847 \text{ grms. } \text{Na}_2\text{CO}_3.$$

Each 100,000 parts of water will require therefore 10.847 parts of sodium carbonate—that is every 1,000 cubic feet

## FUEL, WATER AND GAS ANALYSIS

will require  $\frac{10.847 \times 10 \times 100}{16 \times 98} = 6.9$  lbs. of 98 per cent. alkali.

### IV. SUSPENDED SOLID MATTER.

Water which contains more than five parts of suspended matter per 100,000 of water, should be filtered or allowed to settle in large tanks, before admitting to the boilers.

Sand filters with an upward flow are the most suitable for removing suspended impurities, since these can be quickly cleansed by washing out in the reverse direction with clean water. When softening plant is in use, special filtration is unnecessary, for the suspended matter in the untreated water is carried down with the carbonate of lime; and the only danger in such cases is that this lime is not allowed time to settle. The water from the softening plant may therefore at times contain suspended carbonate of lime, the remedy for which is a larger softening plant. As a rule the precipitation of lime and other insoluble matter in a water softening plant occurs more quickly with hot feed water, and it is advisable, wherever possible, to use heated water in the softening plant, and to take the necessary steps to avoid loss of heat *during the settling process*. Water in a vessel exposed to the outside air will necessarily lose much heat by radiation, and the convection currents set up by this loss will interfere with the settling of the insoluble matter.

### V. TOTAL SOLIDS.

The total solids in feed water should not exceed 20 parts per 100,000, and where this limit is exceeded the water must be submitted to the action of softening chemicals.

The principal salts found in feed water are the carbonates and sulphates of lime and magnesia, while the chlorides and sulphates of these elements and of sodium occur seldom and in smaller amount. The danger of large amounts of sodium chloride being present at times of flood tide in water drawn from tidal rivers, has already been referred to; and for boiler plants located in such positions it is necessary to have some means for quickly noting the change in the character of the water supply.

The chemist in charge in such cases, either should test the

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water daily *at full tide* for chlorides, or should provide the fireman in charge of the boilers with a salinometer of a reliable type. A test based on the use of capsules of silver nitrate containing a weighed quantity of this salt with potassium chromate as indicator, may also be devised for showing when the feed contains more than 10 parts of sodium chloride per 100,00 of water.

As regards the treatment by chemicals for removal of the total solids, this subject will be dealt with at length in the next chapter, and it is only necessary to state here that carbonate of soda is the chemical usually employed in conjunction with lime.

### VI. TEMPORARY AND PERMANENT HARDNESS.

Waters testing above 15 English degrees of temporary and permanent hardness ought not to be used without chemical treatment in steam-boilers.

The heat losses and disadvantages resulting from the formation of scale are so great, that in nearly all cases in large works a positive saving results from the installation of softening apparatus.<sup>1</sup> Permanent hardness, i.e. that due to sulphates of lime and magnesia is the more dangerous, since these salts form a more compact and adherent scale than the corresponding carbonates. The removal of hardness by chemicals will be dealt with in Chapter VIII, but it may be remarked here that the removal of permanent hardness is only effected by substitution, and that an equivalent amount of another salt remains in solution in the water. The lime and magnesia sulphates are converted into the insoluble carbonates, while the sulphuric acid radicle remains in the water, in the form of sodium sulphate, a very soluble salt.

Where waters with a high permanent hardness test are employed for boiler-feed purposes, the total dissolved salts will therefore always remain high even when a softening plant is in use, owing to the presence of this sodium sulphate. In such cases it is advisable to blow off the boilers oftener than would otherwise be required, since a concentrated solution of sodium sulphate is corrosive in its action upon the gun metal and brass fittings of the boiler.

<sup>1</sup> A scale  $\frac{1}{16}$  inch in thickness is the limit that ought to be allowed to form on the boiler plates.

## FUEL, WATER AND GAS ANALYSIS

In all cases it is in fact advisable to test the water remaining in the boiler at weekly intervals, and to blow off the boiler when the total dissolved matter exceeds 250 parts per 100,000 of water.

The Appendix contains some typical tests of feed waters.

## CHAPTER VIII.

### The Use of Softening Re-Agents and the Tests Necessary to Regulate their Amount.

#### I. ADVANTAGES OF SOFTENING.

THE importance of pure water for the supply of steam-boilers has only been recognized in recent years, and the great extension of the water-softening industry since 1895 is largely due to this fact. There is some danger now, however, that boiler engineers may run into the other extreme, and that they may by unwise use of softening re-agents produce greater evils than those they desire to remove.

A water containing chemical salts in solution is just as likely to produce harmful results inside the boiler, when these salts have been added by the user for the purpose of purification, as when they occur naturally. The excessive use of caustic soda and sodium carbonate in many boiler plants is undoubtedly responsible for some of the corrosion of boiler plates and fittings.<sup>1</sup> For steaming purposes a water containing little or no foreign matter in suspension or in solution is desirable, and the purer the water is, the more free from trouble will be the boiler, in which it is used. Even dissolved gases (oxygen and carbonic acid) may produce much harm when liberated inside a boiler, and a large proportion of the pitting of boiler plates noticed just above the entrance of the feed water supply pipe, is due to these gases. The water used for steam generation in steam boilers should therefore be as free from solid, liquid and gaseous impurities, as it is possible to obtain it. As already stated in the previous Chapter, water containing more than 20 parts total solids per 100,000 of water,

<sup>1</sup> See abstract of paper upon *The Action of Slightly Alkaline Waters upon Iron*, read before the Society of Public Analysts by Messrs. Cribb and Arnaud, *Mechanical Engineer*, January 13, 1906.

## FUEL, WATER AND GAS ANALYSIS

or 15 degrees of total hardness, ought to be purified before use.

The treatment of the water with softening chemicals should occur in special apparatus outside the boiler. To carry out the softening treatment inside the boiler, is likely to aggravate some of the evils it is desired to avoid.

The proper control of the feed water of the boiler, can only be exercised by aid of systematic and constant sampling and testing of the water as it enters and leaves the softening apparatus. Occasional tests of the feed water before and after softening treatment are useless.

In the first place the character of the supply may change from week to week and even from day to day. In many localities the rainfall is the chief agent in causing this variation in the amount of suspended and dissolved impurities present in the natural water supply, in others the dictum of the city water engineer, who, as a rule, has more than one available source of supply. Secondly, the softening apparatus even when of the automatic type requires checking, for owing to this variation in the composition of the natural supply, there is grave danger of excessive chemicals being used at times in the softening operation, and these, as already stated, may be almost as harmful as the original impurities of the water.

With pure water a boiler may run from 1,000 to 2,000 hours without cleaning, and the evaporative efficiency during this period, owing to the absence of scale, will remain high. With dirty and impure feed water on the other hand, the limit of safe work is 500 or less hours, and the evaporative efficiency will fall rapidly towards the end of this comparatively brief working period. It is evident therefore that in the majority of works, a water softening plant will prove a wise expenditure of capital, for it will increase the capacity of the existing boiler plant and reduce the fuel consumption at one and the same time, with only a slight addition to the daily working expenses.

### II. THE CHEMISTRY OF THE SOFTENING PROCESS.

The chief salts that can be removed from water by the use of softening chemicals are the carbonates and sulphates of lime and magnesia. Taking these seriatim we have the following :—

## WATER

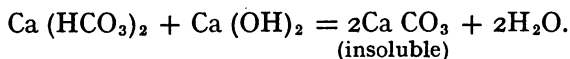
1. *Calcium Carbonate*.—Chemical symbol  $\text{CaCO}_3$ , always present in natural waters as bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$

This salt can be removed :—

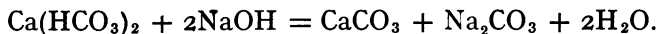
(a) *By boiling the water*. This method yields a precipitate of calcium carbonate which may either form a hard scale, or a soft mud, according to the slowness or rapidity of separation. The chemical equation for this change is :



(b) *By adding slaked lime or lime to the water*. This method yields double the amount of calcium carbonate which occurs in method *a* as a flocculent precipitate, but it avoids the evolution of carbonic acid gas. The chemical equation is :—



(c) *By adding caustic soda to the water*. This chemical combines with the second  $\text{CO}_2$  molecule of the bicarbonate, and precipitates the calcium carbonate as before, while sodium carbonate remains in solution. The chemical equation is as follows :—



2. *Magnesium Carbonate*.—Chemical symbol  $\text{MgCO}_3$ , always present in natural waters as bicarbonate,  $\text{Mg}(\text{HCO}_3)_2$ . This salt can be removed :—

(a) By boiling.

(b) By adding slaked lime or lime water.<sup>1</sup>

(c) By adding caustic soda.

The chemical equations are similar to those given for calcium carbonate, with the substitution of Mg for Ca in the molecular formulae. Both calcium and magnesium carbonate are loose flocculent precipitates when first caused to separate from water by the use of lime water, but boiling renders these precipitates dense and crystalline.

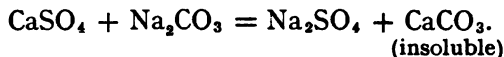
3. *Calcium Sulphate*. Chemical symbol,  $\text{CaSO}_4$ .

This salt can be removed from water :—

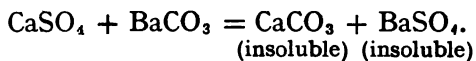
(a) *By heating with sodium carbonate*. The chemical equation for this change is :—

<sup>1</sup> Magnesium carbonate is converted into magnesium hydrate by heating with lime water. This further change complicates the reactions for softening water by lime, when magnesium salts are present.

## FUEL, WATER AND GAS ANALYSIS



(b) *By heating with barium carbonate.* This chemical produces two insoluble compounds instead of one, and the sulphate is removed from the water as barium sulphate. The chemical equation is :—



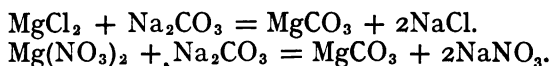
### 4. *Magnesium Sulphate.* Chemical symbol $\text{MgSO}_4$ .

This salt can be removed from water by heating it with sodium carbonate or with barium carbonate. The chemical equations are as in 3, with the substitution of Mg for Ca in the molecular formulae. As before, the magnesium carbonate is converted into the hydrate, if excess of lime be present.

It will be observed that when sodium carbonate is the chemical used for removing sulphates, calcium and magnesium carbonates are again the precipitated salts, but that an equivalent amount of sodium sulphate remains in solution.

The precipitated carbonates, as before, are flocculent when first separated, but become dense and crystalline on boiling. Barium carbonate on the other hand, removes both the base and the acid radicle of the calcium or magnesium sulphate, and for this reason would be generally employed, if cheaper and more easily applied to this purpose. As barium salts are extremely poisonous their use is attended with some danger in a large works, where only one water supply is available for all purposes.

5. *Magnesium Chloride and Magnesium Nitrate.* These two salts are occasionally present in natural waters in appreciable amounts. They can be decomposed in the same manner as the sulphate, namely, by heating the water with sodium carbonate. The chemical equation for the changes are as follows :—



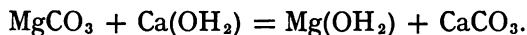
Here again an equivalent amount of sodium chloride or nitrate remains in solution, and the change is from a dangerous salt to a less dangerous one, for magnesium sulphate, chloride and nitrate are all salts which may decom-



## WATER

pose and liberate corrosive gases, if heated to a high temperature as a scale upon boiler plate.

Magnesium carbonate is stated by some authorities to be slightly soluble in water, and they recommend that it should be converted into the insoluble hydrate, by the addition of an excess of lime water, according to the equation :—



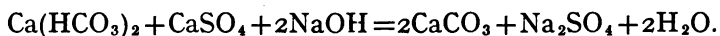
The solubility of the carbonate is very slight—100 parts of cold water dissolve only .02 parts of the carbonate—and, moreover, the deposit obtained when precipitating a hot solution of magnesium sulphate with sodium carbonate, is a mixture of hydrate and carbonate, and not carbonate alone. An excess of lime, however, is required to obtain the separation of the other carbonates when magnesium is present, and its use will add to the bulk of the precipitate which remains to be dealt with in the softening apparatus. Magnesium hydrate alone is a gelatinous precipitate likely to cause stoppage of the filters attached to the softening apparatus.<sup>1</sup>

### III. THE CALCULATION OF THE AMOUNT OF SOFTENING CHEMICALS REQUIRED.

The tests upon which the additions of the softening chemicals are based are those for temporary and permanent hardness. It is not advisable to attempt to remove the temporary hardness by boiling, for long continued boiling is required to remove the whole of this, and such an expenditure of fuel or of waste heat would not prove economical. It is, in fact, best to reduce the hardness to the lowest degree possible, by the use of lime, and sodium or barium carbonate ; and all modern water-softening plants are operated upon this basis. It is possible to remove both carbonates and sulphates by the use of caustic soda alone, when the two salts are present in molecular proportions, for the carbonate of soda produced by the reaction with the carbonates then reacts with the sulphates. The reaction in this case is expressed by the following equation :—

<sup>1</sup> The only other case in which an excess of softening chemicals is required, is when the water contains silica in solution. This is a most dangerous impurity, and it can only be removed by use of an excess of lime and soda.

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Carbonates and sulphates do not, however, occur often in water in molecular proportions. Caustic soda is also dearer than caustic lime.

The calculations of the necessary amount of chemicals are made from the chemical equations given in section 2 of this chapter. These show that one molecule of calcium carbonate or magnesium carbonate requires one molecule of calcium hydrate or two molecules of sodium hydrate to precipitate it, and that one molecule of calcium or magnesium sulphates requires likewise one molecule of sodium or barium carbonate for its decomposition.

The molecular weights are as follows :—

Salts	{	CaCO <sub>3</sub>	.	.	100	
present in		Mg <sub>2</sub> CO <sub>3</sub>	.	.	84	
water as		CaSO <sub>4</sub>	.	.	136	
impurities		MgSO <sub>4</sub>	.	.	120	
		CaO	.	.	56	or Ca(OH) <sub>2</sub> . 74
Softening	{	NaOH	.	.	40	or 2Na(OH) . 80
Chemicals		Na <sub>2</sub> CO <sub>3</sub>	.	.	106	
		BaCO <sub>3</sub>	.	.	197	

Since the English degrees of temporary and permanent hardness in water are expressed in grains of calcium carbonate per gallon, and the molecular weight of this salt is just 100, the calculations are considerably simplified. It is only necessary to multiply the degrees of temporary or permanent hardness by .56 or by 1.06 to find the grains of lime or sodium carbonate required for each gallon of water. The further calculation is equally simple, since the result

multiplied by  $\frac{1,000}{7,000}$  (that is divided by 7)<sup>1</sup> gives the pounds avoirdupois required to soften 1,000 gallons of water. Fig. 31 is a diagram showing the pounds of softening chemicals required per 10,000 gallons of water, for the various degrees of hardness from 1° to 25°.

For the other chemicals the method of calculation is similar, the factor for caustic soda being .80 and for barium carbonate 1.97, in place of those given above. It must be remembered in making these calculations that commercial chemicals are seldom pure, and that some allowance for impurities and losses in making up the solutions must be

<sup>1</sup> One pound avoirdupois contains 7,000 grains.

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made, in the final calculations for water softening. For caustic lime an allowance of 20 per cent. is advisable; for sodium carbonate 5 per cent., and for caustic soda an allowance of 10 per cent.

It is, however, unnecessary to purchase high grade chemicals for softening purposes, and if a chemist be in charge of the softening plant, a considerable saving can be effected in the annual expenditure upon chemicals, by purchase of low grade

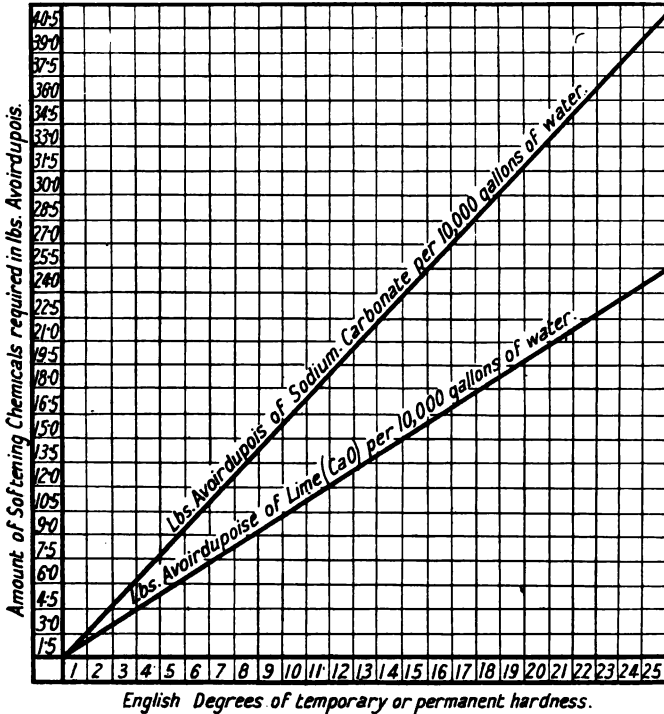


FIG. 31.—DIAGRAM TO SIMPLIFY WATER SOFTENING CALCULATIONS.

or damaged products from the manufacturers, at 50 per cent. below the usual market prices. Thus in the manufacture of caustic soda an impure product known in the trade as "caustic bottoms" is produced which sells at less than half the price of white caustic soda, and yet contains over 50 per cent. of  $\text{Na}_2\text{O}$  as compared with 70 per cent. in the standard product. Should it be desired to use caustic soda in the softening plant instead of caustic lime, this

## FUEL, WATER AND GAS ANALYSIS

impure product is quite good enough for the purpose. Carbonate of soda is usually bought in the form of a "*soda-ash*," and here again a low grade product can be bought with advantage. Sulphides in solution, however, may be dangerous, and should be removed by chemical treatment, before using the soda solution in the softening apparatus.

### IV. THE SOFTENING APPARATUS.

All the well-known and patented forms of water-softening apparatus are based on the chemical reactions given in section 3. They differ one from the other simply in the mechanical arrangement of the plant, and in the devices used for rendering the apparatus automatic in its action. The best illustrated description of water softening apparatus is to be found in a paper read by Messrs. Stromeyer & Baron before the Institution of Mechanical Engineers in December, 1903. This paper was printed in full in many of the technical journals of that date, and readers desiring further information upon the subject of water-softening apparatus are referred to it.

The use of secret compositions for putting into boilers, in order to prevent scale and grease troubles, is unwise and should never be practised. Apart from the excessive prices paid for such compositions, the impurities of a boiler feed water ought to be removed before the water enters the boiler, and should not be separated inside it. The addition of caustic soda to the water as it enters the boiler is another practice which must be condemned except when carried out under expert control, for under certain conditions this use of caustic soda does more harm than good, and also increases the tendency of the boiler to produce wet steam.

The water therefore must be treated with the softening chemicals in some apparatus, outside the boiler plant. If a chemist be available to take charge of and control the operations, the writer considers the intermittent type of apparatus in which the chemicals are allowed a considerable time to act in large tanks, in which the precipitate can settle by gravitation, to be the best. Any chemical engineer could design such a water-softening installation, and the payment of heavy royalty fees or of an excessive first cost for the plant would thus be avoided.

If no chemist be available to control the work of the plant, one of the automatic and continuous types of soften-

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ing apparatus must be selected. A discussion of the comparative merits of the large number of automatic softeners now in the market would, however, lead the writer beyond the proper limits of this work and only two general principles for guidance in the selection can be given. In the first place the softening apparatus must be sufficiently ample in capacity to deal with the whole of the boiler feed. A softening apparatus worked beyond its rated capacity is certain to lead to dissatisfaction.

In the second place, the filtering or separating chamber of the softener must be large, efficient in action, and easy of access for cleaning. The success of a softening apparatus depends largely upon the complete separation of the precipitated carbonate of lime from the water. To allow this carbonate of lime to get into the boilers is to throw away the advantages gained by the use of chemicals. In some automatic softeners the filters and settling chamber are not satisfactory. Finally, whenever possible, the water should be passed into the softening apparatus warm or hot. Nearly all chemical reactions are accelerated by heat, and when working with little above the calculated amount of softening chemicals, the speed of reaction is of great importance to the successful operation of the plant.

### V. THE CONTROL OF THE SOFTENING PROCESS.

The water sampling apparatus described in Chapter V must be employed to check the work of the softening plant. The samples of water collected in this way ought to be tested daily by the engineer, or chemist in charge of the plant.

It is advisable to have two sets of twelve or twenty-four sampling vessels in use, one set collecting hourly samples of the untreated water, and the other set collecting hourly samples of the softened water as it flows from the softening apparatus to the boilers. A selection from these samples is then made each day for the chemical examination, the general appearance of the water when examined in a tall glass cylinder (Fig. 32) and its effect upon neutral litmus paper, being used as a guide in this selection.<sup>1</sup> The presence

<sup>1</sup> A weak solution of silver nitrate in water is of use in this preliminary examination of the samples. Carbonates in solution produce a white precipitate with this reagent; hydrates produce a light brown precipitate of silver oxide.

## FUEL, WATER AND GAS ANALYSIS

of calcium or sodium hydrate in the treated water can also be detected by the use of turmeric paper, which will turn reddish brown when these chemicals are present. This effect will of course signify either that an excess of lime and soda is being used in the softening plant or that the water is being passed too rapidly through the plant and that the chemical reactions described in section 2 have not had time to be completed. The time element is in fact much more important than many makers of automatic softening apparatus have realized, and it is this time factor which gives the non-continuous tank system of softening a decided advantage.

When taking samples of water from the tanks shown in Fig. 22 (p. 69) it will be necessary to thoroughly mix

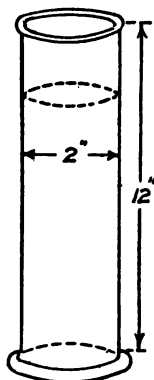


FIG. 32.—GLASS JAR FOR EXAMINING WATER SAMPLES.

the water with a wooden plunger, for a sediment of calcium carbonate may be found at the bottom of each vessel, due to unsatisfactory working of the softening plant. When such a sediment is found, either the rate of flow through the softening apparatus is too rapid or the filtering chamber is out of order, and an investigation must be made to find and remedy the fault without delay. Having selected certain samples for further examination, the temporary and permanent hardness of these must be determined by the methods described in Chapter VI. The difference between the tests of the untreated and treated water will show the working efficiency of the softening plant, and will also

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provide the necessary data for any alterations in the amount of chemicals used. Once weekly, or daily if this be possible, an average sample of the water flowing from the softening plant is tested for total solids and for oil. As already pointed out the use of sodium carbonate or caustic soda has the disadvantage that sodium sulphate remains in solution in the treated water; and thus the use of these chemicals will not cause any reduction in the total dissolved solids but actually increase them. The softening of a water containing 10 degrees of permanent hardness, will add over 10 per cent. to the amount of dissolved salts in the softened water. For this reason, boilers fed with hard waters that have been softened by use of sodium carbonate, require frequent blowing off, otherwise the sodium sulphate becomes concentrated to a dangerous extent and attacks the boiler fittings. As regards the presence of oil, this will not often be found in the water flowing from the softening apparatus, since the precipitation of calcium carbonate in this will carry down the particles of oil. Should oil be found, however, it will be necessary to erect a special oil separator for treating the water as it flows into the softening apparatus, a separator working on the electrolytic principle being most suitable for works where electric power is generated.





**PART III : WASTE GASES.**



## CHAPTER IX.

### The Chemical and Physical Characteristics of the Waste Gases—Sampling the Gases.

#### I. CHEMICAL CHARACTERISTICS.

**T**HE burning of ordinary bituminous fuel in the furnaces of steam boilers is in reality a chemical oxidation of the hydrogen and carbon of the fuel, this oxidation being sufficiently intense to produce light and heat. When this oxidation or combustion of the fuel has been properly carried out, one obtains as products of the chemical changes only carbon dioxide and aqueous vapour, these two being diluted, however, with the nitrogen and unconsumed oxygen of the air. Sulphur dioxide gas is also generally present as an impurity derived from the sulphur in the coal. As already pointed out, it is this ingredient of the waste gases and not the soot which destroys vegetation, and damages stone work in all great industrial centres where coal is burned on a large scale.

The chemical products of the perfect combustion of bituminous fuel in air are therefore :—Carbon dioxide, aqueous vapour, and sulphur dioxide, with oxygen and nitrogen as diluent gases derived from the air.

Should the combustion process have been improperly carried out, particles of unconsumed carbon, and carbon monoxide gas will be present in the exit gases from the furnace of the boilers ; while with very bad management, entirely unconsumed hydrogen and hydrocarbon gases may be found in addition to those already named.

Semi-anthracite and anthracite fuels contain less hydrogen, and when heated produce less hydrocarbon gas than bituminous coal. The waste gases from boiler furnaces fired with these classes of fuel, as a rule, therefore, contain little soot or undecomposed hydrocarbons ; but on the other hand, the proportion of carbon monoxide may be high, owing to insufficiency of the air supply.

Coke also is a fuel which may produce large amounts of

## FUEL, WATER AND GAS ANALYSIS

carbon monoxide when the management of the furnace and of the air supply is at fault. Sulphur dioxide is generally present in large amounts in the waste gases from furnaces fired by coke manufactured from cheap classes of fuel.

It may be pointed out here, that with coke and anthracite, the appearance of the waste gases gives no indication of the composition of the gas, and a clear and apparently satisfactory waste gas may contain large amounts of carbon monoxide and be associated with very bad conditions of combustion in the furnaces of the boiler.

Chemical tests of the exit gas are therefore required to discriminate between good and bad work with coke and anthracite.

When semi-anthracite or bituminous fuels are employed, insufficiency of air supply will cause, as before, carbon monoxide to be present in the exit gases, but in this case, owing to the larger amount of hydrocarbons liberated on heating the coal, smoke will be produced, and will serve as a signal that the combustion of the fuel is incomplete.

With these cheaper and more generally employed classes of fuel, a chemical examination of the waste gases therefore is not required to prove the existence of bad management of the furnaces and incomplete combustion. The freedom from smoke of the gases issuing from the chimney top is sufficient to indicate whether good or bad conditions exist within the furnaces.<sup>1</sup> It is somewhat depressing to have to state that, although bituminous coal of all grades *can* be burned entirely without smoke production in the furnaces of steam-boilers, in nine cases out of ten the correct conditions for perfect combustion are absent, with the result that soot and carbon monoxide with unconsumed hydrocarbon gases are allowed to escape in large quantities into the atmosphere.

### II. PHYSICAL CHARACTERISTICS.

*Temperature.*—The temperature of the waste gases depends very largely upon the amount of excess air allowed to pass into the boiler furnaces, and upon the cleanliness of the boiler. A large excess of air causes a low initial temperature in the furnace, and a low heat transmission to

<sup>1</sup> Excess of air may lead to a "clean chimney top," but does not produce efficiency in steam raising.

## WASTE GASES

the water in the boiler. With badly scaled boiler plates the heat of the furnace gases will not be transmitted so rapidly to the water on the other side of the plates, and the gases will consequently carry a larger proportion of their heat into the economizers and flues.

The temperature of the gases is therefore no indication of good or bad work, for it depends upon causes which operate in different directions. An excess of air lowers the temperature of the furnace and of the exit gas, while dirty and scaled plates increases it.

Good work and a high evaporative efficiency of the boiler demand a minimum of air and a high initial temperature within the furnace, combined with a rapid transfer of heat through the plates to the water. The temperature of the exit gases may thus be exactly the same, in a boiler which is converting 80 per cent. of the heat value of the fuel into steam, and in one which is converting only 60 per cent., and is allowing over 30 per cent. to escape into the flues and chimney. The temperature of the gases issuing from the boiler flues is therefore not a safe guide to the working efficiency of the boiler, though, as a general rule, the lower the temperature of the exit gases, the higher is the evaporative efficiency of the boiler.

*Specific Heat.*—The specific heat of the exit gas varies with the chemical composition, and can be calculated when this is known by the aid of the following figures:—

Carbonic acid	(CO <sub>2</sub> )	.	.	.216	}	At constant pressure with water = 1·000.
Carbonic oxide	(CO)	.	.	.248		
Hydrogen	(H) <sub>2</sub>	.	.	3·404		
Nitrogen	(N) <sub>2</sub>	.	.	.244		
Oxygen	(O) <sub>2</sub>	.	.	.218		
Aqueous vapour	(H <sub>2</sub> O)	.	.	.475		

It is evident that the amount of heat carried away by the exit gases will depend very largely upon the percentage of aqueous vapour present. This, however, varies with the amount of hydrogen present in the fuel, and with the wetness or dryness of the fuel when charged into the furnace. The specific heat of the moisture laden exit gases from furnaces using ordinary bituminous fuel may therefore lie between .240 and .300. Poole in his work on *The Calorific Power of Fuels* gives a series of specific heats ranging from .312 for 5 per cent. of CO<sub>2</sub> to .323 for 15 per cent. of CO<sub>2</sub>; but the writer considers that these

## FUEL, WATER AND GAS ANALYSIS

values are too high unless a very excessive amount of aqueous vapour be present in the exit gases. The importance of specific heat is recognized when calculating the heat lost with the exit gases. Chapter XII will deal with this subject, and in the calculations there given a constant value of  $\cdot 240$  for the specific heat of the dry exit gases will be employed, this being the condition in which they are generally analysed.

*Specific Gravity.*—The specific gravity varies like the specific heat, with the chemical composition of the exit gases, and can be calculated when this is known. The following are the figures for the specific gravity of the gases likely to be present :—

Carbonic acid	(CO <sub>2</sub> )	.	.	1·529	} Experimental figures with air = 1·000.
Carbonic oxide	(CO)	.	.	·967	
Nitrogen	(N) <sub>2</sub>	.	.	·971	
Oxygen	(O) <sub>2</sub>	.	.	1·105	
Hydrogen	(H) <sub>2</sub>	.	.	·069	
Aqueous vapour	(H <sub>2</sub> O)	.	.	·615	
Sulphur dioxide	(SO <sub>2</sub> )	.	.	2·217	

A large percentage of carbonic acid or of sulphur dioxide in the exit gases is therefore accompanied by a high specific gravity. The variations in specific gravity are used in one form of CO<sub>2</sub> testing apparatus, to indicate the percentage of CO<sub>2</sub>. Further details of this instrument will be given in Chapter XI.

*Refractive Index.*—The refraction index of furnace gases has not until lately been regarded as of any value as a guide to their chemical composition. An apparatus based on accurate observations of variations in the refractive index has now however been designed by F. Haber, and has quite recently been placed upon the market by Carl Zeiss of Jena. This instrument allows percentage variations down to  $\cdot 10$  per cent. of CO<sub>2</sub> to be easily detected, the refractive index of the furnace gas being compared with that of air or some other standard gaseous mixture. A difference of 1 per cent. of carbon dioxide makes a difference of  $\cdot 000015$  in the refraction co-efficient, and this corresponds to 1·1 divisions upon the scale of the instrument.

Further details of this instrument will be given in Chapter XI.

*Colour.*—The colour of the gases passing away from the furnace or combustion chamber of a boiler is some guide

## WASTE GASES

to the completeness of the combustion process. Gases in which all the carbon has been burnt to  $\text{CO}_2$  and the hydrogen to  $\text{H}_2\text{O}$  are colourless and transparent; while incandescent particles of carbon produce yellow tongues of flame; and unconsumed hydrocarbon gases appear as dark streaks upon the bright background of the furnace walls.

It is advisable to use a dark blue glass when examining the furnace gases in this way, and to study first the various phases of combustion, with a Bunsen burner flame held against a cherry, red background of card or paper. By varying the amount of air admission at the base of the burner all degrees of combustion can be obtained with the hydrocarbon gases supplied to the burner; and in this way an artificial reproduction of the conditions prevailing in a boiler furnace may be obtained. It is unfortunate that the combustion process in the furnaces of the ordinary internally fired Lancashire boilers cannot be studied in this way, and that the method is only applicable to the furnace gases from water-tube boilers. In these latter and in externally fired Lancashire boilers, slight holes closed with sheet mica can easily be made at suitable points in the brickwork setting, and a valuable check upon the combustion process can be exercised by observations made through blue glass in the manner already described. The observations should be made as far from the boiler furnace as possible, but before the gases come into contact with the water-cooled plates or tubes of the boiler.

### III. SAMPLING THE WASTE GASES.

For regular and systematic control of the work of the boiler plant, it is necessary that frequent tests should be made of the exit gases from each boiler, both for temperature and for chemical composition.

The best place for taking the sample of the gases is at a point about 18 inches or two feet on the boiler side of the damper which is used to cut off the boiler from the main flue to the economizers or chimney. If Lancashire boilers are installed and a separate damper be provided for each side flue, two sampling holes will be required. The holes should be made large enough to take a thirty inch length of  $1\frac{3}{4}$ -inch wrought iron pipe, provided with a flanged top which can be closed with a bolt or plug when the pipe

## FUEL, WATER AND GAS ANALYSIS

is not in use. This pipe is set with fire-clay in the brick-work setting of the boiler, and is always ready for use when required. When fixing new boilers in position it will save time and trouble if a number of these sampling holes be provided in the brickwork setting, at points suitable for testing purposes. Similar holes ought to be provided at one or more places in the main flue, and in the breast of the chimney, since the chemical composition of the waste gases at these points serves to indicate the amount of air leakage through faulty brickwork that is occurring between the boiler and the chimney. The sampling hole on the chimney breast must be made at a height of at least 15 feet from the ground, as baffle walls are generally provided at the chimney base to direct the gases from opposite flues in an upward direction, and a sample of the mixed gases cannot therefore be obtained at a lower level.

For withdrawing the sample of gas from the flues, tubes of hard (potash) glass must be employed in 3 feet lengths, and of  $\frac{3}{8}$ -inch external diameter. Arrangements for attempting to sample the gases across the whole width of the flue by use of a perforated or split wrought iron tube are of little use, and it is best to simply insert the hard glass tube, so that its far end projects about 18 inches into the flue. A large bung  $1\frac{1}{4}$  inches in diameter is fixed upon the glass sampling tube, so that it is firmly held in position in the flanged end of the wrought iron pipe, and no air leakage into the flue occurs at this point. A second or third length of hard glass tube is now joined to the first by thick red rubber tubing of good quality (black rubber is not suited for work with hot gases), and the sampling apparatus is then connected to the free end of the sampling tube or tubes. No filtering arrangement for retaining soot is used at this stage of the sampling, since it is better to have the freest possible passage between the flue and the sampling vessel. Soot and moisture will collect upon the inner walls of the glass tubes, and these must be well washed after each sampling operation, and allowed to drain and dry before use again.

Three methods for collecting the sample will now be described :—

(a). *Snap-samples of the waste gases taken by aid of the dry method and Honigman's gas-burette.*—Honigman's original gas-burette was designed for testing the amount of carbonic



## WASTE GASES

acid present in gas-mixtures containing a large percentage of this gas ; it has been largely used in the manufacture of sodium bicarbonate and other chemicals. In its earlier form the burette was not well adapted for boiler work, and the form of burette and sampling apparatus has been modified by the writer, to render it more suitable for use in testing the waste gases from boiler plants, and also more accurate in its results. This improved form of the Honigman apparatus is shown in Fig. 33. *A* is the special gas-

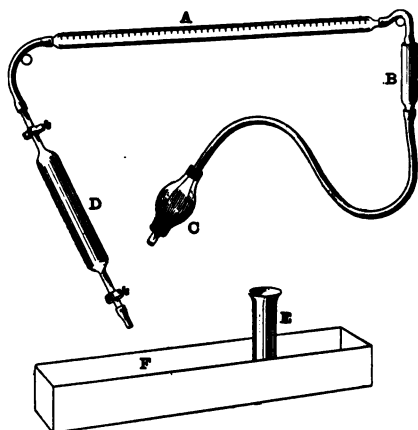


FIG. 33.—HONIGMAN'S MODIFIED GAS-SAMPLING APPARATUS.

burette holding about 110 c.c. of gas, and graduated in fifths of a cubic centimeter for the first 25 c.c. of its contents. A space of 10 c.c. between the zero mark and the end of the burette is essential. *C* is a rubber finger-pump provided with valves, so that the gases pass through it only in one direction. It passes 35 c.c. of gas at each compression, and is employed for "*drawing*" the sample of waste gases into *A* from the flue. *B* is a small rubber stop-valve which is inserted between *A* and *C* to prevent all possibility of air leakage through *C* back into *A*. By drawing 600 c.c. of gas through *A*, all the original air will be displaced by flue-gas ; with a finger-pump of the above dimensions this can be effected in seventeen compressions, occupying a time of less than one minute. If a check sample of gas for more complete analysis be collected at the same time in the gas sample tube *D*, the amount of gas drawn through the

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apparatus must be increased correspondingly, to allow for the increased volume of air requiring displacement.

The glass stop-cocks on *D* are then closed, the spring clips are placed on the rubber at each end of *A*, and the sampling apparatus can then be disconnected, and the sample taken away for analysis.

Since no liquid is used in this method of collecting gas samples, no absorption of carbonic acid gas can occur before testing. As a general rule the soot will be removed by deposition upon the inner walls of the sampling tubes, before the gas arrives in *D* or *A*. With very smoke laden gases, a little glass wool must be inserted in the rubber tube connecting *D* to the tubes that pass to the flue, in order to filter out the particles of unconsumed carbon.

(b). *Average samples extending over one hour.*—When an average sample of the waste gases over a period less than one hour is required, the apparatus shown in Fig. 34 is

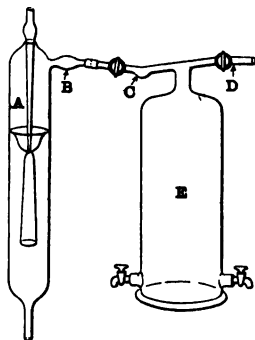


FIG. 34.—SAMPLING APPARATUS FOR TAKING AVERAGE SAMPLES OVER ONE HOUR.

employed. *A* is a water-jet air pump which works upon the injector principle, and draws air through the arm *B* at a rate dependent upon the pressure of the water supply. The arm *B* is connected to the limb marked *C* of a Stead gas sampling bottle, *E*, and the other limb of this *D* is connected to the glass tube or tubes leading to the flue. The sampling vessel *E* is filled up to the point where it joins the horizontal limb, with mercury, or with water saturated with carbonic acid. The pump is now set to work and gas is drawn from the flue at a constant rate through the horizontal limbs *C*, *D*

## WASTE GASES

of the gas sampler. One of the lower cocks of this is then opened to allow a slow trickle of mercury to pass out. A mercury bottle provided with a funnel is placed below to receive this and store it for the next sampling operation. The rate of flow of the mercury must be arranged so that the sampling bottle will still contain some of the metal at the end of the period over which the sampling is to extend. During this time, gas drawn from the flues will have been passing continuously through *C*, *D*, and a small proportion of this gas will have been continually passing into *E* to replace the mercury which has flowed away. At the end of the period, therefore, *E* will contain a fair average sample of the flue gases, and on closing all the cocks the apparatus can be disconnected, and the vessel *E* containing the gas sample can be taken to the laboratory for chemical examination.

If the waste gases are very smoky, a small bottle containing glass wool must be used to filter out the soot, this being inserted between *D* and the first length of sampling tube. The wool must be renewed for each test, as owing to the large volume of gas passing through the apparatus, a large quantity of soot will soon be collected. The mercury also will require frequent cleaning. This is best carried out by filtering through a large dry filter paper having a pin-hole in the apex, and by then washing the mercury with tap-water and drying with filter paper or blotting paper. When quite clean no reaction occurs between the dry flue gases and the mercury, and the sample can be kept for some hours in the vessel *E* without change.

(c). *Average sample extending over twelve hours.*—When an average sample of the flue gases extending over a period longer than one hour is required, the apparatus shown in Fig. 34 cannot be employed, for the weight and cost of the mercury required would be prohibitive.

It is then necessary to use an apparatus depending upon the flow of water from one vessel to another, and a difficulty arises due to the variation in the head of water at different stages of the sampling operation. The head being greatest when the sampling vessel is quite full of liquid, the outflow of water and inflow of gas will start at a maximum and gradually become reduced as the water is displaced by gas. The sample of gas obtained in this way cannot therefore be regarded as a true average of the waste gases in

## FUEL, WATER AND GAS ANALYSIS

the flue, during the twelve hours over which it has been collected.

Fig. 35 shows a gas-collecting apparatus in use at Messrs. Crosfield's Soap Works at Warrington which is free from this defect, the rate of flow from the upper to the lower vessel being constant for all variations in the water level.

The water from the upper gas collecting vessel *A* passes through the intermediate water-seal bottle *B*, and then into the lower reservoir *D* by the delivery tube *C*. This delivery tube falls as the water level in *D* rises, on account of its

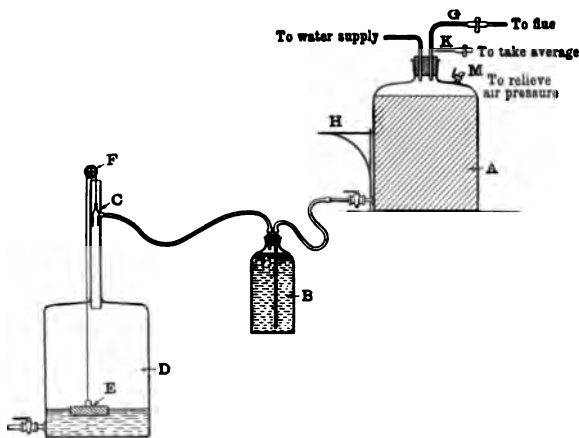


FIG. 35.—SAMPLING APPARATUS FOR TAKING AVERAGE SAMPLES OVER TWELVE HOURS.

attachment to the float *E* by a cord passing over the pulley *F*.

The head of water is thus seen to depend upon the vertical distance between the level of water in the vessel *A*, and the position of the delivery tube *C*, and a study of Fig. 35 will show that this is constant for all positions of the water level in *A*. The gases will thus be drawn into *A* at a constant rate during the whole of the twelve hours, and the sample therefore may be regarded as a true average of the flue gases during this period.

Two precautions must be observed in using this apparatus. The water in *A* must be covered with a film of oil to prevent  $\text{CO}_2$  absorption; and the tube *G* leading to the flue must be connected not direct to the flue, but to a T

## WASTE GASES

piece as in Fig. 34, through which the gases are being drawn at a rapid rate by the water pump. Otherwise the sample of gases collected in *A* will hardly be representative of the flue gases. If only one sampling apparatus be in use, the top vessel is filled by hand when empty. If one apparatus be provided for each boiler of a large battery, a small pump is used for discharging the water from the lower storage vessels into the top vessels, all of these being connected to one water main. It is, of course, necessary that each vessel should be quite filled with water before starting the sampling. For this purpose the air cock at *M* is opened to allow the imprisoned gas to escape when the vessel is being filled with water.

The apparatus described above has been patented by Messrs. Crosfields, in the name of Crosfield & Dale, Patent No. 9,099 of 1906.

## CHAPTER X.

### The Approximate Analysis of the Waste Gases.

HAVING obtained a satisfactory sample of the waste gases by one of the methods described in the previous chapter, the sample is brought to the laboratory for further examination. As a general rule it is advisable to test the gas sample as soon as possible after its withdrawal from the flues or from the collecting vessel, since there is always some danger of air leakage at the glass cocks or clips of the retaining vessel. It is also best to make the chemical tests in the laboratory, away from the dust and heat of the boiler-house, for no gas testing apparatus will give accurate results when operated in a dusty atmosphere and subjected to rapid changes of temperature. Each of the sampling methods described in Chapter IX permits the final sample to be transferred to the laboratory for the chemical examination. The Stead's Gas Sampling vessel shown in Fig. 34 is used to withdraw a sample from the larger vessel shown in Fig. 35 by placing it upon the bracket *H* and by connecting it to the tube *K*, while the clip at *G* is closed and the bottle *B* is raised to relieve the suction in *A*.

It is important to note that neither the soot nor the moisture in the waste gases are estimated by the ordinary methods of analysis, and that special apparatus is required when the amounts of these are to be separately determined.

The soot and moisture collect to a large extent upon the inner walls of the glass tubes and vessels through which the gases are drawn from the flues, and the water used in the measuring burette during the test of the sample of course condenses the remaining moisture.

To prevent any soot from getting into the gas-testing apparatus, it is usual to place a plug of glass wool in one of the connecting tubes and to renew this as often as required.

Two methods of testing the samples of waste gases will now be described in detail :—

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### I. TESTS WITH THE HONIGMAN GAS BURETTE.

(See Fig. 33, p. III.)

The burette *A* is first immersed for two minutes in the trough *F*, which is four-fifths filled with water, in order to bring the gas contents of the burette to a standard temperature. The spring clip on the zero end of the burette is then removed, and the burette is held upright in a vertical position with its lower end immersed in the water contained in the glass jar *E*. The zero mark of the burette is placed level with the brim of *E*, and the upper clip is opened to allow of the excess of gas to escape into the air, water being poured into *E* from the trough, until the gas contents of *A* measure exactly 100 c.c.

The burette is then removed from the jar *E* and is placed in a slanting position in the trough, with its upper end resting on one of the ends of the same. A small 1 gram piece of solid caustic potash is taken in the forceps provided for the purpose, and is inserted in the rubber tube at the lower end of the burette. It is then pushed up into the same by the short length of glass rod, this being left in the rubber tube as stopper.

The burette is now removed from the trough, and is gently shaken, the purpose being to dissolve the small lump of caustic potash in the water contained in the burette, and to bring the resultant solution into use as an absorbing liquid.

Two minutes' agitation is usually sufficient for this purpose, and the burette is then again immersed in the water contained in the zinc trough, in order to bring back the contents to the original temperature. The final operation is to withdraw the glass rod from the rubber tube on the lower end of the burette, to hold the latter in a vertical position in the glass jar, and to read off the volume of gas after levelling the liquid within and outside the burette. The loss in volume equals the percentage by volume of  $\text{CO}_2$  contained in the gas sample.

This apparatus yields accurate results, and tests with it can be completed within five minutes, but some little practice is necessary to obtain this accuracy and speed. The precautions necessary in its use are as follows:—

1. The rubber tubing at the upper end of the burette

## FUEL, WATER AND GAS ANALYSIS

*must not* be immersed in the water, since if any liquid collects inside it the expulsion of the excess gas above 100 c.c. is rendered exceedingly difficult.

2. No air must be allowed to enter the burette at the lower end when removing the spring clip. To expel the air in the rubber tube it is advisable to squeeze the fingers along the rubber towards the open end before the clip is opened, keeping the end of the rubber tube meanwhile under water.

3. Both before and after the absorption of  $\text{CO}_2$ , the gases must be reduced to the standard temperature—that of the water in the trough.

4. No air must be allowed to enter the tube and burette when it is being placed in the jar for levelling purposes, or when inserting the caustic potash in the solid form. This last operation must be carried out under water; and speed is necessary, as this chemical dissolves very rapidly in water.

5. After each test, the burette, jar, and trough must be thoroughly washed out with clean water in order to remove all the caustic potash solution. The burette itself should be filled and emptied three times, the simplest method of filling being to immerse it, in a slanting position in the zinc trough, after the latter has been emptied and refilled with clean water. The burette must be well drained before using for another test of the flue gases.

By using the tabloids of pyrogallic acid which are now prepared and sold for photographic purposes, the use of the Honigman burette can be extended to tests for oxygen. These tests are made by pushing the tabloid of pyrogallic acid, and one additional piece of caustic potash, into the burette from below, after absorption of the carbonic acid gas. The remainder of the test is then carried out as before.

## II. TESTS WITH THE IMPROVED FORM OF ORSAT APPARATUS.

When the percentage of oxygen and of carbonic oxide are required in addition to that of carbonic acid gas, the Orsat apparatus shown in Figs. 36 and 37 is the most convenient for general use. The writer does not recommend that this apparatus should be carried to the boilers and the sample of gas drawn directly into it from the flues by use of the finger pump G. For snap samples and tests of this kind, the Honigman burette is the most useful apparatus. The Orsat



## WASTE GASES

apparatus yields the most trustworthy results when kept in the laboratory at one temperature with all its parts scrupulously clean. The sample of gas collected in the gas sample tube *D*, Fig. 33, or in the Stead Gas Sampler (Fig. 34) is transferred to the measuring burette of the Orsat apparatus by mercury displacement. For this purpose the upper end of the tube or vessel containing the sample of gas is

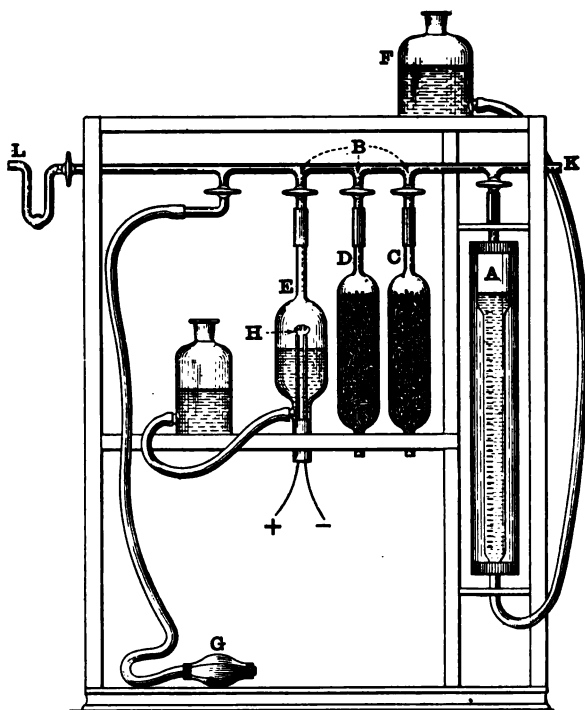


FIG. 36.—IMPROVED FORM OF ORSAT'S GAS-TESTING APPARATUS.

connected by thick rubber tubing to the **U** tube marked *L* in Fig. 36. By raising the mercury or water reservoir and opening the cocks, the gas is caused to flow out of the sampling vessel along the glass **T** piece, *B*, *K* in Fig. 36. The **U** tube *L* contains glass wool, and this serves to remove the last traces of soot from the waste gases. When all air has been expelled from the tube *B*, *K*, the free end at *K* is closed, the cock on the measuring burette *A* is opened, and by lowering the reservoir bottle *F*, 100 c.c. of the gases are

## FUEL, WATER AND GAS ANALYSIS

drawn into *A*. The cock at *L* is now closed, and the final adjustment is made by raising the bottle *F* cautiously and allowing the excess of gas to escape by *K*. It is advisable to allow the gas sample to remain *under pressure* in the gas burette *A* for two minutes before commencing the test. This gives time for the last traces of moisture and sulphuric acid gas to be removed from the sample, and prevents error



FIG. 37.—IMPROVED FORM OF ORSAT'S GAS-TESTING APPARATUS.

from these causes in the  $\text{CO}_2$  test. Any leakage at the taps or joints can also be discovered by this means before the test is made.

The Orsat apparatus comprises a measuring burette *A*, holding 100 c.c., and graduated in tenths of a c.c. for the first 25 c.c. of its contents; a glass T-piece *B*, with three glass stop-cocks; two absorption pipettes, *C*, *D*, filled with caustic potash and pyrogallic acid solution respectively;

## WASTE GASES

and a modified form of Winkler's combustion pipette *E* for determining the carbonic oxide, methane, and other combustible gases. The water aspirator-bottle *F*, and the rubber finger-pump *G*, are the remaining accessories of the apparatus.

The measuring burette *A* is enclosed in a water-jacket to preserve the gas from temperature changes during the test, and the absorption pipettes *C* and *D* should have caoutchouc balloons fixed on their free limbs to preserve the contents from contact with the outside air. The pipettes *C* and *D* are filled with narrow glass tubes, in order to provide a large surface moistened with the absorbing reagent when the gas is passed into them, and the caustic potash or pyrogallic acid solution is displaced.

The method of using this apparatus is simple in principle, but details of manipulation, which can only be understood by actual practice with it, require to be attended to in order to obtain accurate results. After 100 c.c. of the gas have been carefully measured in *A*, and time has been given for this to assume the temperature of the surrounding water, note being taken of any alteration in volume during this interval, connexion is made between *A* and *C*, and the gas is made to travel backwards and forwards three times by alternately raising and lowering the reservoir bottle *F*. The liquid in *C* is finally drawn up to the mark, the cock is closed, and the reduction in volume of the 100 c.c. represents the per cent. of carbon dioxide gas in the gas sample. With fresh caustic potash solution the absorption in  $\text{CO}_2$  is rapid; with a solution containing 30 or more per cent. of carbonate the absorption of  $\text{CO}_2$  is slow. It is necessary, therefore, to repeat the absorption procedure, and to make two measurements of the residual gas, in order to be certain that all the  $\text{CO}_2$  is removed. The caustic potash solution must also be renewed, when its absorption power for  $\text{CO}_2$  has become too slow for quick work.

For the determination of the oxygen, the same process is repeated in the absorption pipette *D*, which contains an alkaline solution of pyrogallic acid. Here again at least two absorptions and measurements of the residual gas must be made, in order to be certain that all the oxygen has been removed by the pyrogallic acid solution.

The volume of the residual gas should now be about 81 c.c. If more than this, there is reason to suspect the pres-

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ence of carbonic oxide gas, or of unconsumed hydrogen and hydrocarbon gases of the methane or ethylene type. The amount of these gases is determined by burning in the combustion pipette *E* with an excess of oxygen. For this purpose 50 c.c. only of the residual gas are used, and are mixed with 50 c.c. of the outside air drawn in by *K*, care being taken that these gas measurements are correct. This air provides the oxygen required for the further combustion of the carbonic oxide, hydrogen and hydrocarbons. The total volume of gas is carefully measured, and the gas is drawn over into the combustion pipette *E*, the platinum coil meanwhile being kept at a bright red heat, by means of an electric current of two amperes at 10 volts from any convenient source of electric energy. As the combustible gases pass over this coil they are burnt to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively. The gas is now drawn back into the measuring burette, and the diminution in volume is noticed and recorded. If no diminution occurs, it signifies that no carbonic oxide, hydrogen or hydrocarbons have been present. Should any diminution have occurred, it is necessary to distinguish between that due to carbonic oxide, and that due to hydrogen or hydrocarbons. For this purpose the residual gas is first passed over into the absorption pipette *C*, and the carbon dioxide gas produced by the combustion of the carbon monoxide is determined as before by the loss of volume. As one unit volume of carbon monoxide produces the same volume of carbon dioxide, the decrease in

volume due to  $\text{CO}_2$  absorption in *C*, multiplied by  $\frac{x}{50}$  ( $x$  being

the volume of the original gases left after absorption of the  $\text{CO}_2$  and  $\text{O}$ ) represents directly the percentage of carbon monoxide in the original gas sample. The percentage of hydrogen is now found by calculation, according to the following method :—

Contraction on combustion = 2.3 c.c.

Carbon monoxide found by  $\text{CO}_2$  absorption = 1.6 c.c.

$\frac{1.6}{2} = .80$  c.c. or oxygen corresponding to 1.6 c.c. carbon

monoxide.

2.3 — .8 = 1.5 c.c. or contraction corresponding to the unknown percentage of hydrogen and hydrocarbons.

But this contraction was due to the union of two volumes

## WASTE GASES

of hydrogen and one volume of oxygen, or three volumes of gas, and therefore the percentage of hydrogen in the original gas sample must have been—

$$1.5 \times \frac{2}{3} \times \frac{x}{50} = y \text{ per cent. of hydrogen.}$$

This method of determining the amount of the combustible gases was first used by Coquillon, but his original apparatus has been modified as shown, by Winkler and by Sodeau; and full details of the procedure to be followed will be found in the original article by the last-named chemist, published in the paper named below.<sup>1</sup> This method of testing for carbonic oxide and other combustible gases is much to be preferred to the more customary method of using an acid or ammoniacal solution of cuprous chloride for their absorption in the ordinary form of pipette, since such a solution does not yield accurate results unless freshly made for each test. This precaution is troublesome, and is seldom taken by users of the ordinary Orsat apparatus; hence the carbonic oxide tests recorded for flue-gases are seldom correct.

The Orsat apparatus, as modified by Sodeau, is the most convenient and practical form of gas-testing apparatus for works use; and when in charge of a man having experience in its use, the results obtained are sufficiently accurate for all technical purposes.

Only two solutions are required for this modified Orsat apparatus, namely, *Caustic potash* of 1.20 sp. gr., and an alkaline solution of *pyrogallic acid*.

The former solution is best made as required, by dissolving 23 grams (or 1½ sticks of the usual make) of pure caustic potash in 140 c.c. of distilled water. This solution should be transferred to the absorption pipette which holds about 150 c.c., without delay or exposure to the air. It is not advisable to make large quantities of caustic potash solution at one time. If stored in corked bottles it rots the corks and absorbs CO<sub>2</sub> from the atmosphere; while if kept in stoppered bottles it causes the stoppers to bind themselves fast in the necks.

The pyrogallic acid solution is made by dissolving 20 grams of pyrogallic acid in caustic potash solution of 1.20 sp. gr. The caustic potash solution (150 c.c.) is first pre-

<sup>1</sup> *The Chemical News*, February 5, 1904.

## FUEL, WATER AND GAS ANALYSIS

pared as above, and when cold is poured upon the weighed amount of pyrogallic acid contained in a small flask. This must be kept corked while solution occurs, and the solution must then be quickly transferred to the second absorption pipette.

The solution of pyrogallic acid in caustic potash is of a dark brown tint, and deepens rapidly in colour, as it becomes further oxidized. It absorbs oxygen rapidly when warm, but only slowly in the cold, and the Orsat apparatus should therefore be kept in a room rather above the normal temperature.

The Orsat apparatus will only yield correct results when kept clean and in good order, with all the stop-cocks and joints well attended to. At monthly intervals the glass stop-cocks ought to be removed from their sockets and thoroughly cleaned with soft paper. A thin coating of refined lard, or other suitable lubricant, may be employed to make them turn easily after cleaning. Any mishap with the 1.20 sp. gr. caustic potash solution in C, whereby it is drawn up past the stop-cock, must be followed by the removal and washing of this. Inattention to this precaution may result in much delay and expense, owing to the stop-cock sticking fast in its seat, as a result of the wetting with caustic potash solution.

### III. TESTS FOR MOISTURE AND SOOT.

Owing to the high specific heat of aqueous vapour (*see* p. 107), the percentage of moisture present in the waste gases from boilers is of more importance than is generally recognized, and it is unfortunate that so little accurate information is available relating to this constituent. This absence of accurate data is partly accounted for by the difficulty of obtaining correct results in the tests made for moisture. Condensation of the moisture occurs upon the inner walls of the sampling tubes before the weighed absorption apparatus is reached, and the soot and dust present in the chimney gases also add to the difficulty of the determination.

The following method is as satisfactory as any that can be devised, the soot and dust being determined at the same time by actual weighing in the filter tube, shown in Fig. 38.

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The glass tube shown is of hard potash glass, 9 inches in length, and about  $\frac{1}{4}$  inch in internal diameter. The lower end is rounded off and is provided with an opening  $\frac{1}{16}$  inch in diameter. The upper end is provided with a tubulus and ring, by the aid of which it is firmly attached to a screwed  $\frac{3}{4}$  inch wrought iron pipe, by means of a cap, which holds the glass ring firmly against the end of the iron pipe. Asbestos packing may be used to render this joint gas tight. The glass tube is filled through the lower opening with long and silky asbestos fibre, excluding all fine dust, and after heating carefully over a

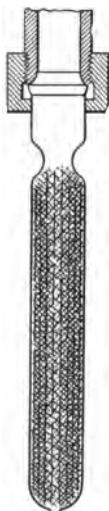


FIG. 38.—SOOT FILTER.

Bunsen burner flame, the tube and its contents are allowed to cool, and are weighed as accurately as possible on a balance or scales reading to 1-100th of a gram.

The filter tube is now attached by the screwed cap to the wrought iron carrier, and this is fixed in the sampling hole of the flue in such a position that the lower opening of the filter tube is about the centre of the flue and of the passing gases. From the increase in the weight of this tube, the amount of soot and dust can be calculated. Care must, of course, be taken to clean the exterior of the tube thoroughly before the second weighing.

The projecting end of the iron carrier tube is attached

## FUEL, WATER AND GAS ANALYSIS

by thick rubber tubing to the moisture absorption apparatus shown in Fig. 39. The wash-bottle contains 150 c.c. of cold water and serves to condense the main portion of the moisture, while the two calcium chloride tubes retain the

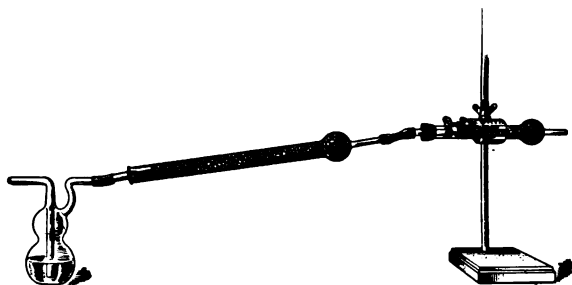


FIG. 39.—MOISTURE ABSORPTION APPARATUS.

remaining portions of moisture present in the waste gases. The complete apparatus is weighed before and after making the test, with as much accuracy as the scales allow, and from the gain in weight the moisture present per cubic foot of waste gas is calculated. If any condensation of moisture occurs between the soot filter and the water absorption

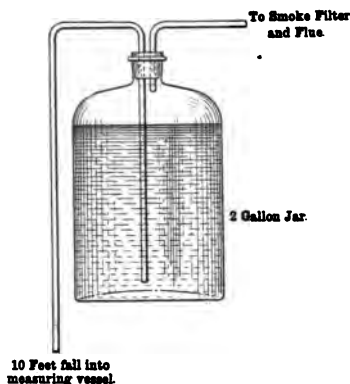


FIG. 40.—WATER-ASPIRATOR FOR TAKING SAMPLES.

apparatus, both tests will be spoiled. For this reason it is necessary to have the wrought iron pipe carrying the filter entirely sunk in the flue, and to use only a very short length of rubber tube for connecting it to the second apparatus.

The aspiration of gas through the smoke filter and water



## WASTE GASES

absorption apparatus is best effected by a water aspirator of simple design (shown in Fig. 40), the volume of gas which has passed being calculated from the volume or weight of water which is collected in the lower vessel.

The degree of accuracy which can be obtained with the apparatus described above depends largely upon the carefulness with which the measuring and weighing operations are carried out ; and a special balance will be required if many tests of this kind are to be made. A large water aspirator and a fairly rapid current of gas through the apparatus are the other conditions of success.

The solid matter retained in the filter tube will consist partly of unconsumed carbon, and partly of fine particles of ash and other inorganic matter.

If it be desired to determine the proportion of each of these, it will be necessary to place the tube in a special form of combustion furnace, and to burn the carbon of the soot to  $\text{CO}_2$ , by heating in an atmosphere of oxygen. This  $\text{CO}_2$  is then absorbed by caustic potash and by caustic lime, and from the increase in weight of the absorption apparatus, the percentage of carbon in the soot is calculated. Details of the method will be found in any text-book dealing with the analysis of organic substances ; but it is one which is obviously beyond the scope of the present work, and requires a trained chemist for its successful operation.

## CHAPTER XI.

### The Use of Continuous and Recording Gas-Testing Apparatus.

A LARGE number of automatic and recording gas-testing instruments of various types have been devised and are now being sold to steam-users, for checking the work of the firemen engaged upon the boiler plant. These instruments are costly to instal, and require skilled attention to maintain them in satisfactory working order. When placed in the charge of men who will give the necessary time and trouble to the work, they yield in most cases, however, satisfactory results.

The tests obtained with these automatic and recording gas-testing instruments can only be regarded as supplementary to the gas-testing methods described in the previous chapter, for neither hydrogen nor carbonic oxide gas are recorded by the apparatus. The heat losses due to the presence of these two constituents in the waste gases from the boilers are, however, so great that no method of control which ignores their possible presence can be considered satisfactory. This matter will be further dealt with in Chapter XII. Even the carbon dioxide test is liable to be incorrect, and independent check tests once a week or oftener with an Orsat apparatus are necessary, to ascertain the margin of error with the automatic apparatus.

The automatic gas-testing instruments may be divided into two classes—those depending for their action upon carbon dioxide absorption in caustic potash, and those based upon the observation of some physical characteristic of the waste gases, which varies in definite ratio and within fixed limits, with different percentages of the same gas. To the first of these classes belong the *Ados* and *Uehling*; to the second the *Krell*, *Arndt* and *Haber* instruments. Of these various types the *Ados* and the *Krell* are the most widely used in the United Kingdom.

## WASTE GASES

### I. THE CONNECTIONS BETWEEN THE TESTING INSTRUMENTS AND THE FLUES.

As generally arranged, one automatic instrument with a recording attachment is installed in a closed cabin or case in the boiler-house, and connection from this instrument to the side flues of each boiler of the installation is made by one long main of  $\frac{3}{4}$  inch wrought iron pipe, with branch connections of the same diameter. Each branch pipe to the boiler flue is provided with a cock. A filter filled with glass or wood wool is employed on the main suction pipe to retain dirt and soot.

By means of a fan or pump, gas is drawn continuously from the flues through these connecting pipes to the testing apparatus, and by opening only the cock leading to the flue of the boiler or boilers under test, the gas sample can be varied as required.

Many objections, all bearing upon the accuracy of the results obtained, may be urged against this method of obtaining the sample. The distance of the testing apparatus from the boiler flues and the presence of a very large number of cocks and soot filters on the one line of pipes, may cause air leakage, and consequently incorrect  $\text{CO}_2$  tests. The use of iron pipe leads to corrosion by the chimney gases, and to absorption of some portion of the constituents. In some cases so serious is this corrosion and formation of salt deposits within the pipes, that great difficulty is experienced in keeping these open for the passage of the gas sample. The large volume of stale gas contained within the long length of sampling pipe, and in the soot filters, is another cause of incorrect results, since the speed of the fan or pumps is not sufficiently high to clear this gas out in reasonable time. Six times the volume of gas must be drawn through these pipes and filters before all the stale gas can be considered to have been removed.

The following recommendations are therefore made for connecting the automatic recording apparatus of any type to the boiler flues; and only when these have been strictly followed can confidence be placed in the test results.

A water jet pump of the type shown on p. 112 should be employed for drawing the gases from the boiler flues. This pump should be fed from a water tank placed 20 or more feet above the ground, fed from the general water supply by a ball tap, and provided with a filtering arrangement at

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the run-off pipe which carries the water to the water-jet pump. This plan ensures a constant head of clean water and constant work of the pump at a uniform rate, with all freedom from stoppage due to the collection of grit or dirt in the water jet.

The connecting pipe to the flues should either be of iron enamelled inside, or of six feet lengths of glass tube. If glass be used the pipes must be placed over-head, and not laid along the boilers, and a T piece provided with a glass stop-cock must be used for each branch to the boiler flues. The vertical branch into the flue must be of hard potash glass,  $\frac{3}{8}$  inch external diameter. All connections of glass tube must be made with the best red rubber tubing and fastened with wire; and once a week the tightness of the system must be tested by closing all the cocks and working the water-jet pump, until a 20 inch vacuum is registered by the pressure gauge attached to the system near the pump.<sup>1</sup>

The dependent glass tubes into the flues must be fixed in flanged guard pipes by cork bungs, as described in Chapter IX, and once a week they must be withdrawn and cleaned, both internally and externally, from the adherent soot.

The main lengths of enamelled iron or glass tubing must be set with a fall away from the testing instrument, and these should also be cleaned monthly, or oftener if required by withdrawn steam through them.

The vessel or vessels which act as soot-filters must be placed close to the water-jet pump, and must be designed without any water seal, and of small dimensions. They should be cleaned weekly or oftener if required.

Finally, it is advisable to have one automatic instrument installed for each six boilers, and to place the cabin or cupboard in a position central to this battery of boilers, in order that the connecting pipes to the furthest boiler of the system may not exceed 30 feet in length. A connection should also be made to the nearest point in the main flue, leading to the chimney. A separate apparatus should be installed for testing the exit gases *at* the chimney, and from the flue midway between the economizers and the chimney. By this plan of arranging the testing system, a battery of 24 boilers would be provided with five testing instruments, and continuous tests of the gases from any

<sup>1</sup> A 29 inch vacuum can be obtained with these water-jet air pumps, when a sufficient pressure of water is available in the supply.

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boiler of the 24, from five points on the main flue, and from the chimney, could be obtained.

As already stated, the present methods of connecting up the automatic testing instruments are in most cases defective, and only by following some such plan as that described above can these defects be removed.

### II. AUTOMATIC TESTING AND RECORDING INSTRUMENTS.

(a) *The "Ados" or "Sarco" Recorder.*—The Ados recording apparatus is widely used in this country and in Germany

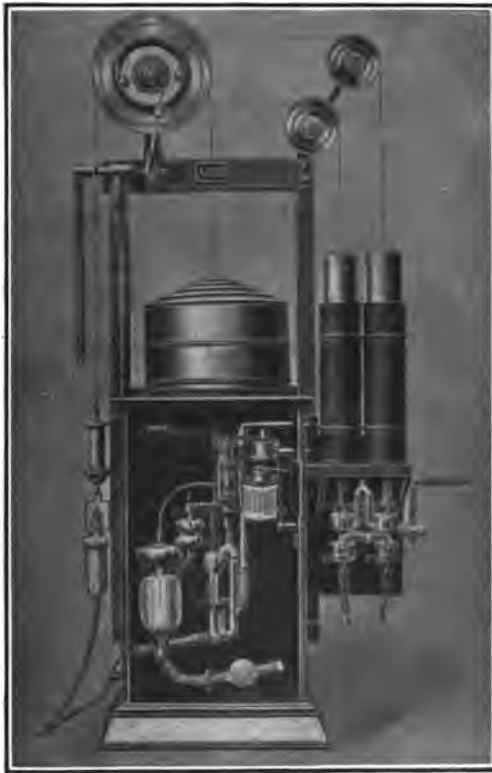


FIG. 41.—ADOS RECORDING APPARATUS (OLD FORM).

for testing the waste gases of boiler plants. Fig. 41 shows the front view of the older form of this instrument, and Fig. 42 the new form which has been recently introduced. The

## FUEL, WATER AND GAS ANALYSIS

two cylindrical vessels shown on the right hand of Fig. 41 contain samples of the flue-gases drawn by suction from the flues. While one of these is filling, the other is delivering a sample of the gas into the measuring and absorption pipettes of the apparatus. 100 c.c. of the gas are used for each test, and the percentage of  $\text{CO}_2$  is determined by ab-



FIG. 42.—ADOS RECORDING APPARATUS (NEW FORM).

sorption with caustic potash solution, exactly as in the two forms of testing apparatus already described and illustrated. The absorption takes place in the disc-like glass vessel shown on the left in Fig. 41, in order to obtain a large surface of  $\text{KOH}$  solution in contact with the exit gases. The volume of the gas remaining after the absorption of the  $\text{CO}_2$  is recorded by means of a float and lever upon paper

## WASTE GASES

carried on a revolving drum, a vertical line being marked by the pen attached to the lever for each separate test. When the volume of remaining gas is 100 c.c. (i.e. when no  $\text{CO}_2$  is present), this line extends the full width of the lined paper; when 10 per cent. of  $\text{CO}_2$  is present, the vertical line extends only up to line 10. The clear space above the line thus measures the percentage of  $\text{CO}_2$  present in the flue gases at any particular time during the day, and as the frequency of testing can be varied at will, the average of the day's work can be ascertained by means of this apparatus. It is customary to arrange the controlling mechanism so that samples of gas are drawn from the flues and tested every ten minutes. The "Ados" apparatus requires careful adjustment and control, and the  $\text{KOH}$  solution must be renewed at intervals depending upon the

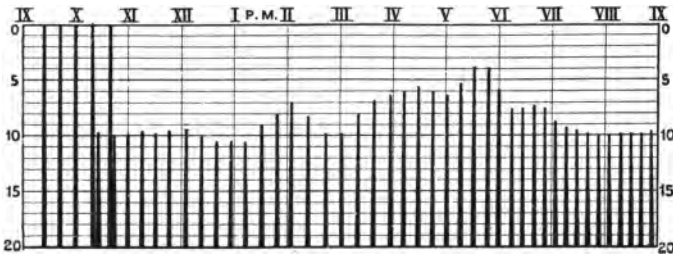


FIG. 43.—TYPICAL RECORDS OF THE ADOS APPARATUS.

frequency of the tests. Fig. 43 shows a record made with this instrument over a period of 12 hours.

(b) *The Uehling Gas Composimeter.*—This instrument is an American invention, and is not much known in this country, although a pyrometer based on the same principle is widely used in iron works in America and in the United Kingdom. The gas composimeter is shown in Fig. 44. Its working is based upon the law which governs the flow of gases through small apertures. A constant suction is applied by means of a steam jet at one end of a gas tube provided with an inlet smaller than its outlet, and connected to the exit flue. In this tube the chimney gases are submitted to the action of a caustic potash solution. The variations in pressure of the gases within this tube give the measure of the absorption which is occurring, and therefore of the amount of  $\text{CO}_2$  present. The

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exact measurements of pressure variations by means of a mercury column is consequently all that is required to yield the percentage of  $\text{CO}_2$ . This instrument can be provided with a recording pen and drum, in order to obtain continuous records of the  $\text{CO}_2$  present in the waste gases. Since the Uehling apparatus requires a caustic potash

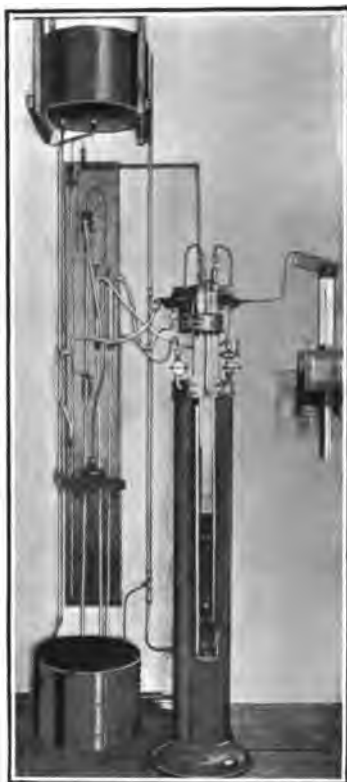


FIG. 44.—UEHLING RECORDING APPARATUS.

solution, and takes no account of the carbonic oxide present, it is open to the objections already mentioned.

(c) *Arndt's Econometer or Gas Balance*.—The two instruments described above depend for their action upon the absorption of carbon dioxide gas by solutions of caustic potash. The three remaining recording instruments depend for their action upon the variation in some physical property



## WASTE GASES

of the mixed gases. The Arndt gas balance is shown in Fig. 45.

Carbonic acid gas is considerably heavier than air, the respective weights of one litre being 1.97 grams and 1.29 grams. Thus an increasing percentage of carbonic acid will be indicated by an increase in the relative weights of a measured volume of the waste gases and of air. This fact is made use of in Arndt's Econometer, which is, in reality, a gas balance. The waste gases are weighed while being continually drawn from the flue at *E*, through the weighing bulb *C*, by means of a steam jet fixed at *D*. *A*

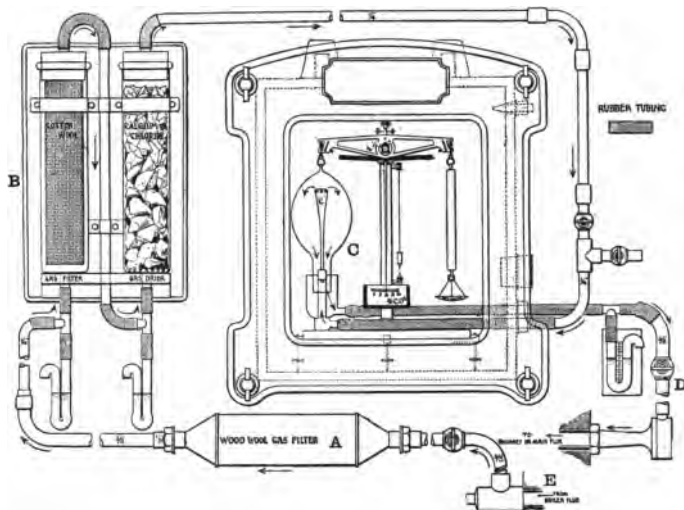


FIG. 45.—ARNDT'S GAS BALANCE.

and *B* are filters and drying tubes to remove soot and moisture before the gases are passed into the bulb *C*. The scale of the balance is graduated so that the percentage of  $\text{CO}_2$  at any given moment can be read off directly. If desired, the apparatus can be provided with a recording attachment, in order that a continuous record of the  $\text{CO}_2$  may be obtained.

The filters and drying tubes of this apparatus require constant attention; in other respects the apparatus is less troublesome than the "Ados" apparatus, since no caustic potash solution is required. If provided with a recording drum, the test records are also continuous, and not inter-

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mittent, as in the "Ados" apparatus. The possible presence of carbonic oxide in the exit gases is, however, ignored, as in all other forms of automatic recording apparatus. Since this gas is lighter than air (1 litre weighing only 1.25 grams) its presence in any quantity will render determinations of the  $\text{CO}_2$  from the readings of the Arndt apparatus incorrect.

(d) *The Krell Recorder*.—This apparatus is shown in Figs. 46 and 47. In principle it is allied to the Arndt gas balance, since its action depends upon the relative weights of the flue gases and of air. In this case, however, the difference is measured by a delicate differential gauge, attached to two tubes of equal height, one containing air and the other the sample of gas from the flues. The pressure gauge readings are taken by means of a slightly inclined glass tube filled with coloured alcohol, which projects from the pressure gauge box. The position of the end of this thread of coloured alcohol varies with the pressure in the gauge box, and by means of a scale marked in percentages of  $\text{CO}_2$  corresponding to certain pressures, the percentage of this gas present in the flue gases at any given moment can be read off directly on the scale. This instrument is usually provided with accessories by which the position of the thread of coloured alcohol is continuously photographed on a recording cylinder and paper. A continuous record of the percentage of  $\text{CO}_2$  present in the waste gases is thus obtained.

The defects of this apparatus are : first, that no account is kept of the carbonic oxide which may be present in the exit gases : this gas, if present, will render all the readings for  $\text{CO}_2$  incorrect, for the reasons already given when discussing the Arndt instrument. The second defect is, that the necessity for developing the records photographically, adds considerably to the trouble and expense of keeping the apparatus in working order.

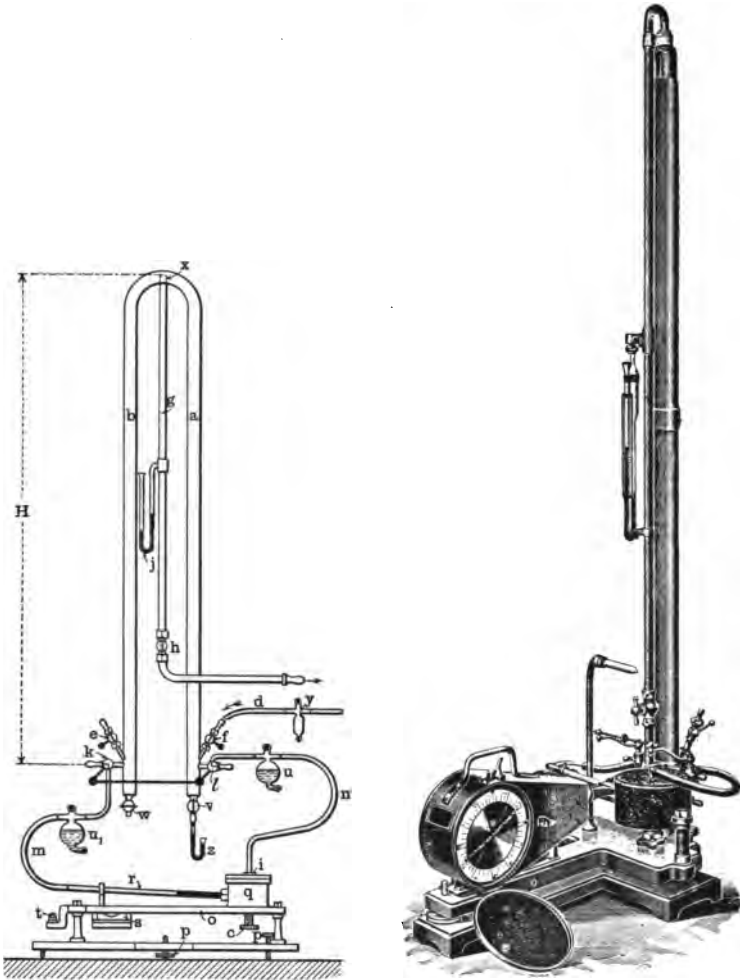
The Krell apparatus is now installed at several electric light stations in this country.

(e) *The Haber-Loewe  $\text{CO}_2$  Testing Instrument*.—This instrument differs from all others in that the variations in the refractive index of the waste gases are made use of to determine the percentage of  $\text{CO}_2$  by direct observation. The method is therefore an optical one, and resembles in some respects the optical methods for determining temperature.

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The instrument consists of the following essential parts :—  
a prism, a telescope and a microscope.

The gas to be tested flows through the prism which is



FIGS. 46 AND 47.—KRELL RECORDING APPARATUS.

hollow, is made of varnished metal, and is provided with windows for the incident and refracted rays of light. The gas used for comparison flows through a casing. When observations are made with the telescope and microscope

## FUEL, WATER AND GAS ANALYSIS

in position, the observer sees in the field of vision a scale which is partly light and partly dark. In pure air the boundary of the dark zone would coincide with  $0^{\circ}$  on the scale; in air containing .9 per cent.  $\text{CO}_2$  this boundary would coincide with  $1.0^{\circ}$  on the scale; and in air containing 9.0 per cent. of  $\text{CO}_2$  the boundary of the dark zone would be at  $10.0$  on the scale.

The instrument can be graduated so as to yield the percentage of  $\text{CO}_2$  in the waste gases by direct observation, air being generally used as the basis of the comparison.

If desired, the instrument can be made to record the readings by a photographic attachment, as in the Krell recorder.

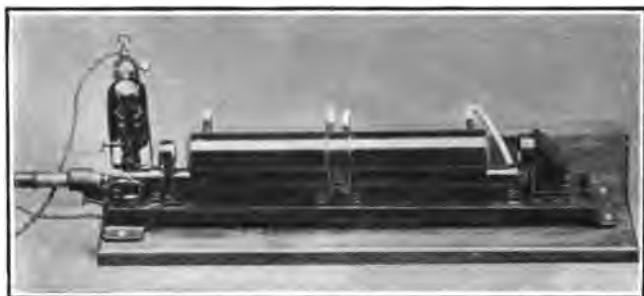


FIG. 48.—HABER-LOEWE GAS-TESTING INSTRUMENT.

The refractive indices upon which the instrument is based are as follows :—

Hydrogen . . . . .	1.000139
Aqueous vapour . . . . .	1.000261
Oxygen . . . . .	1.000270
Dry air . . . . .	1.000291
Nitrogen . . . . .	1.000297
Carbon monoxide . . . . .	1.000340
Methane . . . . .	1.000444
Carbon dioxide . . . . .	1.000452
Acetylene . . . . .	1.000610
Sulphur dioxide . . . . .	1.000665
Ethylene . . . . .	1.000678

The method is only applicable with success to gas mixtures containing two gases whose indices of refraction differ by considerable amounts, and the figures given above show that the presence of hydrogen, aqueous vapour, and sul-

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phur dioxide will all influence the results unfavourably. Carbon monoxide gas will also be returned as carbon dioxide by this method of observation. Fig. 48 illustrates the form of this new instrument which is being manufactured by Carl Zeiss of Jena.

## CHAPTER XII.

### The Practical Applications of the Gas-Test Results.

#### I. CALCULATION OF THE TOTAL HEAT LOSSES DUE TO THE VOLUME AND SPECIFIC HEAT OF THE EXIT GASES.

**I**N order to be able to calculate the heat lost daily with the waste gases from any boiler plant, it is necessary to obtain figures showing the mean temperature, and the mean  $\text{CO}_2$  and  $\text{CO}$  contents<sup>1</sup> of these gases for the 12 or 24 hours. These returns may be based either upon the average of a stated number of snap-tests, or upon the results obtained with one of the automatic recording instruments.

As already pointed out in Chapter XI, the automatic gas-testing apparatus only records percentages of  $\text{CO}_2$ , and where any apparatus of this kind is installed, it is still necessary to make occasional tests of the gases with the modified Orsat apparatus, in order to be certain that no carbonic oxide is present in the waste gases. This precaution is all the more necessary since the tendency where automatic apparatus has been installed, is to work the furnaces with too little rather than with too great an excess of air, in order to obtain carbonic acid gas averages above 10 per cent. A simple calculation will show *that it is better to have 10 per cent.  $\text{CO}_2$  and no  $\text{CO}$  in the exit gases, than 14 per cent.  $\text{CO}_2$  and 2 per cent.  $\text{CO}$ .* This is a fact which is not sufficiently recognized by boiler engineers who have installed automatic apparatus, and trust to the records of this alone in controlling the working of their boiler plant. The modified form of Orsat apparatus described in Chapter X ought, therefore to be installed in any works using over fifty tons of fuel per week. Tests of the waste gases should be made with this apparatus daily, both as a check upon the automatic recording apparatus, and as a guide to the economic working of the whole plant.

<sup>1</sup>  $\text{CO}_2$  is the chemical symbol for carbon dioxide, and  $\text{CO}$  that for carbon monoxide.

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Air contains, in round numbers, 21 per cent. by volume of oxygen and 79 per cent. of nitrogen. When this oxygen is employed for burning solid carbon, it yields the same volume of carbon dioxide gas. If, therefore, the whole of the oxygen of the air could be used up in burning fuel on the grates of steam-boiler furnaces, and if this fuel contained nothing beyond carbon and ash, a maximum percentage of 21 per cent.  $\text{CO}_2$  by volume in the waste gases would be attainable.

Two facts render this maximum impossible of attainment. In the first place, all solid and liquid fuels contain hydrogen, and the oxygen likewise contained in fuel is not sufficient to combine with this hydrogen, and to yield with it aqueous vapour. Therefore some portion of the oxygen of the air is required to burn the excess hydrogen contained in the fuel.

Further, under actual conditions of work, it is impossible to burn solid fuel properly with only the theoretical amount of oxygen. An excess varying from 50 per cent. to 100 per cent. above this theoretical amount is required to obtain perfect combustion of the fuel.

The hydrogen present varies considerably in different classes of solid fuel: in bituminous fuels it ranges, as a rule, from 3 to 6 per cent. By calculating the weight of oxygen required to burn the hydrogen present in the fuel, and by deducting from this the oxygen contained in the fuel, one obtains the oxygen required from the air. Deducting the equivalent volume of this from 20.8, we have the *percentage by volume of oxygen available for combustion of the carbon*. This figure for most bituminous fuels is about 19.2 per cent., and this therefore represents the maximum percentage of  $\text{CO}_2$  which could be obtained by perfect combustion, with the theoretical amount of air. Now supposing we have an average test for the day of the waste gases of 10 per cent.  $\text{CO}_2$ , and an average temperature of  $465^\circ \text{F}$ . at the base of the chimney, how are these figures to be used to calculate the 2,304 British Th. Units given on p. 58 as the thermal loss, under these conditions of work?

The calculation is as follows:—

Ten per cent.  $\text{CO}_2$  equals an air-consumption of  $19.2/10$  or 1.92 times that theoretically necessary. As 12 lbs. of air are theoretically required for the combustion of 1 lb. of fuel, this excess of air represents  $12 \times 1.92 = 23$  lbs.

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of air consumed per lb. of fuel, yielding 24 lbs. of waste gases.

The specific heat of these gases may be taken as 0.240. The loss of heat with the waste gases per lb. of fuel burnt is therefore—

$$24 \times 0.24 \times 400^1 = 2,304 \text{ British Th. Units.}$$

The calculation for any other percentage of  $\text{CO}_2$  in the exit gases is similarly made, the maximum percentage of  $\text{CO}_2$  (19.2) being used as a means for finding the excess of air represented by any given percentage of  $\text{CO}_2$ .

### II. CALCULATION OF THE HEAT LOSSES DUE TO IMPERFECT COMBUSTION.

The gases due to the imperfect combustion of fuel are carbon monoxide, free hydrogen, and certain hydrocarbons of the methane and ethylene series. Since the heat produced by the combustion of fuel is dependent upon the complete oxidation of the carbon and hydrogen to carbon dioxide gas and aqueous vapour respectively, it is evident that incomplete oxidation must be accompanied by loss of heat, and that the amount of this loss will depend upon the volume of the unburned hydrogen, hydrocarbons, and carbonic oxide gases. The following methods can be applied for calculating these losses from the results of the approximate analysis of the waste gases by the improved Orsat apparatus described in Chapter X; the percentage of carbon in the fuel and percentage by volume of hydrogen, carbonic oxide, and carbon dioxide in the waste gases being the test figures required for the calculation.

(a) *Losses Due to Carbonic Oxide.*—Fuel contained 80 per cent. carbon, waste gases contained 2.0 per cent. carbonic oxide, with 8.0 per cent. of carbon dioxide. Since carbonic oxide yields on combustion its own volume of carbon dioxide, the total volume of carbon dioxide, if the oxidation of the carbon had been complete, would have been 2.0 + 8.0 or 10.0 per cent. Therefore 2-tenths or 1-5th of the carbon had escaped complete oxidation. This is equivalent to  $0.80 \times 1/5$  or .16 lb. of carbon.

Now it has been proved by experiment that when 1 lb.

<sup>1</sup> It is assumed that the air temperature is 65° F. and that the net loss of heat in the exit gases is  $465 - 65 = 400^\circ \text{ F.}$



## WASTE GASES

of carbon is burned to carbonic oxide it produces 4,415 British Th. Units of heat, while when it is burned to carbon dioxide it produces 14,646 British Th. Units. (The difference between the heat produced by the union with the first atom of oxygen, and that with the second atom of oxygen, is believed to represent the work done in converting the solid carbon into the gaseous form.) The heat loss arising from incomplete combustion of the carbon is therefore 14,646-4,415 or 10,231 British Th. Units, and the heat loss in British Th. Units for the particular case under discussion is  $10,231 \times \cdot 16 = 1,637$  British Th. Units for every pound of fuel burnt. Supposing that the fuel in this case had a thermal value of 14,320 British Th. Units, the heat lost by imperfect combustion of the carbon and production of 2 per cent. of carbonic oxide in the waste gases would amount to 11.40 per cent. of the total heat value of the fuel. These figures prove the great importance of testing for carbonic oxide, and the inadequacy of any system of control which ignores its possible presence in the exit gases.

The general formula for calculating the losses due to carbonic oxide is :

$$X = \frac{\text{Per cent. CO}}{\text{Per cent. CO}_2 + \text{per cent. CO}} \times \frac{\text{Percentage of carbon in fuel} \times 10,231}{100}$$

in which X represents the British Th. Units lost per pound of fuel burnt.

(b) *Losses Due to Hydrogen.*—The older theory of combustion assumed that oxygen had a preferential attraction for hydrogen in presence of carbon, and that all the hydrogen would be burned to aqueous vapour before any of the carbon was oxidized to carbonic oxide or carbon dioxide.

The recent researches of Bone and others upon the chemistry of the combustion process have shown that this theory is incorrect, and that hydrogen can still exist in the free state in the combustible gases after the oxidation of the carbon has commenced. On the other hand, Sodeau has proved that by the use of improved methods, notable amounts of free hydrogen can be found in the exit gases from boiler plants worked with an insufficient air supply; and in the article referred to below<sup>1</sup> he gives the following analyses of the exit gases from a 1,000 h.p. water tube boiler of the Express type, fired with Welsh coal :—

<sup>1</sup> *Chemical News*, February 5, 1904.

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CO <sub>2</sub>	9·0	11·0	9·9	9·2
CO	2·15	2·8	1·65	1·3
H.	·65	·55	·47	·4

These tests prove conclusively that free hydrogen may exist in the exit gases from boiler furnaces in the presence of considerable percentages of carbon dioxide, and that the older view that the hydrogen must be first completely burnt to aqueous vapour before the combustion of the carbon occurred is incorrect. It is therefore always advisable to test for the presence of hydrogen in the exit gases from boilers worked under close supervision as regards air excess, since with the escape of 1 per cent. of unconsumed hydrogen considerable heat losses may arise.

The method of calculation is less simple than in the case of carbonic oxide, since in the absence of any test for the aqueous vapour, one is unable to state the loss as a proportion of the total hydrogen present in the fuel. It is therefore necessary first to calculate from the volume percentages of the gas analysis, the weight of the various gases by aid of the sp. gravity figures given on p. 108. Taking the first sample given above by Sodeau we have the following figures :—

	Percentage by volume.	Sp. Gr. Factor.		Equivalent by weight.
Carbon dioxide .	9·0	×	1·529	= 13·76
Carbon monoxide .	2·15	×	·967	= 2·07
Hydrogen . . .	·65	×	·069	= ·045
Oxygen . . .	8·00	×	1·105	= 8·84
Nitrogen . . .	80·20	×	·971	= 77·87
	100·00			102·585

The figure ·045 in 102·585 of waste gases is equivalent to ·0439 per cent. hydrogen by weight.

By application of the method described in Section I of this Chapter we find that a percentage by volume in these gases of 9·0 per cent. CO<sub>2</sub> and 2·15 per cent. CO, corresponds to an air supply of 20·52 lbs. of air, and to a production of 21·52 lbs. of waste gases per pound of fuel burnt. The weight of hydrogen which is escaping combustion per pound of fuel burned in the above case is, therefore,  $\frac{·0439 \times 21·5}{100}$

## WASTE GASES

or 009438 lb. Now 1 lb. of hydrogen gas, when burned completely to  $H_2O$ , produces 62,100 British Th. Units of heat;<sup>1</sup> and the loss of heat in the particular case named above is therefore  $009458 \times 62,100$  or 586 British Th. Units, equivalent to 4 per cent. of the total heat value of the fuel. Although the percentage of free hydrogen in the waste gases by volume may be small, it is thus seen to be of considerable importance in its effect upon the heat losses, and its presence ought always to be made the subject of special tests.

(c) *Heat Losses Due to Unburned Hydrocarbon Gases.*—Since the hydrocarbon gases, methane, ethylene, etc., will have been burned to carbon dioxide and aqueous vapour respectively, in the combustion pipette described in Chapter X, and have been returned in the test as carbon monoxide and free hydrogen, it is unnecessary to make any separate calculations for the heat losses due to the presence of these gases. The error in the final result is negligible, for both elements exist in combination in the gaseous state in the hydrocarbon gases, and the thermal energy required to render them free is probably small. The thermal values given for the combustion of free hydrogen and of the gaseous atom of carbon in carbon monoxide are therefore applicable; and the calculations given under *a* and *b* include the losses due to the possible percentage of these hydrocarbon gases.

### III. CALCULATION OF THE HEAT LOSSES DUE TO AIR LEAKAGE.

(a) *At the Dampers.*—Tests of the  $CO_2$  present in snap samples of the exit gases drawn *simultaneously* from the sampling hole just within the damper (on the furnace side of it) and from the nearest sampling hole on the chimney side of it, at a distance of at least two yards, are made. If the tests differ by less than half of one per cent. the air leakage may be regarded as slight.

In some cases, however, it will be found that a difference of 2.0 or more per cent. exists between the tests of the two samples. The excess of air and heat loss represented by this difference is then calculated by the method given under

<sup>1</sup> This assumes that the latent heat of the steam produced is recovered. If the water passes away from the apparatus as vapour at 212° F. this figure is reduced to 53,406 B. Th. Units.

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Section I of this Chapter. It is advisable when making use of this method to check the air leakage at the dampers, to make the test when the boiler fires are burned red, and to see that no interference with the fires occurs during the sampling operation. Both sampling tubes should be inserted an equal distance into the flues; and it is of course necessary to take the second sample of gas from the flue at a point where the exit gases from other boilers have not had a chance to mix with it, and to change its composition.

Air leakage at dampers and through the flues of incompletely dampered off boilers is a prolific cause of bad draught in most boiler plants, and attention to this defect is urgently needed. Since the cold air drawn into the flues in this way does not pass through the furnace of the boiler it may be argued that the heat loss is negligible. In most modern boiler plants, however, economizers or feed water heaters are employed for extracting some portion of the heat from the waste gases; and the dilution with cold air, drawn in through the dampers of the boilers, diminishes greatly the efficiency of this accessory plant. The use of gas testing apparatus for discovering and checking this leakage is, therefore, of considerable importance.

(b) *Through the Brickwork of the Boiler Setting, Economizer and Flues.*—The method of making the test is described under (a). *Simultaneous* snap samples are drawn from different sections of the flue, and are tested for the percentage of  $\text{CO}_2$ . The gradual reduction in the percentage of  $\text{CO}_2$ , as the sampling approaches the chimney, is the measure of the air leakage. The calculation of the air excess and of the heat loss, is carried out as already described in detail under Section I of this Chapter. In nearly every case where special attention has been devoted to this subject, considerable air leakage through the brickwork of boilers and flues has been found; and the casing in of the rough setting of these, in glazed bricks or in sheet iron, has been found to result in considerable economy. It must be pointed out here that leakage through the brickwork setting of a boiler, or through the economizer walls is a direct source of heat loss, since the cold air which leaks into the flues in this way is raised to the boiler or economizer temperature by heat abstraction from the boiler plates and economizer tubes. The ordinary direction of heat transfer is therefore reversed,

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with direct loss to the efficiency of the boiler or economizer plant.

### IV. CALCULATION OF THE INITIAL FURNACE TEMPERATURE.

The test results of the exit gases can be made use of to calculate the temperature attained in the combustion area of the boiler furnace. The method is based upon the calorific value of the fuel, and the weight of the products of combustion per lb. of fuel burnt. The former figure is obtained by one of the methods of direct test described in Chapter III; the latter is calculated from the results of the approximate analysis of the waste gases, as described in Section I of this Chapter.

Taking the case there given, in which the gases contained 10 per cent.  $\text{CO}_2$  and no carbonic oxide or unburned hydrogen, this was found to correspond to an air excess of 1.92 times the volume demanded by theory, or to 24 lbs. of waste gases per pound of fuel. The specific heat of these gases was, however, .24; therefore 5.76 British Th. Units would be required to raise the temperature of these 24 lbs. of waste gases through 1.0 F. Taking the heat value of fuel in this case, at 14,200 British Th. Units, it is evident that the furnace temperature must have been  $\frac{14,200}{5.76}$  or 2,465° F.

Should the combustion of the fuel be incomplete, and carbonic oxide, hydrocarbon gases or free hydrogen be present in the exit gases, it is necessary to deduct from the thermal value of the fuel the thermal units corresponding to the amount of these gases per pound of fuel burnt. These are calculated by the method given under Section II of this Chapter. The balance of heat units produced by the combustion of 1 lb. of the fuel is then divided by the factor 5.76 as in the previous example.

Since the rate of heat transfer from the hot gases on the one side of the boiler plate to the water on the other side of the plate is dependent upon the difference in temperature between the two, and increases directly as the temperature, it is evident that a high initial furnace temperature is requisite for the most economical working of boilers. The method of calculation described above is the simplest and

## FUEL, WATER AND GAS ANALYSIS

quickest method of ascertaining and controlling this factor in good boiler working.

### V. CALCULATION OF THE HEAT LOSSES DUE TO AQUEOUS VAPOUR.

As pointed out on p. 124, the amount of aqueous vapour in the waste gases from steam boiler plants is rarely determined, and the heat losses due to this constituent of the final exit gases are therefore largely unknown. The following calculations however prove their importance, and the necessity for keeping the moisture in the coal as low as possible, as well as the advantage of using fuels containing a low percentage of hydrogen. The superior steam-raising efficiency of South Wales steam coal is no doubt due to its low percentage of hydrogen.

Taking the coal, the analysis of which was given in Chapter I, we find that there was 3.05 per cent. moisture and 4.65 per cent. hydrogen present in the fuel as delivered.

Since hydrogen yields nine times its own weight of aqueous vapour on combustion, every 100 lbs. of this coal would produce  $3.05 + (4.65 \times 9)$  or 44.90 lbs. of aqueous vapour in the furnace gases, and 1 lb. of the coal would correspondingly produce .449 lb. of aqueous vapour. This aqueous vapour had, however, all to be raised from the temperature of the external air to the temperature of the exit gases. In addition to the loss of heat due to the high specific heat of aqueous vapour, there was also that due to the fact that the water passing off as aqueous vapour from the furnace of the boiler had first to be raised to 212° F. and then vaporized. Now 966 British Th. Units of heat disappear in the vaporization of 1 lb. of water, and this value is known as the latent heat of steam. The calculation for the heat lost with the moisture present in these gases is therefore made as follows: the temperature of the exit gases being taken as 665° F., and the external air temperature at 65° F.

1. Heat required to raise the moisture from 65° F. to 212° F.— $449 \times (212 - 65) = 66$  British Th. Units.

2. Heat required to convert this moisture into steam at 212° F.— $449 \times 966 = 433$  British Th. Units.

## WASTE GASES

3. Heat required to raise this steam from  $212^{\circ}$  F. to  $665^{\circ}$  F.<sup>1</sup>— $449 \times (665 - 212) \times .540 = 109$  British Th. Units. The total heat loss due to the presence of this aqueous vapour in the exit gases is therefore :—

$$66 \times 433 \times 109 = 608 \text{ British Th. Units.}$$

With the fuel under consideration this loss was equivalent to  $\frac{608}{12600}$  or to 4.8 per cent. of the total heat value of the fuel.

The chief loss is due to the latent heat of the steam, and this heat cannot be recovered from the waste gases unless they be cooled below  $212^{\circ}$  F. before passing up the chimney. Since the efficiency of chimney draught is dependent upon the temperature difference of at least  $400^{\circ}$  F. between the vapour within the shaft and the air outside it, it will be seen that until fan draught is more general, the loss of this heat is largely unavoidable. It can, however, be minimized by the use of dry fuel, and the prevention of all unnecessary steam escapes into the furnaces of the boilers. The fuel tests given in the Appendix show that great differences exist between the moisture tests for various classes of coal, and that in washed slacks of bituminous character, the moisture may rise to a very high figure.

It is therefore questionable whether the freedom from ash obtained by washing is not purchased at too high a cost ; and it would be well to stipulate in buying such washed slacks or "peas" that the moisture shall not exceed 5 per cent. in the fuel as delivered.

## VI. CALCULATION OF THE HEAT BALANCE.

The method of ascertaining the evaporative efficiency of the boilers by means of a "heat balance" was described in Chapter IV. It is unnecessary to repeat here the details of this method of calculating the efficiency of the steam-raising plant. The second entry in the heat balance given in Chapter IV may, however, be expanded to include all the heat losses discussed in Sections II, IV and V of this Chapter.

The heat balance is then set out as follows :—

<sup>1</sup> The specific heat of steam rises with the temperature, and at  $665^{\circ}$  F. is about .600.

# FUEL, WATER AND GAS ANALYSIS

## HEAT VALUE OF FUEL IN CALORIMETER.

	B. Th. Units.
1. Losses by radiation, etc. . . . .	.
2. <i>Losses by waste gases</i> :—	.
(a) due to excess air . . . . .	.
(b) due to unburned carbonic oxide . . . . .	.
(c) due to unburned hydrogen and hydrocarbons . . . . .	.
(d) due to moisture . . . . .	.
3. Losses by unburned carbon in cinders and ash . . . . .	.
4. Losses by heat carried in cinders and ash . . . . .	.
5. <i>Balance</i> heat converted into steam . . . . .	.

The difference between the total of the items 1-4, and the heat value of the fuel as ascertained by the calorimeter then gives the total units of heat converted into steam, and from this the evaporative efficiency of the boiler or boilers is obtained, by expressing the result as a percentage of the total heat available. It is important that the heat value of the *undried fuel* be used in these calculations, and not the heat value of the *dry fuel*, as usually returned by the chemist. The former can be calculated when the latter is known.

Fig. 49 shows in graphic form the percentage of fuel wasted by heat losses in the exit gases at various temperatures. It is based upon a table given in the Appendix of the book named below.<sup>1</sup>

As an illustration of the use of the diagram, we may take the case of waste gases containing 8 per cent. CO<sub>2</sub>, and having a temperature of 600° F. At the point where the lines representing these values intersect in the diagram, we find the figure 24.9, which represents the percentage loss of fuel under these conditions. If the percentage loss is not marked for the particular case under consideration, the value is obtained by interpolation. Taking a case in which the waste gases contain 10.5 per cent. CO<sub>2</sub>, and pass away again at 600° F., the percentage fuel loss at 10 per cent. CO<sub>2</sub> at 600° F. is 20.2, and at 12 per cent. CO<sub>2</sub> it is 17.1. The loss at this temperature with 10.5 per cent. CO<sub>2</sub> is therefore evidently  $20.2 - \left( \frac{20.2 - 17.1}{4} \right)$  or 19.4 per cent.

<sup>1</sup> *Smoke Prevention and Fuel Economy*, by Booth and Kershaw Constable, 1904.



# WASTE GASES

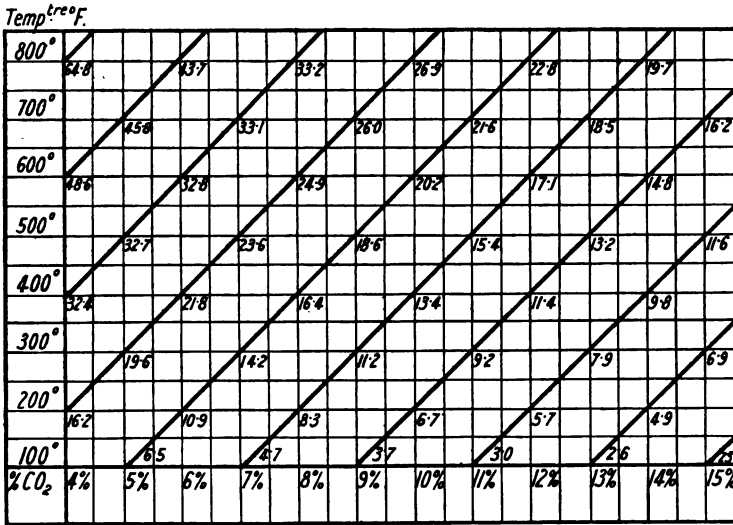


FIG. 49.—DIAGRAM OF HEAT LOSSES IN EXIT GASES.

The other losses for the intermediate temperatures and CO<sub>2</sub> percentages are arrived at by aid of the diagram by use of a similar method.



**APPENDIX.**



## I.

### RULES FOR SAMPLING FUEL.

**A**S each barrow load or fresh portion of fuel is taken from the pile or store heap, a count is kept of the number used, and *the whole contents of each tenth or twentieth barrow or portion* are placed on one side, in a cool place, under cover. Care must be taken that the barrow or portion selected for the sample does not contain an unfair proportion of lumps or smalls.

At the end of the day, or period for which the sampling is to be carried on, the heap of fuel obtained for sampling purposes, as described above, is transferred to a sampling plate, and the larger lumps are all crushed down to walnut size. Should no sampling plate be available, four of the iron plates used for covering man-holes and boiler-flues may be utilized to obtain a *hard clean* surface on the floor of the boiler-house, and the crushing down of the sample may be carried out on these plates, with any heavy and flat lump of iron at hand. The heap of fuel, after this first crushing, is thoroughly mixed by turning over and over with a spade. The heap is then flattened down, two lines are made across it at right angles with the edge of the spade, and two of the four opposite sections are selected to form the reduced sample. The lumps in this are again crushed, the sample is again mixed, and the quartering operation repeated, until about 8 or 10 lbs. of fuel only remain, with no lumps that will not pass through a  $\frac{1}{4}$ -in. sieve. Two 1 lb. tins, with patent lids, are filled from this remaining heap of fuel, after thoroughly mixing the same with the hands or with a small shovel. One of these tins is to be sent per parcels post to the fuel expert for analysis; the other is to be kept for reference in case of dispute.

II.

APPROXIMATE ANALYSES, CALORIFIC VALUES (CALCULATED AND OBSERVED), PRICES AND COMPARATIVE COSTS OF VARIOUS ENGLISH AND WELSH COALS.

General Description of Coal.	1	2	3	4	5	6	7	8	9	10
	Particular description of Coal.	Per cent. Moisture.	Per cent. Ash.	Per cent. Coke.	Per cent. Volatile Matter.	Per cent. Fixed Carbon.	Calorific Value Observed.	Calorific Value calculated.	Price per Ton delivered in Bunkers.	Calorific Value per Penny of Cost.
									s. d.	
Hard South Wales Coals	Standard Merthyr	1.21	8.85	84.50	15.50	75.65	7,942	7,950	21 0	70,784
	Cwmmwr Main	1.46	10.00	87.50	12.50	77.50	7,935	7,855	17 3	85,792
	Dynevor Duffryn	1.25	8.10	84.10	15.90	76.00	7,987	8,028	19 1	77,952
	Pontardame Smokeless	2.66	8.40	87.90	12.10	79.50	7,875	7,995	17 3	85,120
	Ocean Steam Coal	3.13	13.95	87.00	13.00	73.05	7,590	7,511	15 10	89,376
Loughor & Mynydd	Newydd	2.20	17.05	86.00	14.00	68.95	7,360	7,545	9 6	144,480
	Werfa	1.34	14.95	90.00	10.00	75.05	7,331	7,405	11 11	128,128
Soft Bituminous Coals	North Hetton	2.51	13.80	69.00	31.00	55.20	7,590	7,347	11 10½	119,168
	Bowley Washed Slack	2.76	5.85	67.40	32.60	61.55	8,365	8,123	10 6	148,512
	Wigan	4.94	16.85	69.90	30.10	53.05	7,192	7,089	8 3	162,624
	Wigan and Skelmersdale	6.76	16.50	71.20	28.80	54.70	7,245	7,203	8 4	162,176
	Digby Bright Peas	10.44	6.50	63.50	36.50	57.00	7,935	7,703	7 9	191,072
Shipley Peas	Shipley Peas	7.72	7.75	66.00	34.00	58.25	7,891	7,764	7 11	185,920
	Marchay Rough Slack	7.80	3.05	64.70	35.30	61.65	8,314	8,214	8 8	178,976
	Manners Peas	7.44	10.75	66.40	33.60	55.65	7,675	7,490	7 5	193,088

NOTES

(1) The results in columns 3, 4, 5, 6 and 7 are all based on the sample dried at 110 degrees C.

(2) Columns 7, 8 and 10 give the calorific values in Centigrade units.

(3) The first five samples are from a South Coast Electricity Supply Station, and the costs delivered in Bunkers are correspondingly high.

III.

GOUTAL'S FORMULA FOR CALCULATION OF THE CALORIFIC VALUE OF THE FUEL, FROM THE RESULTS OF THE APPROXIMATE ANALYSIS.

Goutal in 1902 published <sup>1</sup> the formula given below for calculating the calorific value of the fuel from the results of the approximate analysis, the formula being based upon a very large number of tests of various French coals. The author has used this formula for some years, and has compared the results obtained with it with the actual

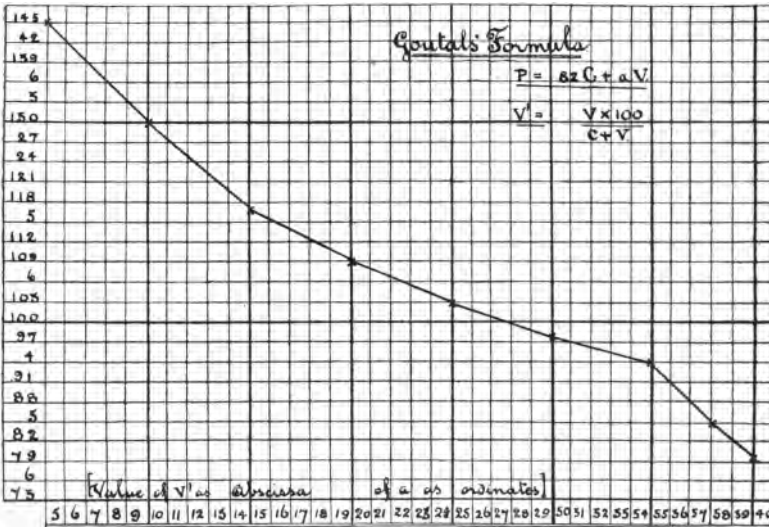


FIG. 50.

calorific values obtained with the bomb calorimeter. In the majority of instances the differences are small, and the formula may be used with advantage for determination of the calorific value, when no direct test is possible. It is a mistake, however, to place too great reliance upon the calculated value, and in all cases of importance, the direct test with one of the approved forms of calorimeter should be made.

The formula is as follows:—

$$P = 82C + aV,$$

<sup>1</sup> *Comptes Rendus.*—Sept. 1902.

## APPENDIX

in which P is the calorific value of the fuel in Centigrade units ; C is the percentage of fixed carbon ; V is the percentage of volatile matter ; and (a) is a variable depending upon the percentage of hydrocarbons and of hydrogen in the actual combustible of the coal.

Using the formula :—

$$V^1 = \frac{V \times 100}{C + V}$$

the following values are obtained for a

$V^1 =$  5.    10.    15.    20.    25.    30.    35.    38.    40.  
 $a =$  145.   130.   117.   109.   103.   98.   94.   85.   80.

Figure 50 is a diagram giving the curve based upon the above figures, and this may be used with advantage in calculating the corresponding value of (a) for any value of ( $V^1$ ), between the limits 5 and 40.

The following are a few results selected to show the fairly close agreement between the calculated and observed thermal values— for different coals tested by the author (results in Centigrade units) :

<i>Observed.</i>	.	.	.	.	<i>Calculated.</i>
8321	.	.	.	.	8107
7906	.	.	.	.	8081
7874	.	.	.	.	7952
6968	.	.	.	.	7006
7169	.	.	.	.	7351



#### IV.

### THE USE OF FUELS OF LOW CALORIFIC VALUE FOR STEAM-RAISING PURPOSES.

The tables given on p. 156 of the Appendix indicate that great economies may be effected, by the use of cheap fuels, for steam-raising purposes. Under correct conditions of combustion with properly designed grates, these cheap fuels may be burned completely without smoke, and as large a proportion of the total heat value of the fuel converted into steam, as in the case of the more expensive fuels.

But one can obtain in these cheap fuels two or even three times the number of thermal units per penny of cost, that one obtains when buying South Wales steam coal or the higher class bituminous coals. By their employment, therefore, it is possible to reduce by 50 per cent. or more the cost of the fuel for the boiler plant. It is unwise, however, to attempt to use cheap fuels in this way unless the boilers be placed in the sole charge of a man who understands the scientific principles underlying combustion, and is ready to adopt the methods of attaining economical work, details of which are given in Chapters IV, VII and XII of this volume. Further, in burning low grade fuels, there is always a large increase in the weight and volume of ashes and cinders, and special provision must be made for removing these without undue cost. The arrangement for trapping and removing flue-dust, also require most careful consideration when burning fuels high in ash contents, and a considerable alteration in the present methods of removing flue-dust is demanded by the necessities of the case. The removal of cinders, ashes and flue-dust in such circumstances ought to be automatic and continuous; but there is no difficulty in designing suitable mechanism for this purpose, and the question of its adoption simply resolves itself into one of "will it pay"? In many, if not in the majority of large plants, the answer to this question would be the affirmative; and the annual savings effected by the use of cheap fuel would balance many times over the interest upon capital cost and working expenses of automatic machinery for the removal of flue-dust and ashes.

V.

TESTS OF WATER FROM VARIOUS SOURCES.

*Results expressed in parts per 100,000.*

Description.	Total Solids.	Temporary Hardness.	Permanent Hardness.	Total Hardness.
LIVERPOOL CORPORATION WATER.				
1. Lake Vyrnwy . . .	4.46	—	—	1.7
2. Rivington . . .	10.36	—	—	3.9
3. Dudlow Lane . . .	19.2	—	—	8.8
4. Green Lane . . .	33.1	—	—	20.8
5. Windsor . . .	41.7	—	—	28.5
6. Waterloo District . .	6.8	1.5	4.1	5.6
VARIOUS DISTRICTS.				
7. Spring water . . .	17.6	5.6	7.2	12.8
8. Surface water . . .	56.8	34.9	3.8	38.7
9. Surface water . . .	47.00	—	—	—
10. <i>From a Boiler in need of washing out</i> . . .	689.2	—	—	—

NOTES.

Lake Vyrnwy is in North Wales ; Rivington is a catchment area near Bolton.

Samples 3, 4 and 5 were from the old pumping stations of the Liverpool Corporation, and are samples of well waters. Sample 6 is the combination of Vyrnwy, Rivington and well water supplied to Liverpool and district for domestic uses. It is an exceptionally pure water. Sample No. 9 contained 8.8 parts of organic matter per 100,000, and gave an acid reaction with phenol-phthalein. The acidity required 10.847 parts  $\text{Na}_2\text{CO}_3$  per 100,000 of water, to neutralize it.

Sample No. 10 contained 43.2 parts of organic matter per 100,000 of water, and showed the danger of running boilers too long without blowing off. In this case the fittings were always leaking.

## VI.

## TYPICAL TESTS OF EXIT GASES.

No.	Per cent. CO <sub>2</sub> (Carbon dioxide).	Per cent. O (Oxygen).	Per cent. CO (Carbonic oxide),
1	6.80	12.80	nil
2	5.80	13.80	nil
3	8.90	10.60	nil
4	8.50	10.80	nil
5	10.60	6.20	2.00
6	13.40	5.40	.20
7	12.40	6.70	.30
8	9.30	9.10	.80
9	8.80	10.40	.20

## NOTES.

All the above tests were made upon samples drawn from the flues of boilers under actual working conditions, the samples being taken from the side flues on the furnace side of the dampers.

Tests 1 to 4 show low CO<sub>2</sub> percentages and excess oxygen; while tests 8 and 9 indicate that even with a comparatively large excess of oxygen it is possible to produce carbonic oxide under bad conditions of firing. In these two cases it is possible that the fire was thick in places and burnt through in others, and that the air excess was rushing in at these thin and bare places in the grate.

Tests 5, 6 and 7 show fairly good CO<sub>2</sub> percentages, but No. 5, with its 2.00 per cent. of carbonic oxide, indicates the danger of attempting to attain high CO<sub>2</sub> percentages, except under scientific control. The thermal losses due to carbonic oxide formation are discussed in Chapter XII (p. 142).



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Butler & Tanner, The Selwood Printing Works, Frome, and London.

