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QUANTITATIVE ANALYSIS OF SULPHUROUS ANHYDRIDE IN THE PRESENCE OF NITROUS PRODUCTS AS APPLIED TO THE CONTROL OF LEAD CHAMBERS.

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The method of quantitative analysis of sulphurous anhydride in the presence of nitrous products formed the subject of a paper, presented at the international meetings relative to analyses and experiments (Paris - November 1950).

The method of analysis usually employed for the determination of SO₂ in gases (discoloration of liquor titrated with iodine in a given volume of gas) cannot be applied if the gas contains nitrous products. Nitrogen peroxide reacts, in fact, with the hydroiodic acid formed with liberation of iodine. The buffer solutions, used hitherto, gave no satisfactory results, if gases contained sulphuric acid mist, which usually was the case. Experiments in regard to the control of chambers by this method presented difficulties, the results obtained varying as much as 100%, according to the rate of aspiration, whilst the buffer solutions did not prevent any secondary reactions. The determined content also varied with the analyser. In addition, it was almost impossible to ascertain where the loss in sulphur had occurred in an installation for intensive production (SO₂ or mist) until the method described in the following paragraphs had been employed.

The process consists in the main of eliminating nitrous products in the gases before they get mixed with the iodine solution, by making them pass through a urea solution.

APPLICATION.

I. LEAD CHAMBERS.

The usual technique of controlling lead chambers is based on the colour of the vapours from the Gay Lussac, from which the condition which has to be maintained for a smooth running is deduced, under given exterior conditions (difference in temperature between top and bottom). The vapours between the first and second Gay-Lussac should be neither white nor yellow, but what has been agreed upon as "green".

If this technique gives satisfactory results when working to full capacity or in summer, when the difference between yellow and white is very small, and when any irregularity makes

itself felt very soon, it is inaccurate in the case of a low production, and especially in winter. As a matter of fact, in that case, the difference between yellow (chamber with an excessive quantity of nitrous products - insufficient SO_2 at bottom) and white (chamber with too small a quantity of nitrous products - excessive quantities of SO_2 at bottom) is very great and the colour, which it has been agreed upon to call green, extends over a wide production area. It is very difficult to control the operation of the chambers otherwise than by getting very close to yellow: this is not indicated because the chamber contains excessive quantities and the last sections do not work; they are too cold and nitric acid is produced, which is harmful to the preservation of the apparatus.

The method of analysing SO_2 has made it possible to be completely independent of the colour of the vapours and to determine with accuracy the standard applicable to all cases. In winter and when working at low rate, the vapours between the two Gay-Lussacs are colourless, if not white, and the old technique would lead one to believe that the reaction in the chamber is much too feeble. According to the analysis of SO_2 this is, however, not the case, and the results obtained after one year's experiment make it possible to give the following precise information in the case of a chamber working to capacity:-

Consumption of ammonia per 100 kgs H_2SO_4	-0.16 as against 0.23
General loss in sulphur at works	5% as against 5.3%
Loss in sulphur in the chimney	0.15 as against 0.40%

II. INSTALLATIONS WITH INTENSIVE PRODUCTION: KACHKAROFF.

In an installation with intensive production, such as the Kachkaroff system, it is very difficult to determine the oxidation of SO_2 in any other way than by analysing the gas content.

It is in this instance that the necessity of eliminating nitrous products becomes imperative, if an exact analytical result be desired, in view of the high nitrous nitrogen content of the gases.

Prior to the application of the quantitative analysis with elimination of nitrous products, a Kachkaroff works had a loss in sulphur of 3% in the chimney, and it has been thought that it was caused by the sulphuric mist, because, according to the usual quantitative analysis, practically no SO_2 had been found. Experiments in retaining the mist in petroleum which, in other cases, had always given good results, revealed a very feeble content of acid mist, whilst the analysis of total sulphur by immediate sampling gave a fairly high content.

A systematic study has been undertaken, aiming at the urea method for the quantitative analysis of SO_2 in the presence of nitrous products. It revealed that the loss originates from unoxidised SO_2 . After having carried out the necessary alteration to the installation the loss in sulphur in the chimney was soon reduced to 0.37%.

The content of nitrous products in the residual gases, expressed in terms of N_2O_3 , decreased during the same period from 3.6 grammes per cubic metre to 0.9 grammes per cubic metre, owing to the more favourable ratio NO .

NO_2

In summarising, it may be said that, judging by the results which this method has made possible, the method of quantitative analysis of SO_2 , described below, appears to be suitable for a number of purposes. The relative precision, which can be expected, is of the order of 10%, a precision which the old methods with buffer solutions were far from giving.

MODUS OPERANDI.

A sintered glass scrubber is placed in series in the gas line between the vessel, containing the gases to be analysed and the standard iodine scrubber, used in the Reich method, containing a urea solution in concentrated sulphuric acid (92 or 98%), heated to a temperature of 100° centigrade (about 10 cubic centimetres of urea to 250 cm³ of acid are sufficient for quite a number of analyses). At first about 10 litres of the gas to be analysed are passed through the urea scrubber, in order to obtain the equilibrium of the solution with the SO₂, contained in the gas, then the analysis with the iodine is carried out (generally 5 cc N/10 iodine are used in 300 ccs. of water).

The rate of aspiration should be of the order of 3 to 5 litres/minute to avoid oxidation of SO₂ between the enclosure and the scrubber.

The heating of the urea solution aims at avoiding too great a dissolution of SO₂ in the acid and at obtaining a rapid equilibrium between this solution and the gases. It is possible to do without this heating in the case where the SO₂ content of the gases does not vary greatly with the weather, without, however, going much below the temperature of the gases, so as not to risk oxidation of SO₂ by nitrous products owing to a sudden drop in temperature.

CHECKING THE METHOD.

- (1) It has been verified that the reaction of urea on sulphuric acid does not liberate SO₂.
- (2) It has further been verified that, after mixing with the urea solution, gases, containing up to 35 grammes of nitrogen per cubic metre, (which is much more than the content encountered in chambers, which are of the order of six grammes per cubic metre and, even with the Kachkeroff system, 25 grs per cubic metre) had no action on an iodine solution which previously had only just been coloured by SO₂. A re-colouring of iodine had not been observed, even an hour after the experiment, although the same experiments, conducted without the mixing with urea, resulted in an immediate liberation of the total quantity of discoloured iodine.
- (3) This method has been checked by using a totally different method (very thorough filtration of acid mist and quantitative analysis of SO₂ by absorption in sodium and titration with barium chloride after oxidation with brone) a method which, moreover, is too complicated to be utilised normally in works. The analyses carried out with the same gases by the two processes has never resulted in a difference of more than 10%.

It is understood that this method is only a modification of the Reich method and, consequently, has also all the disadvantages inherent in this method, namely, the necessity of correcting the temperature and pressure in order to evaluate the volume of the drawn-off gases and, on the other hand, a slight inaccuracy, due to a minute quantity of iodine which may be carried away by the gas. It should be noted in addition that, contrary to what may be thought, the fact that the gases are passed through a solution of hot urea has hardly any influence on the temperature of the scrubber and does not cause loss in iodine.