

## A METHOD FOR THE QUANTITATIVE DETERMINATION OF MINUTE AMOUNTS OF PEROXIDES IN ETHER.\*

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The U. S. P. X test for peroxides in ether is a qualitative one which requires that a 10-cc. sample, treated with cadmium-potassium-iodide T.S., must not produce a color within one hour. It will not reveal the presence of small amounts of peroxides. In view of the importance of freedom from peroxides in anesthetic ether, it appeared desirable to develop a quantitative and more sensitive method.

After consideration of various published methods and modifications of the U. S. P. method, by increasing the size of sample, providing a homogeneous solution for reaction rather than two phases and acidification, we reached the conclusion that a modification of the U. S. P. method based on the above points would yield the desired result. Accordingly, the method given below was developed and found, by extended laboratory application, to give satisfactory results. It will reveal and measure ether peroxides in quantities less than 1 part per million.

## METHOD.

Place 100 cc. of the ether under examination in a 250-cc., glass-stoppered flask. In a similar flask, conduct a blank determination, omitting the ether sample. Add 20 cc. of absolute alcohol and mix. Then add a freshly prepared solution of 1 Gm. of cadmium and potassium iodide in 5 cc. of 36% acetic acid. Mix thoroughly and allow to stand in the dark for one hour. Observe the flasks in a good light against a white background, and, if any yellow color is visible titrate with *N*/50 sodium thiosulphate without the use of starch T.S. Toward the end of the titration, stopper the flask and shake vigorously. Before again opening the flask cool under running water. Vigorous shaking is important if one is to avoid passing the end-point, since two layers are sometimes formed during titration.

Calculate results and express them in terms of parts per million of ethyl peroxide, " $(C_2H_5)_2O_2$ ."

Each cc. of *N*/50 sodium thiosulphate is equivalent to 9.008 parts per million ethyl peroxide.

The following precautions must be observed:

Use carbon dioxide free distilled water to prepare the *N*/50 sodium thiosulphate solution.

The solution of cadmium and potassium iodide in 36% acetic acid turns yellow on standing and must, therefore, be prepared just prior to its use.

Should cadmium and potassium iodide be precipitated, add a few drops of water, drop by drop, until it redissolves.

In developing this method, we conducted several series of determinations, varying each factor in turn while keeping the other factors constant. In this way experiment showed, that,

One gram of cadmium and potassium iodide was necessary,

The proper amount of 36% acetic acid was 5 cc.; a lesser amount was insufficient and a greater amount caused low results,

One hour was the minimum time for the complete liberation of iodine,

The effect of atmospheric oxygen was nil, and

Working under nitrogen was, therefore, unnecessary.

Finally, it was shown, by experiment, that the presence of acetaldehyde did not interfere.

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\* Scientific Section, A. P. H. A., Toronto meeting, 1932.

In order to determine the accuracy of the proposed method, we applied it to samples of ether containing varying amounts of ether peroxide. We first developed a high concentration of peroxide in ether by exposing it to sunlight and then aging. This peroxide ether was diluted with different amounts of an almost peroxide-free ether. The mixtures as well as the almost peroxide-free ether and the peroxide ether were then assayed for peroxides by the above method with the results recorded below.

Sample.	Cc. Peroxide-Free Ether.	Cc. Peroxide Ether.	Cc. N/50 Thio.	P. p. m. (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> Found.	P. p. m. (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> Calculated.
I	100	0	0.05	0.5	.....
II	75	25	7.99	71.9	71.4
III	50	50	15.99	144.0	142.8
IV	25	75	23.88	215.1	214.2
V	0	100	31.65	285.1	.....

The figures in the last column are calculated from the proportions of ether used and they agree closely with the results obtained by the proposed method.

The method for the determination of peroxides was also applied to minute amounts of aqueous hydrogen peroxide, as follows:

An approximately 0.03% hydrogen peroxide solution was prepared, and by the U. S. P. X assay method found to contain 0.00031 Gm. hydrogen peroxide per cc. Small amounts of this solution, measured in a micro burette, were then assayed by the proposed method. The results are given in the following table:

Sample.	Cc. 0.03% H <sub>2</sub> O <sub>2</sub> .	Cc. N/50 Thio.	P. p. m. H <sub>2</sub> O <sub>2</sub> Added.	P. p. m. H <sub>2</sub> O <sub>2</sub> Found.
I	0.25	0.240	0.8	0.8
II	0.75	0.610	2.3	2.1
III	1.25	0.985	3.9	3.4
IV	1.75	1.500	5.4	5.1
V	2.25	1.960	6.9	6.7
VI	2.75	2.405	8.5	8.2
VII	0.00	0.000	...	...

Parts per million of hydrogen peroxide as ethyl peroxide are calculated on the basis of a 100-cc. sample. In assaying Samples IV, V and VI, small amounts of glacial acetic acid were added to correct for the decrease in acidity caused by the water introduced with increasing amounts of aqueous hydrogen peroxide. Examining the above results, we find that the largest error in the six assays was one-half of one part per million, while the average error was only one-fourth of one part per million.

#### CONCLUSIONS.

1. A method for the quantitative determination of minute amounts of peroxides in ether has been developed.
2. This method is sensitive and accurate to less than one part per million of ethyl peroxide.
3. It is not affected by acetaldehyde or atmospheric oxygen.

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