# Notes

## Gas chromatographic analysis of hydrogen peroxide solutions*

The usual methods for analysis of $H_2O_2$ solutions are time consuming and require samples of at least 0.1 ml, the more highly concentrated samples requiring weighing because of bubble formation. They are further burdened with interference by organic materials[1]. We report here a rapid ($\sim$ 10 min) method applicable to samples in the $\mu$l range which requires no precise knowledge of the sample size. We have found no inherent limitations to the accuracy and precision of our method other than the normal limitations of gas chromatographic techniques in general.

Sometimes it is desirable to analyze for $H_2O_2$ along with organic materials (*e.g.* products from combustion reactions). We tested our method on mixtures of $H_2O_2$, $H_2O$, $CH_3OH$ and $CH_2O$ to get an idea of its applicability to these systems.

The principle of the method is the quantitative catalytic decomposition of $H_2O_2$ into $H_2O$ and $O_2$ on hot platinum gauze with quantitative analysis of these two products on a gas chromatographic column.

*Apparatus and operating conditions*

A Consolidated Electrodynamics Corporation Type X26-201 gas chromatograph with thermal conductivity detectors and a 6 ft. long $\times$ 1/4 in. diameter column filled with 10 % Carbowax 20M on Haloport F (F and M Scientific Corp.) was used for analysis. A tube 5 in. long $\times$ 1/4 in. diameter between the injection port and the column was filled with tightly rolled platinum gauze (52 mesh, 0.004 in. diameter).

We used a column temperature of 150° (at temperatures much below this $CH_2O$ did not get through to the detector). The catalyst section had to be kept somewhat above 150° with a heating tape. Lower catalyst temperatures permitted some undecomposed $H_2O_2$ to reach the column, giving a distorted $O_2$ peak, when the highest concentrations of $H_2O_2$ (97 %) were used. The He carrier gas flow rate was 100 cc/min.

Several commercial solutions of $H_2O_2$ in $H_2O$, nominally 3, 30 and 97 wt. %, were used to test the method on a range of $H_2O_2$ concentrations. Commercial $CH_2O$ solution (37 % $CH_2O$, 10–15 % $CH_3OH$) was used as a source of $CH_2O$ and $CH_3OH$.

*Procedure and discussion*

(*A*) *$H_2O_2$ solutions in water.* A volume of the solution to be analyzed ranging from 0.5 to 10 $\mu$l was injected into the apparatus and the chromatogram recorded. A 10 $\mu$l syringe was used to inject known volumes of $H_2O$ for calibration. Oxygen for calibration was drawn into a gas syringe from a rubber hose through which $O_2$ was being passed into a shallow beaker of water, corrections being made for ambient temperature and pressure.

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The $H_2O_2$ in the sample was calculated from the $O_2$ found using the following stoichiometry:

$$H_2O_2 \longrightarrow H_2O + {}^1/_2\, O_2 \qquad (1)$$

The amount of $H_2O$ in the solution was calculated by subtracting the amount of $H_2O$ evolved by reaction (1) from the total amount of $H_2O$ indicated by the chromatogram. The ratio $H_2O:O_2$ obtained from the chromatogram unambiguously establishes the $H_2O_2$ concentration without requiring knowledge of the sample size. The sample size is limited only by the sensitivity of the detector for $O_2$. The limit for our instrument was $\sim$ 50 $\mu$g of $H_2O_2$.

To give an idea of the standard deviation to be expected over a range of concentrations, we made consecutive runs using $\sim$ 5 $\mu$l of liquid on shelf samples of nominal 97, 30 and 3 wt. % $H_2O_2$. In analyzing the chromatograms we assumed concentrations were proportional to the product peak height $\times$ peak width at half peak height. We used manual injection. The results are shown in Table I. The true standard deviation for the method should be close to the sample standard deviation for 6 to 8 determinations. Refinements in analysis of chromatograms and injection (*e.g.*, planimetry and automatic injection) should improve the precision to some extent.

TABLE I

GAS CHROMATOGRAPHIC ANALYSIS OF VARIOUS $H_2O_2$–$H_2O$ SOLUTIONS

| | *Stated strength (wt. %)* | | |
|---|---|---|---|
| | *97–98* | *29.0–32.0* | *> 3.0* |
| *Run No.* | *Observed strength (wt. %)* | | |
| 1 | 100.1 | 25.2 | 1.88 |
| 2 | 95.7 | 23.7 | 1.94 |
| 3 | 97.4 | 24.6 | 2.04 |
| 4 | 97.1 | 25.7 | 1.90 |
| 5 | 94.7 | 24.3 | 1.89 |
| 6 | 96.4 | 27.4 | 2.05 |
| 7 | 94.9 | 26.1 | |
| 8 | 99.1 | 26.1 | |
| Average | 96.9 | 25.4 | 1.95 |
| Standard deviation | 1.9 | 1.2 | 0.08 |

(*B*) *Analysis of $H_2O_2$–$H_2O$–$CH_3OH$–$CH_2O$ mixtures.* A few experiments were done to see if $CH_3OH$ and $CH_2O$ would be affected by the decomposition of $H_2O_2$ on the platinum gauze. A few $\mu$l of the $CH_2O$ solution was drawn into the syringe, then a small amount of air to separate the two quantities of liquid to prevent reaction in the syringe, and finally a few $\mu$l of 97 % $H_2O_2$ solution. This sample was injected into the chromatograph and the chromatogram recorded. By comparison with blanks ($H_2O$ in place of $H_2O_2$) no consumption of the $CH_3OH$ was evident, but the $CH_2O$ peak was diminished by $\sim$ 30 %.

*Conclusions*

We propose the above method as a general one for analysis of $H_2O_2$ solutions,

especially when rapid analysis is desired or small samples must be used. Methanol can be analyzed simultaneously with $H_2O_2$ by this method, but some interference between $CH_2O$ and $H_2O_2$ is noted.

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1 W. C. SCHUMB, C. N. SATTERFIELD AND R. L. WENTWORTH, *Hydrogen Peroxide*, Reinhold, New York, 1955.

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## Errors in peak areas due to irregular travel of recorder charts

In quantitative gas–liquid chromatography (GLC) where concentrations are determined from peak areas it is widely appreciated that a detector–amplifier–recorder system with a linear response is required to give meaningful peak heights, and various methods for the determination of the linearity have been proposed. It is usually tacitly assumed that the rate of chart movement, on which depends the peak width, is perfectly regular, but it has been found that serious short-term variations in the rate of travel can occur with some recorders. AAKER[1] has discussed other aspects of recorder performance.

During precise determinations of detector response factors it was observed that the repeatability of the results was governed by the peak widths in successive chromatograms and that there were variations in width that could not be attributed to the operation of the column but rather to the recorder. The regularity of the chart movements of seven potentiometric recorders was investigated by applying to them a signal pulse from an electronic timer at regular intervals and measuring the distances between consecutive pulses on the charts with a travelling microscope. The charts were run at or near maximum speed to minimise measurement errors. A pulse interval of 15 sec was taken as being comparable with peak elution times in many applications. The pulse interval was derived ultimately from mains frequency but as a check on the regularity it was arranged that the pulses applied to the recorder also interrupted a steady signal supplied to a digital integrator and initiated the print-out mechanism so that a digital measure of the interval was obtained.

The results shown in Table I include the mean pulse intervals as measured on the charts and by the integrator, together with the ranges and standard deviations of both measurements. It may be seen that with recorders 1 to 5 there was considerably more variation in the intervals on the chart than on the integrator, indicating