LXX.—*The Estimation of Small Quantities of Nitrogen Peroxide.*

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The following method was worked out primarily for the purpose of following the evolution of nitrogen peroxide in the decomposition of explosives, but is equally applicable to other gaseous mixtures where this gas is present in small proportions.

It is based upon the characteristic absorption spectrum of nitrogen peroxide, which consists of a large number of fine dark lines extending throughout the visible spectrum and a general absorption strongest in the violet and diminishing gradually as it approaches the red end.

It was found that the lines could be distinguished in very dilute mixtures of nitrogen peroxide and carbon dioxide or air, a few of the more prominent groups of lines being still visible at a concentration as low as 0·05 per cent. of nitrogen peroxide. As the proportion of nitrogen peroxide was raised the lines increased in intensity and number, and in mixtures approaching 1 per cent. the violet end of the spectrum was completely absorbed. These differences were sufficiently well marked to enable one to estimate the concentration by comparison with standard mixtures to within 0·02 per cent. in the case of the more dilute mixtures and 0·05 per cent. in the case of the stronger ones.

For the sake of convenience, greater accuracy and the elimination of the personal equation as far as possible, it was decided to make photographic records in cases where quantitative results were desired. For this purpose a series of standard photographs covering a range of concentration of nitrogen peroxide from 0·5 to 1 per cent. was prepared.

Preparation of Standard Photographs.—The spectroscope was a Hilger No. 1 table spectroscope with a single dense flint glass prism. It was provided with a camera attachment, which allowed seven photographs to be taken on a $3\frac{1}{4}''$ by $2\frac{1}{8}''$ plate. The Ilford chromatic plate was found most suitable on account of its fine grain, freedom from fog, and the convenience of being able to use a fairly bright dark-room light.

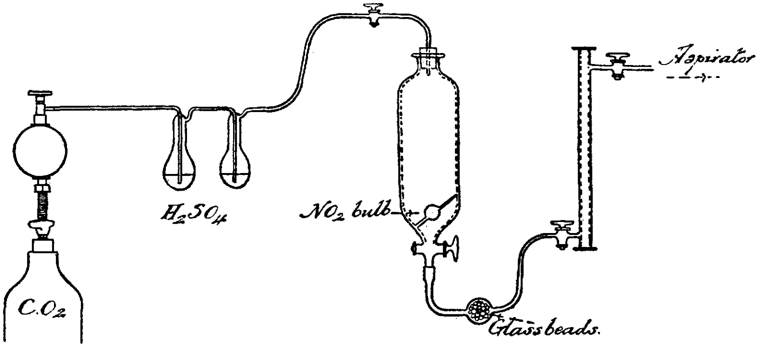
A Welsbach incandescent mantle was used as the source of light.

The vessel for containing the gas under observation was a straight glass tube 40 cm. long with side tubes provided with stopcocks. The ends were closed by glass discs, attached by means of a cement.

Owing to the small volume of the tube and the low concentration of the nitrogen peroxide it was found necessary to make the mixture in a large vessel and then to fill the observation tube. Small glass bulbs of capacity from 0·5 to 12 c.c. with two capillary ends were filled with nitrogen peroxide at atmospheric pressure from a U-tube, in which it had previously been liquefied. In some cases the capillary tubes were quickly sealed with a small blow-pipe flame, and in others simply closed by holding the bulb by the tubes between the fingers before dropping it into the large cylinder which had been filled with dry carbon dioxide.

The bulb was then broken by shaking the cylinder, and when diffusion was complete from one-third to one-half of the gas was aspirated through the observation tube (Fig. 1). A small trap containing glass beads was interposed to prevent pieces of broken glass from the bulb being carried over and deposited on the flat ends of the tube, where they were found to interfere with the passage of light. The stopcocks were then closed and the absorption spectrum of the gas was photographed.

FIG. 1.



Apparatus for preparing standard mixtures of CO_2 *and* NO_2.

The direct light from the mantle was shielded by a screen of thin sheet copper with a circular aperture which allowed the light to pass through the tube to the spectroscope.

The source of light and the slit of the spectroscope were 15 cm. and 1 cm. distant from their respective ends of the tube. The slit was closed down to 0·05 mm., and under these conditions an exposure of forty seconds was sufficient, although as a rule several different exposures were given to allow for slight variations in the negatives with which the standards were to be compared.

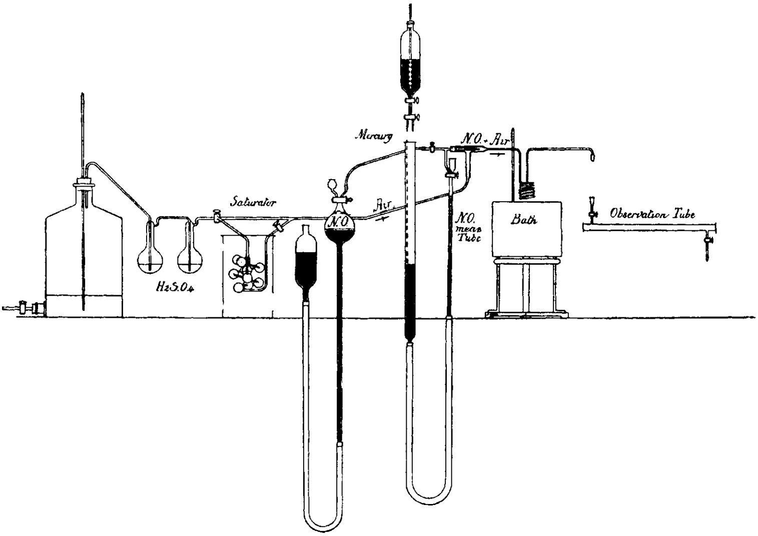
The plates were developed in the Ilford pyro-soda developer, using the full quantity of pyrogallic acid but no potassium bromide.

The composition of the gaseous mixtures used in the preparation of the standard photographs was calculated on the assumption that the nitrogen peroxide would be dissociated into NO_2 at the degree of dilution used in these experiments. The gas was measured at 27°, and its composition was taken to be 80 per cent. of N_2O_4 and 20 per cent. of NO_2 (Deville and Troost, *Jahresb.*, 1867, 177).

Photographs were taken of the mixtures of nitrogen peroxide and carbon dioxide referred to on p. 761, and these photographs are reproduced in Fig. 2 (see plate facing p. 775).

Application to the Estimation of Traces of Nitrogen Peroxide in Air.—In studying the effect of water vapour on nitrogen peroxide in connexion with the decomposition of explosives, an apparatus was devised for the production of mixtures of two gases in definite proportions, which were then passed through a tube and examined with the spectroscope. Advantage was taken of this to prepare a series of mixtures of air with small quantities of nitrogen peroxide. The apparatus used for this purpose is shown in Fig. 3.

FIG. 3.



A slow steady current of nitrogen dioxide was obtained by dropping a very fine stream of mercury into the compensating tube of a gas burette connected to a capillary tube. This slow current of nitrogen dioxide was blown through the capillary tube into a comparatively faster stream of dry air, the rate of which had been measured by passing it through two gas washing bulbs of sulphuric acid. The nitrogen dioxide became oxidised to nitrogen peroxide on coming in contact with the air, and the absorption spectra of the mixtures were photographed, the proportion of nitrogen dioxide present being estimated by comparison with the set of standard photographs of absorption spectra of nitrogen peroxide in carbon dioxide.

Experiment.	Rate of NO c.c. per hour.	Rate of air c.c. per hour.	Concentration of NO_2 in air, calculated from NO used.	Concentration by comparison of photographs with standard photographs of NO_2 in CO_2.
1	3·00	1970	0·0015	0·0013
2	2·40	1020	0·0023	0·0020
3	2·40	690	0·0034	0·0027
4	5·40	1020	0·0052	0·0045
5	4·80	410	0·0114	0·0095

The results given in the preceding table show that the concentrations found by the method described in the present paper agree very fairly with those actually present.

It will be observed that the concentration of nitrogen peroxide as arrived at from the spectroscopic comparison is slightly lower in all cases than that calculated from the proportion of nitrogen dioxide used. This is possibly due to the fact that a distinct interval of time in seconds is required for the formation of nitrogen peroxide in this manner, as is shown by Raschig (*Zeitsch. angew. Chem.*, 1905, **18**, 1281) and Lunge (*ibid.*, 1906, **19**, 861).

An extended trial of the method has proved it to be trustworthy and capable of employment in practically all cases where nitrogen peroxide is present in small quantity, and it has been successfully used in the investigation of the gaseous products of decomposition of explosives.

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