# Liverpool Section.

*Meeting held at University, on Wednesday, April 8, 1908.*

DR. JAMES T. CONROY IN THE CHAIR.

## AN ARRANGEMENT TO FACILITATE THE USE OF HEMPEL'S PIPETTES.

BY J. S. STUDER.

The Orsat gas analysis apparatus is very useful[?] for testing the exit gases of steam boilers, and its portability adds considerably to its practical value in various investigations and technical processes. To obtain, however, a full analysis of a producer gas, I consider that the adoption of Hempel's method is essential, but having recognised the possibility of the results being slightly inaccurate, I introduced some two or three years ago a new method of manipulation of Hempel's pipettes. The adoption of this new method has the effect of reducing the margin of error so much that for works purposes and general technical operations it may be ignored.



— PLAN —
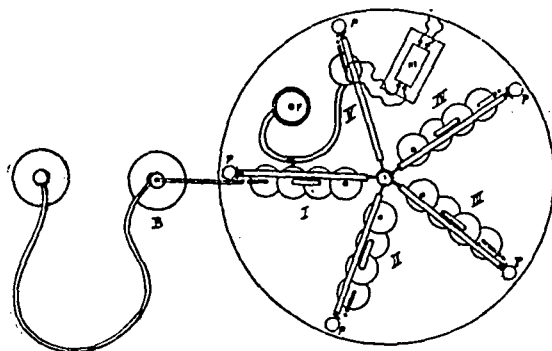
The new arrangement consists of a circular disc, C, which rests horizontally on the central support, D. This support is of metal and is hollow from the top to the point, e. On this point rests the small piston, which projects from the centre of C. In this manner a free circular horizontal movement can be given to the disc, and the various absorbing vessels, and the explosion pipette can be easily brought in consecutive order to the point where the gas surettes are manipulated. When it is necessary to agitate the solutions in one of the pipettes, the small bemi-circular fork bolt. b, is drawn back, and an easy backward and forward movement can be given to the absorbing vessels. The movement is facilitated by the arrangement of small fulcrums, a, which are the only supports of the pipettes.

By rotating the disc, C, consecutively about 72°, each pipette is brought in position of that of No. 1, and in transferring the gases under examination from the burette, B, to the various pipettes, and then again to No. 1, an analysis of the principal constituents of a producer gas can be carried out in about 20 minutes.

On comparing this arrangement of Hempel's pipettes with that generally in use, it will be obvious that by suspending the various pipettes, with the exception of the explosion pipette, on a fulcrum, and yet maintaining great stability of the whole arrangement, the shaking of the pipettes is easily carried out without the risk of drops of the reagent finding their way to the capillary tubes. Leakage or fracture at the point d is almost impossible.
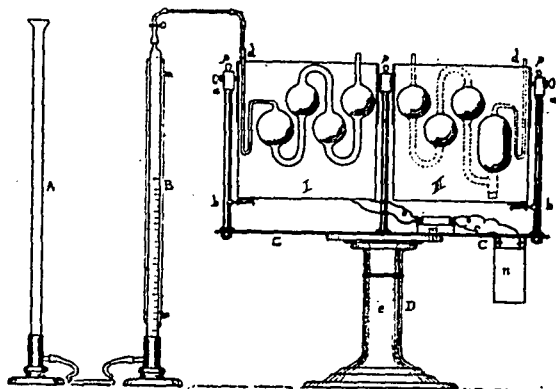


— ELEVATION —

The fact, that the burette, B, is in this method a fixture throughout the whole series of manipulations, enables a water jacket to be more easily placed round it.

The various pipettes are filled with the following solutions :—No. 1 contains caustic soda or potash ; No. 2, bromine water or fuming sulphuric acid ; No. 3, sodium or potassium pyrogallate ; No. 4, an ammonical solution of cuprous chloride ; and No. 5 is an explosive pipette filled with mercury (r, mercury reservoir bulb ; m, induction coil ; n, storage battery.)

The absorption of ethylene by bromine water is very frequently omitted, (published results of analysis of producer gas rarely mention ethylene) and may be a cause of error when testing for methane. The importance of estimating ethylene will be recognised from the fact that its calorific value is much greater than that of any other constituent of a producer gas. The calorific power of gases, expressed as calories per cubic meter, is, according to Lunge, as follows :—Carbon monoxide, 3066 ; hydrogen, 2581 ; methane, 8697 ; ethylene, 14,045. It is evident therefore, that by omitting the estimation of ethylene, appreciable inaccuracies may result. It is well known that cuprous chloride will absorb ethylene, and for this reason alone it is important that the heavy hydrocarbons should be absorbed, either in bromine water or fuming sulphuric acid, before determining carbon monoxide when testing producer gas.

It has been said that, in the analysis of producer gas, the use of water instead of mercury gives rise to some error in the results obtained. In practice, where one is not limited to the use of the quantity of gas to be examined, one meets that objection by saturating all water to be used with the gas to be examined. In a works where a great number of analyses have to be carried out during a day, the use of water is a great and indispensable convenience, especially when the samples to be analysed have to be fetched from various parts of the works.

# London Section.

*Meeting held at Burlington House on Monday, May 4, 1908.*

DR. J. LEWKOWITSCH IN THE CHAIR.

## THE MANUFACTURE OF SODIUM NITRITE.

BY GILBERT T. MORGAN, D.SC.

Sodium nitrite is practically the only salt of nitrous acid which is prepared on a manufacturing scale and it finds extensive use in the production of several classes of artificial colouring matters and also in the preparation of various pharmaceutical products and other fine chemicals.

### I. Production from sodium nitrate.

Hitherto nitrite has generally been prepared from sodium nitrate, and the following are some of the principal methods by which this chemical change can be effected.

1. *Thermal decomposition.*—The alkali nitrates when heated above their fusion point evolve oxygen and furnish nitrites, but this reaction is of no practical importance owing to the simultaneous occurrence of a further decomposition to oxide. The difference in the behaviour of the two alkali nitrates is of some theoretical interest, the potassium salt giving a final residue of the dioxide, whilst the sodium salt yields the monoxide.

2. *Reduction by metals.*—Finely divided copper has been suggested by Persoz and by Müller and Pauly, but owing to the infusibility of this metal at the temperature of molten nitre it is difficult to ensure a uniform reduction throughout the heated materials, and, moreover, this process involves the regeneration of the comparatively expensive copper from the resulting cupric oxide. Zinc dust has been tried but I am not aware that a successful method has been based on the use of this metal. Sturm (Fr. Pat. 321,498 of 1902; this J., 1903, 212) obtains nitrite by heating sodium nitrate with finely divided metals in a muffle furnace. More recently iron has been recommended as a reducing agent for sodium nitrate.

The heating of a concentrated solution of lead nitrate with finely divided lead leads to the formation of insoluble basic lead nitrite, which furnishes sodium nitrite by double decomposition with sodium carbonate. This reaction is, however, only of theoretical interest.

Lead is undoubtedly the most convenient metal for the reduction of sodium nitrate; it is comparatively cheap, and its melting point (330—335° C.) lies so close to that of the nitrate (314° C.), that the two reagents can be brought together in the liquid condition at a temperature considerably lower than that at which the thermal decomposition of nitrite occurs. (Hampe, Annalen, 1863, 125, 336.) The reduction is effected on a manufacturing scale in shallow cast-iron pans, 4 ft. in diameter and about 18 inches deep, fitted with a stirring gear which agitates thoroughly the whole mass of molten material. The pans are supported on perforated fire-brick arches, arranged so that the products of combustion of the coal fires circulate uniformly round the pan before passing to the flues. Each pan is charged with 200 lbs. of sodium nitrate and 3 cwts. of lead, which are heated and stirred until all the metal is oxidised. At this stage 50 lbs. of nitre are added and thoroughly stirred in until the mixture is of uniform consistence when 3½ cwts. of lead are gradually added, with constant agitation, the mechanical stirring being supplemented by the use of long-handled rakes employed to "pull out" the mixture of metal and salt from the central and hottest part of the pan. The success of the reduction depends very largely on the skill and experience of the workman, who generally controls two pans, and whose duties are to regulate the firing of the pan and the rate of addition of the metal.

The reaction occurring in the nitrite pan is not so simple as that represented by the equation, $Pb + NaNO_3 = PbO + NaNO_2$, for the higher oxides of lead are also produced both by aërial oxidation and by further reaction with the nitrate. In this connection it should be noted that litharge itself has been suggested as a reducing agent for nitrate, $3PbO + NaNO_3 = NaNO_2 + Pb_3O_4$, although the large proportion of this oxide required would militate against its adoption.

During the reaction a portion of the lead becomes converted into a singularly inert substance of high specific gravity; this product is regarded as a sub-oxide, but may be a passive form of the metal contaminated with higher oxides and sodium plumbite.

The fusions are allowed to run for one-half to three-quarters of an hour after all the lead has been added, when the product, which now has a yellowish brown tint, is tested for nitrite. With careful working the soluble constituent of the melt should contain 90 per cent. or even more of sodium nitrite. When rich in nitrite the cooled melt has on its surface a characteristic crystalline incrustation which is never noticed on

specimens containing a relatively small percentage of the required salt.

Satisfactory results are, however, only obtained when both the lead and nitrate are of good quality. The former should be good commercial lead which has been remelted, skimmed and cast into small bars. The latter should be crystallised Chili saltpetre of the best quality. The presence of sodium iodate is especially harmful, as this salt appears to act catalytically in promoting the destruction of the molten nitrate and nitrite. The appearance of the characteristic violet vapour of iodine arising from the melt shows that inferior nitrate is being employed and in these circumstances the salt should be recrystallised, when the harmful impurities are eliminated.

The reduction being complete, the molten contents of two pans are ladled into 120 gallons of warm water contained in a covered cylindrical washing box fitted with powerful stirrers rotating on a horizontal axis. The curved lid of this box contains two small circular apertures for the introduction of the melt, and within, the soluble nitrite is separated from the litharge by agitating the mixture for one hour and then allowing the precipitate to subside. The clear liquor is then run off into a neutralising tank and here the solution, which is distinctly alkaline, is neutralised with dilute sulphuric acid or, if possible, with the solution obtained by absorbing nitrous fumes in water.*

This neutralisation causes the decomposition of sodium plumbite and the precipitation of a small amount of lead hydroxide. The neutralised liquors are now evaporated in wrought iron pans heated either directly or with internal steam pipes. At 45° Bé. the concentrated solution shows a thin film of nitrite on its surface and is then run off into rectangular cast iron crystallisers and left for at least 12 hours, when the first crop of sodium nitrite crystals is collected, the mother liquors being again concentrated and allowed to crystallise. These crystals, when dried in a centrifugal hydro-extractor and then in an air-oven, should contain 96 per cent. of $NaNO_2$.

The washing of the oxides of lead is repeated, the more dilute washing liquors being flushed off together with the litharge into settling tanks. These liquors are used to lixiviate subsequent melts, whilst the litharge is either dried for sale or mixed with the "sub-oxide" and smelted to lead in a small blast furnace.

As received from the settling tanks the pasty litharge contains varying proportions of the higher oxides of lead. It may, however, be rendered more uniform by conversion into flake litharge or red lead in suitable reverberatory furnaces.

The working up of these large quantities of lead compounds is one of the chief disadvantages of this process, another is the baleful effect of the lead on the workmen, a certain incidence of plumbism being almost unavoidable.

3. *Reduction by non-metals.*—The well-known detonation of charcoal and nitre leads to the formation of a carbonate and only small quantities of nitrite. When brought under control by the addition of caustic soda and lime the reaction between sodium nitrate and graphite has been patented as a process for preparing sodium nitrite (Grossmann, Eng. Pat. 1452 of 1904; and also Knop, Eng. Pat. 4747 of 1897).

A similar process involving the use of sulphur, which has been successfully worked out on a manufacturing scale by Messrs. Read Holliday and Sons, of Huddersfield, is based on the following reaction:—

$$3NaNO_3 + S + 2NaOH = Na_2SO_4 + 3NaNO_2 + H_2O.$$
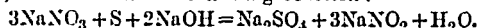
The fusion is carried out in open pans fitted with stirring gear, but of larger capacity than those employed in the lead process. The nitrate containing a portion of the caustic soda (about 1/10th) is melted and treated alternately with sulphur and more molten caustic soda until the nitrate is practically all reduced. The fused product is added while still hot to sufficient warm water to dissolve the whole of the nitrite and only a portion of the sodium sulphate, a large proportion of which is left behind in a granular condition. The liquor is drained

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* These fumes are obtained in such nitric acid oxidation processes as the manufacture of arsenic acid.

through a vacuum filter and evaporated to a smaller bulk when a further portion of sulphate separates and the solution on cooling deposits sodium nitrite while the final mother liquors furnish more Glauber's salt.

This process yields without troublesome by-products a nitrite of good quality, which is obviously quite free from lead, and apart from the separation by fractional crystallisation of the nitrite from the dissolved sulphate, the operations involved present no serious practical difficulties.

Carbon monoxide either pure or in the form of producer gas has no action on molten sodium nitrate but in the presence of fused caustic soda there is an intermediate formation of formate which then reduces the nitrate in the following manner :—

$$NaNO_3 + HCO_2Na + NaOH = NaNO_2 + Na_2CO_3 + H_2O.$$

(Goldschmidt, Eng. Pat. 17066 of 1895.)
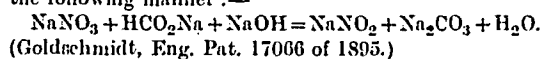
4. *Reduction by metallic sulphides and sulphites.*—Etard formerly recommended sodium sulphite as a reducing agent for sodium nitrate (Bull. Soc. Chim., 1877, **27**, 434), and a modification of his process has recently been patented (D.R.-P. 138,029). The percentage yield of nitrite is excellent but the high proportion of sodium sulphate in the melt—about two-thirds of the total—renders the separation of sodium nitrite somewhat troublesome. Closely allied to this method is the process devised by the firm of Gebrüder Flick, which consists in passing sulphur dioxide over sodium nitrate and calcium hydroxide heated in retorts. The nitrite is then readily separated from the sparingly soluble calcium sulphate.

The commonly occurring sulphides react with fused sodium nitrate, furnishing nitrite. Messrs. McGougan have patented the use of galena which gives a melt containing litharge, sodium nitrite and sulphate with small amount of sodium plumbite (Eng. Pat. 7715 of 1897). I have noticed that stibnite, the fusible sulphide of antimony, very readily reduces the nitrate giving a high percentage of nitrite but the cost of this reducing reagent is prohibitive.

Sodium sulphide and nitrate interact energetically forming a nitrite melt which contains only a relatively small proportion of sodium sulphate. Le Roy has advocated the use of barium sulphide, a mixture of this substance and sodium nitrate being heated in an iron dish when a vigorous reaction sets in and sodium nitrite and barium sulphate result. The intensity of this reduction is moderated by the admixture of barium sulphate (Compt. rend., 1900, **108**, 1251).

## II. *Production of nitrite from nitrous fumes.*

It was shown conclusively by Divers (Trans., 1899, **75**, 85) that pure sodium nitrite could be readily prepared by absorbing nitrous fumes in aqueous sodium carbonate or hydroxide, provided that these gases contain a slight excess of nitric oxide. Excess of nitrogen peroxide would result in the formation of nitrate. Nitric oxide itself was shown by Debray to unite with barium peroxide forming barium nitrite, a similar reaction with the alkali peroxides would lead to sodium and potassium nitrites. Raschig's observation that nitric oxide combines very rapidly with oxygen to form nitrous anhydride whilst the further change of the latter oxide to nitrogen peroxide occurs comparatively slowly suggests a method of utilising atmospheric nitrogen in the production of nitrite. The absorption of the nitrous fumes within a few seconds of their formation in the electric arc is an operation involving considerable practical difficulty, which however has to some extent been overcome by the method recently patented by the Badische Anilin- und Soda- fabrik (Fr. Pat. 363,643 of 1906). According to this patent the nitrous fumes are maintained at a temperature of 300° C. until they are absorbed by an alkaline solution of sodium nitrite from a former operation. A strong solution of this salt is employed in order to reduce as far as possible the vapour pressure of the liquid, and thus minimise the dilution of the hot reacting gases with steam.

According to Eyde (Eng. Pat. 28,613 of 1904) the gases of the electric furnace containing much air when quickly brought into contact with the hydroxides of the alkalis or alkaline earths, yield nitrites

$$2NO + NaOH + O = 2NaNO_2 + H_2O.$$
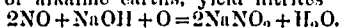
*Electrolytic reduction of nitrates.*—Various attempts have been made to utilise the electric current in the reduction of nitrates to nitrites. Among the most recent are the experiments made by E. Müller and F. Spitzer (Zeit. Elektrochem., 1905, **11**, 509) with cathodes of different metals, the most favourable results being obtained with spongy silver.

*Miscellaneous agents.*—The interaction between barium hydroxide, manganese dioxide and sodium nitrate has been patented by Huggenberg. Zinc and ammonia have been employed by Stahlschmidt. The oxidation of ammonia in the presence of metallic oxides at 650—750° C. leads to the production of " nitrous anhydride " which is absorbed by alkalis (U.S. Pat. 763,491 of 1904). This oxidation of ammonia to nitrite has also been effected electrolytically in aqueous solution in the presence of sodium and cupric hydroxides (Traube and Biltz, Ber., 1904, **37**, 3120).

## III. *Production of nitrite from calcium nitrate.*

As it has been predicted that calcium nitrate will gradually displace the sodium salt as the commercial source of nitre, I have made some experiments on the production of sodium nitrite from calcium nitrate, or from mixtures of this salt with calcium nitrite.

Calcium nitrate melts in its water of crystallisation becomes solid again at higher temperatures and finally fuses. When maintained in a pasty state for some time the anhydrous salt loses oxygen and oxides of nitrogen ; some nitrite is produced but the yield is very small. Reducing agents increase the production of nitrite very considerably and when mixed with sodium sulphide and sulphide the calcium nitrate on heating furnishes a yield of more than 60 per cent. of the calculated amount of sodium nitrite. The object of taking the two reducing agents in these proportions is to ensure the conversion of both sulphur compounds into sparingly soluble calcium sulphate.

i. $2Ca(NO_3)_2 + Na_2S = CaSO_4 + Ca(NO_2)_2 + 2NaNO_2.$

ii. $Ca(NO_3)_2 + 2Na_2SO_3 = CaSO_4 + Na_2SO_4 + 2NaNO_2.$
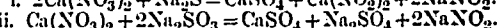
The combined changes may be represented as follows :—

$$3Ca(NO_3)_2 + Na_2S + 2Na_2SO_3 = 6NaNO_2 + 3CaSO_4.$$

By taking the sulphide and sulphite in these proportions the product after lixiviation consists chiefly of very soluble nitrite and sparingly soluble gypsum which are readily separated. The sulphide and sulphite are melted together until their water of crystallisation is driven off and the residue intimately mixed with the calcium nitrate. This mixture is heated until the water contained in the last salt is eliminated. A portion of the dried mixture is then heated strongly until a re-action sets in accompanied by incandescence and the remainder is added sufficiently rapidly to ensure the continuance of this interaction. The greyish white product is lixiviated with warm water, the sulphate removed and the nitrite obtained from the solution.

With a mixture of nitrate and nitrite the sulphide may be omitted as in this case sulphite alone suffices to convert all the calcium into sulphate.

$$Ca(NO_2)_2 + Ca(NO_3)_2 + 2Na_2SO_3 = 4NaNO_2 + 2CaSO_4.$$
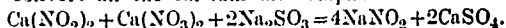
Instead of the sulphide and sulphite, a mixture of sulphur, caustic soda and calcium nitrate may be employed.

$$3Ca(NO_3)_2 + 2S + 6NaOH = 2CaSO_4 + Ca(OH)_2 + 6NaNO_2.$$
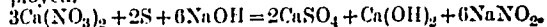
The introduction of carbon dioxide or dilute sulphuric acid into the aqueous solution of the melt ensures the precipitation of the calcium hydroxide in the form of calcium carbonate or sulphate.

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## METANIL YELLOW: ITS USE AS A SELECTIVE INDICATOR.

### BY ERNEST LINDER, B.SC.

In 1906, attention was drawn by Mr. E. G. Ballard to the behaviour of " Dolly Cream "-dye in presence of various acid fumes (43rd Alkali Report, p. 19). He ascertained by direct test in the laboratory that a strip of filter paper stained with the dye and exposed in the dry