# Colorimetric Determination of Peroxide Value with Potassium Iodide-Silica Gel Reagent

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## ABSTRACT

A micro-determination of peroxide value is proposed. The iodine liberated from potassium iodide-silica gel reagent with peroxides in the oil was complexed with starch in 0.01 N hydrochloric acid. The blue color was then measured colorimetrically at 560 nm.

## INTRODUCTION

Peroxide value (POV) is usually determined by volumetric analysis of the iodine liberated from potassium iodide by oxidation with peroxides at room temperature in acetic acid-chloroform medium (1). Colorimetric methods have been reported for micro-determination. Eskin and Frankel (2) presented a method based on the complex formation of titanium and lipid hydroperoxides present in the oil. The colored complex was measured spectrophotometrically at 415 nm. Takagi et al. (3) reported an improvement of the Swoboda and Lea method which depends on the formation of a colored complex of iodine ion with cadmium ion.

In our previous papers (4-6), a POV test paper was proposed as a simplified test for the determination of peroxide in oils. The test paper consisted of a potassium iodide-starch-silica gel sheet. Silica gel is considered to be Lewis acid. Therefore, hydroperoxides can react with potassium iodide without adding any acid, and iodine is liberated. When the test paper is placed in water after contact with deteriorated oil, a blue color developes.

Based upon the same principle, the micro-determination of POV is presented in this paper.

## MATERIALS AND METHODS

### Reagents

1. KI-silica gel reagent. About 100 g of silica gel (Merck silica gel No. 60 for column chromatography, 70-230 mesh) is put into 100 ml of 10% potassium iodide solutions. After filtration, the wet silica gel is dried in a clean air stream. The dried silica gel is further dried for 30 min in an oven at 110 C. It is necessary to keep KI-silica gel reagent in a dark place.
2. Hexane.
3. 50% Ethyl alcohol.
4. 0.01 N hydrochloric acid.
5. 1% Starch solution containing 20% sodium chloride.

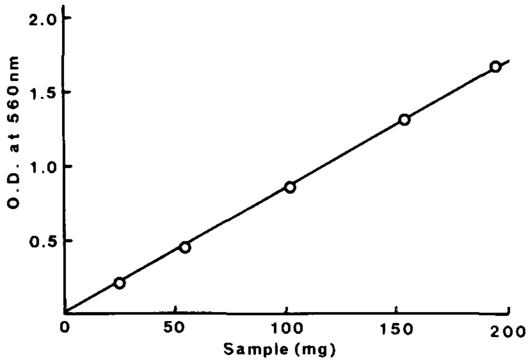

FIG. 1. Relationship between absorbance and sample size. Sample was autoxidized soybean oil, POV = 18.5.

### Procedures

1. Sample (less than 200 mg) is weighed in a test tube, and 1 ml of hexane is added.
2. KI-silica gel reagent (1.5 g) is added and shaken. The test tube is incubated for 5 min at 30 C in a dry-block heater.
3. 50% Ethyl alcohol (2 ml) is added and shaken vigorously.
4. 0.01 N hydrochloric acid (15 ml) and 0.5 ml of starch solution are added and shaken vigorously.
5. The solution is transferred to a centrifuge tube and centrifuged for 3 min at 3,000 rpm.
6. The optical density at 560 nm is read.
7. A blank test is necessary.

### Calibration

A calibration curve is obtained by using known POV samples which have been determined by the standard titrimetric method (7).

## RESULTS AND DISCUSSION

The principle of this method is the same as the routine method (1,7) which depends on the reaction of potassium iodide in an acid solution with peroxides followed by titration of the liberated iodine with sodium thiosulfate. In this case, however, titration was replaced by colorimetry.

An example of the relationship between absorbance and sample size is shown in Figure 1. A linear relationship between the absorbance and sample size is observed for 20 to 200 mg oil. The upper limit of POV is ca. 200 when 20 mg of sample is used. A larger POV sample must be diluted with nonoxidized oil before this method can be applied. When sampling by volume is allowed, depending on the kind of experiment, the sample can be diluted with hexane.

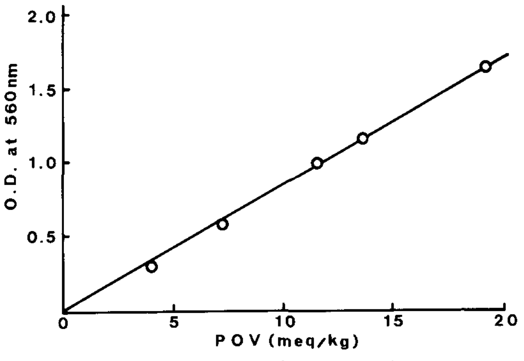

FIG. 2. Relationship between absorbance and different POV samples. Samples were autoxidized soybean oil with POV determined titrimetrically. Amount of each sample was 200 mg. From this data, the optical density per mole active oxygen contained in one tube was calculated to be 0.425.

A good linear relationship was obtained between the color intensities and changes of POV which were determined by the standard titrimetric method as shown in Figure 2. This figure corresponds to the calibration curve. In this case, the POV of the sample can be calculated by the following equation.

$$\text{POV (meq/kg)} = \text{OD}/0.425 \times 1/\text{sample weight (g)}$$

To determine the calibration curve, one sample having 15-20 of POV is selected, and the optical density using a 200 mg sample is obtained. A line is then drawn between this point and the origin.

The scale of this experiment can be enlarged or reduced. However, the ratio of the amount of hexane, KI-silica gel reagent, 50% ethyl alcohol, 0.01 N hydrochloric acid, and starch solution should be kept constant. The concentration of alcohol influences the tone of the color developed. A large amount of the sample also influences the color tone. Therefore, it is necessary to draw the calibration curve with known POV samples which have been determined by the standard titrimetric method (7).

From a larger scale experiment, it was confirmed that the reaction of KI-silica gel reagent and hydroperoxides is completed by titrating the colored mixture containing silica gel with a standard thiosulfate solution. The only problem is that not all the liberated iodine moves to the solution when the extract solution used is limited. An equilibrium of the distribution of iodine between the solution and silica gel seems to be established. There are strict linear relationships between color intensities and sample size (Fig. 1) and also between optical densities and POV (Fig. 2). Therefore, this method seems practical. There is rather good reproducibility of the results.

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