A Coulometric Method for the Determination of Low Peroxide Values of Fats and Oils

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ABSTRACT

The AOCS official method for the determination of peroxide values of fats and oils has been modified to perform more precise analyses, especially in the range of extremely low values (peroxide value < 1). In the newly developed method presented here, the final titrimetric step of an iodometric method has been replaced by an electrochemical technique, based upon coulometric reduction of the iodine at an electrode maintained at a controlled potential. Using this method peroxide values down to 0.06 were determined with reasonable precision. Finally, the influence of different parameters on the peroxide value obtained was investigated.

INTRODUCTION

Under the influence of air, unsaturated lipids are oxidized to give peroxides and other degradation products. This oxidative rancidity is believed to occur by a free radical mechanism, and it has been shown that organic peroxy compounds with a range of reactivity are produced (1). As the precise composition of organic peroxides often is not known, the peroxide content of fats and oils frequently is expressed as the peroxide value (PV). This indicates the ability of oxidation products of the sample to liberate iodine from potassium iodide and is expressed in terms of milliequivalents of peroxide/1000 g sample.

PV obtained by iodometric methods do not represent absolute values. They have no significance, unless the method used for their determination is given. The methods used are highly empirical, and any variation in procedure may cause variations in the results. Thus, to obtain reproducible results it is necessary to control the temperature, the sample wt, the amount of reagents, and the time of contact (2).

For routine laboratory use, standard methods for the determination of PV of fats and oils have been developed. One of these is the AOCS official method (3), which is a frequently used iodometric method, using acetic acid-chloroform as a solvent. Investigating this method, it was found to fail for low PV because of difficulties in the titration end point determination. To improve this standard method, a modified final step was developed. As the main reaction procedure was not changed, comparable results could be expected.

This paper, thus, describes a sensitive coulometric method based upon iodometry for precise determination of PV. The reaction procedure is carried out in an electrochemical cell, and the iodine produced is reduced at a rotating platinum electrode, maintained at a constant potential. By electronic integration of the current, a quantitative result is obtained. PV ranging from 0.06-20 have, thus, been determined with appreciable precision in 9-15 min. Furthermore, this precise method was perfectly suited for a careful study of the influence of different parameters upon the resulting PV.

EXPERIMENTAL PROCEDURES

Coulometric Equipment

The electrochemical cell used has been described earlier for use in coulometric microdetermination of hydrogen peroxide (4) and organic peroxides of different reactivities (5). The sample compartment, provided with a glass jacket for circulation of thermostated water, is separated from the auxiliary compartment by two clay filters with a connecting chamber in between. The electrode system consists of three units: a rotating platinum gauze working electrode located in the sample compartment, a saturated calomel reference electrode close to the working electrode, and a spiralized Pt-wire counter electrode in the auxiliary compartment. The electronic circuitry contains a potentiostat for control of the working electrode potential and an integrator for electronic integration of the current. The digital read-out of the integrator is, thus, a measure of the number of coulombs consumed in the cell reaction.

Reagents

All solutions were prepared from analytical reagent grade chemicals and deionized freshly distilled water. Reagents used agreed with the AOCS method. For the coulometric method a 2M aqueous solution of sodium perchlorate was prepared in addition. Nitrogen (purity

TABLE I

Comparison between Titrimetric and Coulometric Determination of Peroxide Value

Sample	Titrimetric determination PV[a]	PV	Coulometric determination No. of determinations	Standard deviation, %
Soybean oil, deodorized[b]	0	0.060	7	7.7
Soybean oil, deodorized[b]	0	0.110	7	5.1
Soybean oil, deodorized[b]	0.35- 0.45	0.309	5	3.8
Cooking fat, fresh	0.40- 0.50	0.369	3	2.7
Corn oil	0.43- 0.49	0.441	4	1.0
Soybean oil, bleached	0.55- 0.65	0.563	5	1.5
Rapeseed oil	0.80- 0.90	0.830	3	1.3
Soybean oil, phosphoric acid treated	2.06- 2.16	1.885	5	0.44
Soybean oil, neutralized	3.78- 3.88	3.297	6	0.35
Rapeseed oil	3.61- 3.71	3.574	5	0.29
Soybean oil, raw	3.98- 4.08	3.842	5	0.39
Peanut oil	12.30-12.40	11.40	5	0.38
Rapeseed oil	14.53-14.63	13.30	4	0.27

[a] Mean value of two determinations. The range indicates a sliding indicator change. PV = peroxide value.
[b] Analysis of the same oil sample within a month.

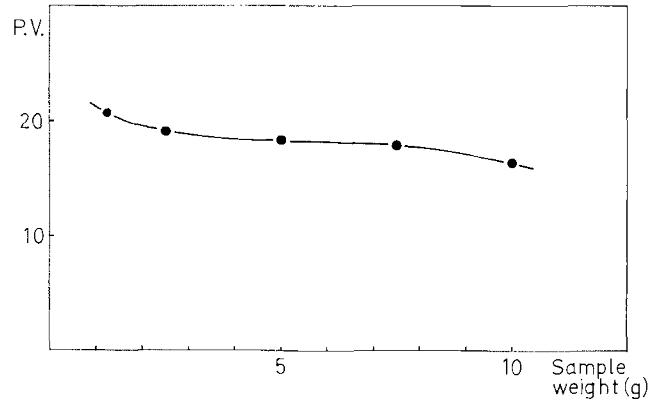

FIG. 1. Effect of sample wt upon the peroxide value.

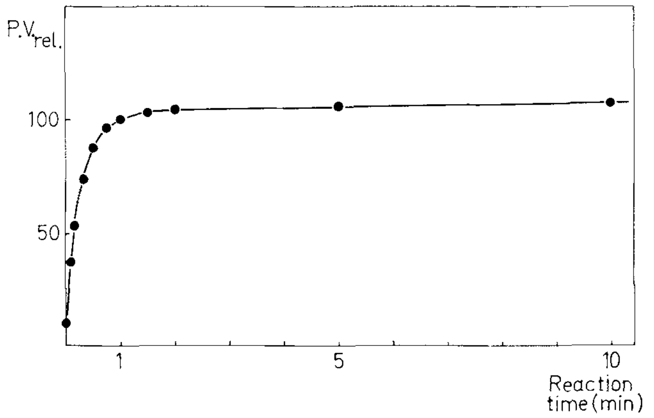

FIG. 2. Effect of time of reaction upon the relative peroxide value. ($PV_{rel} = \frac{P.V._t}{P.V._{1\ min}} \times 100$)

>99.9%; passed over copper at 500 C) was used as a sweep gas. Samples of fats and oils were stored in dark bottles in a refrigerator.

Titrimetric Determination

The AOCS official method was used.

Coulometric Determination

The connecting chamber and auxiliary compartment of the cell were filled with sodium perchlorate supporting electrolyte. Nitrogen continuously was passed through the sample compartment for deaeration. According to the size of the sample compartment (~ 30 ml) it was found convenient to scale down the proportions of the standard AOCS method three times. Thus, the following sequence of operations was used, in close analogy with the titrimetric method: (A) Introduce 1.667 ± 0.017 g sample into the sample compartment of the cell by means of an all glass syringe, weighing the syringe before and after injection. (B) Add 10 ml solvent mixture and mix by means of the rotating working electrode until the sample is dissolved. (C) Add 0.167 ml saturated potassium iodide and mix for exactly 1 min. (D) Add 10 ml 2M aqueous sodium perchlorate solution. (E) Reduce the iodine produced. Read the integrator and timer when the current has reached its residual value (<10 μA). (F) Conduct a blank determination of the reagents.

The integrator reading obtained was converted into PV as follows:

$$PV = \frac{A \cdot U_c \cdot 1000}{F \cdot M}$$

where A = calibration factor for integrator (in this case 0.49750 coulombs/volt), F = Faraday constant (96487 coulombs/mol), U_c = integrator read-out (mV), corrected for blank, and M = wt of sample (g).

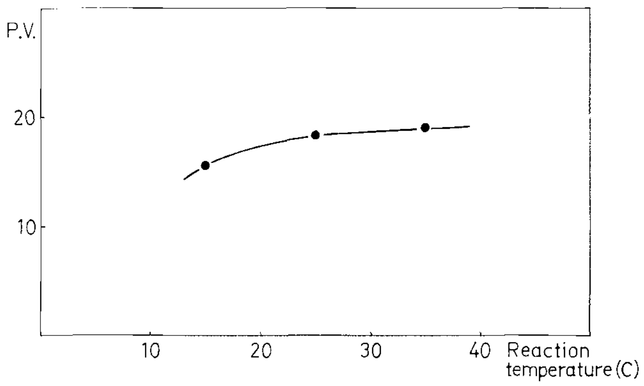

FIG. 3. Effect of reaction temperature upon the peroxide value.

RESULTS AND DISCUSSION

The results from titrimetric and coulometric determination of PV of some different samples are shown in Table I. To obtain a high precision, it was found necessary to deaerate all solutions used; it has been stated (6) that contamination of oxygen is a great source of error, since reaction of peroxide with iodide produces radicals, forming more peroxide under the influence of oxygen. This explains the higher PV obtained by the titrimetric method, where no deaeration is recommended. Furthermore, the blank value of the reagents decreased when deaerated from a value corresponding to PV ~0.06 to PV ~0.03, which is of advantage for the determination of low PV. Finally, the continuous deaeration of the whole reaction mixture resulted in a decrease of the residual current when reducing the iodine produced, since oxygen also is being reduced at the potential used (0 mV vs. the saturated calomel reference electrode). The water added to stop the reaction contained a supporting electrolyte ($NaClO_4$) to reduce the cell resistance to a reasonable level, thereby giving a short reduction time.

As stated earlier, the methods used for the determination of PV are highly empirical, and any change in procedure is reflected in the result. Therefore, an investigation of the influence of five different parameters was performed, i.e. sample wt, amount of potassium iodide, time of reaction, amount of water, and reaction temperature. In all experiments the volume of organic phase was unchanged (10 ml), and, when studying the effect of sample wt, the relation between sample wt and potassium iodide was kept constant (10:1). The results from this investigation using the coulometric method are shown in Figures 1-3, where the PV stated are mean values of three determinations. In Figure 1 the experimental wt have been multiplied by three to facilitate direct comparison with the official AOCS method. Negligible effect upon the PV was observed when varying the amount of potassium iodide and water from half to twice the standard amounts. Thus, it is evident that the three most critical parameters are sample wt, time of reaction, and reaction temperature. This motivates, e.g. that the reaction cell is thermostated, since the temperature dependance is rather high around 25 C.

The coulometric method described here is perfectly suited for the determination of low PV and also can be used for high values when improved precision is required.

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