ANALYTICAL STUDIES CONCERNED WITH THE REACTIONS BETWEEN ORGANIC PEROXIDES AND THIO-ETHERS

I. ANALYSIS OF ORGANIC PEROXIDES

by

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INTRODUCTION

The need for an accurate and precise analytical method for hydroperoxides became evident in these laboratories during chemical and kinetic investigations into the behaviour of such peroxides in the presence of certain organic sulphur compounds.

Methods for the analysis of organic peroxides fall broadly into two main groups. One group comprises procedures based upon the oxidation of ferrous iron, the ferric iron so produced being estimated colorimetrically[1, 2, 3, 4] or volumetrically[5, 6]. Alternatively, the excess ferrous iron may be determined[7, 8]. Such methods have been developed chiefly for the estimation of peroxidic compounds in media such as rubber, fats, edible oils and petroleum products, and their standardisation against peroxides of known purity has been only on a limited scale. YOUNG, VOGT, AND NIEUWLAND[1] reported accurate analyses of hydrogen peroxide and disuccinyl peroxide by their colorimetric technique and a slight modification of this method by BOLLAND, SUNDRALINGAM, SUTTON, AND TRISTRAM[3] gave similar results. ROBEY AND WIESE[4] obtained satisfactory accuracy using benzoyl peroxide and *tert.*-butyl hydroperoxide as standards. It has been shown[8, 9], however, that the values obtained by the ferrous method are reduced considerably when the determination is carried out anaerobically. LAITINEN AND NELSON[8] reported values of 228 and 118 % for the estimation of *tert.*-butyl hydroperoxide in the presence and absence of air and demonstrated that, under similar conditions, the method of ROBEY AND WIESE[4] gave 190 and 24 % respectively. WAGNER, CLEVER, AND PETERS[9], in the course of a thorough study of the colorimetric ferrous techniques, found the method of BOLLAND *et al.*[3], to give reasonably accurate results when applied to pure tetralin and *tert.*-butyl hydroperoxides in air, but 4-63 % of the theoretical in nitrogen. The authors concluded that the peroxide could be destroyed by both reduction and decomposition, the latter becoming appreciable in the absence of oxygen. KOLTHOFF AND MEDALIA[10] reached similar conclusions about the reaction between ferrous iron and cumene hydroperoxide. In the absence of oxygen, molar reaction ratios considerably less than the stoichiometric value of 2 were found, indicating induced decomposition of the peroxide. In the presence of oxygen, molar ratios greater than the stoichiometric indicated that an induced oxygen oxidation of ferrous iron occurs during the reaction.

Considered as a whole, the evidence it makes clear that, owing to their non-stoichiometry, the ferrous methods are unreliable in an absolute sense and warrant practical application only when carried out under carefully standardised conditions.

The second main group of peroxide analytical methods utilises the oxidation of hydriodic acid or iodide ion. Again a critical survey of the published techniques, which differ in their choice of solvent, sample size, temperature and the use of aerobic or anaerobic conditions, is rendered difficult by the fact that few have been standardised against pure peroxides. However, reasonably accurate results have been reported for benzoyl peroxide[11, 12, 13, 14, 15, 16] and for tetralin and *tert.*-butyl hydroperoxides[12]. Several workers have analysed various media peroxidised to unknown extents[17, 18, 19, 20, 21, 22, 23, 24], and compared the results in some cases[3, 25, 26] with those obtained by ferrous methods. In general, the iodometric techniques have been considered to yield the more nearly theoretical results.

Two sources of error have been recognised. First is the possible addition of iodine to olefinic double bonds[12, 27], and the marked dependence of the results on sample size[18, 20, 26, 28] is perhaps attributable to this cause. This error can be minimised by reducing the sample size so that no more than 10^{-5} moles of iodine are liberated[29] but attempts to eliminate it altogether by estimating the potassium iodide decomposed rather than the iodine liberated have met with only partial success[27, 30].

The effect of oxygen, although not so marked as in the ferrous determination, is still important. The factor between aerobic and anaerobic determinations was reported as 1.1-1.5 by LEA[26] for peroxidised fats and 1.2 by SKELLON AND WILLS[11] for benzoyl peroxide. In the latter case, the anaerobic results were the theoretical whereas KOKATNUR AND JELLING[14] and NOZAKI[13], using the same peroxide, found correct results under aerobic conditions. The use of an inert atmosphere has been standardised in several methods[11, 15, 19, 20, 26], the assumption being that more accurate results would obtain. Using a modified form of the DASTUR-LEA method[27], we have demonstrated its sensitivity to traces of oxygen. The use of a nitrogen atmosphere in the estimation of cyclohexene hydroperoxide gave approximately correct results but the rigorous exclusion of oxygen reduced these by 20 %. Under normal aerobic conditions, values higher than theoretical by 14, 26 and 47 % have been obtained for cyclohexene, tetralin and 1-methylcyclohexene hydroperoxides respectively. Although these results, as in the ferrous methods, obviously throw doubt on the stoichiometry of the basic reaction, it appears that fair accuracy and precision can be obtained under suitable conditions. Thus WAGNER *et al.*[12] carried out the estimation in an inert atmosphere in boiling, anhydrous *iso*propanol and reported an absolute accuracy of 2-4 %.

Several other methods of peroxide estimation have been reported including those based on the oxidation of sodium bisulphite[31], arsenious acid and stannous chloride. We have applied the first of these to cyclohexene hydroperoxide with no quantitative success. Similar application of the arsenious acid method, under the conditions described by SIGGIA for benzoyl peroxide[32], has proved satisfactory although the wider usefulness of this method is limited by the discrepancies introduced when solvents other than alcohol are employed.

The remaining method has received comparatively little attention despite its possible advantages. VON PECHMAN AND VANINO[33] reduced phthalyl peroxide with excess stannous chloride, back-titrated with iodine and obtained an estimation correct to 3%. The method has also been used in determinations of amylene peroxide[34] and peroxides in ethereal oils[35]. In a similar manner, STEPHENS[36] succeeded in estimating about 80 % of cyclohexene hydroperoxide. The method was examined in more detail by HOCK AND SCHRADER[37], who applied it to tetralin and cyclohexene hydroperoxides and peroxides in fuel oils. The reduction was carried out at 95° and the excess stannous chloride, in 6*N* hydrochloric acid, back-titrated with ferric chloride solution. Estimations of the order 95-97 % of theory were obtained. Later KOCH AND POHL[38], in a review of this method, reported a precision of only ± 15 % in analyses of peroxidised fuel oils and an absolute accuracy of 85-95 % with tetralin hydroperoxide. SCHILDWÄCHTER[39] obtained similar results on several standard peroxides but recorded the non-reduction of benzoyl peroxide.

One point of note concerned with the work of HOCK AND SCHRADER[37] is the analogy these authors drew between the low titrations of stannous chloride observed in the presence of ethyl alcohol and the low peroxide estimations found in the unavoidable presence of alcohol formed during the reduction of the peroxide. Since the method actually involves back-titration of stannous chloride, such analogy is of course fallacious, and the low results cannot be attributed to any such 'alcohol error'.

As indicated earlier, the objective of the present work was to establish an accurate and precise estimation technique for peroxides, applicable especially in the presence of organic sulphur compounds. The elimination of the ferrous and iodometric methods on the respective grounds of inaccuracy and interference by sulphur compounds left the stannous chloride method as the most promising alternative. We have carried out a full investigation of this method and as detailed below, have found it to be highly satisfactory under the proper conditions.

EXPERIMENTAL

Analytical Solutions

1. Approximately 0.1 *N* stannous chloride solution was prepared by dissolving $SnCl_2.2H_2O$ (11.3 g) and hydrochloric acid s.g. 1.18 (75 ml) in distilled water (925 ml) freed from dissolved oxygen. The solution was stored under nitrogen and was dispensed accurately by means of a simple but effective device, suggested to us by Dr W. T. CHAMBERS, in which the sampling pipette fitted loosely into a hole bored in the rubber stopper of the storage vessel and was filled by the application of nitrogen pressure. The stock solution remained unchanged for many months.
2. Ferric alum solution. Ferric alum (200 g) was dissolved in distilled water (1l) containing concentrated sulphuric acid (60 ml).
3. 0.05 *N* potassium dichromate solution was made up from weighed quantities of the pure substance.
4. Phosphoric acid solution was prepared by the solution of ortho-phosphoric acid (75 ml) and concentrated sulphuric acid (75 ml) in distilled water (350 ml).
5. The indicator was an 0.25 % solution of diphenylamine sulphonic acid in water.

All the reagents used were of AnalaR grade. Potassium dichromate was further purified by twice recrystallising from water and drying at 130°.

Solvents. Acetic acid and benzene were of AnalaR purity. *tert.*-Butanol was purified by fractional distillation up a FENSKE-type column (approx. 10 plates). All solvents were thoroughly outgassed with nitrogen before use. The nitrogen was of 'oxygen-free' standard and further purified by passage through FIESER's solution[40] and a drying train.

Sources of peroxides

1. Benzoyl peroxide — a commercial sample was purified by repeated precipitation from chloroform with methanol and dried *in vacuo*.
2. *tert.*-Butyl hydroperoxide — a commercial sample was purified by precipitation of the sodium salt and the regenerated peroxide fractionated up a FENSKE-type column. The middle fraction was refractionated (b.p. 34.2°/17 mm) and further purified by repeated fractional crystallisation. It then had m.p. 3.5-3.8°.
3. Tetralin hydroperoxide was prepared from pure tetralin by the method of NUSSLE, PERKINS, AND TOENNIES[41]. After five recrystallisations from petroleum ether (b.p. 40°) containing ethyl acetate (5%) it had m.p. 55.3-55.7°.
4. Hydrogen peroxide — a 100 vol. sample was diluted to approximately 0.1 *N* and standardised iodometrically.

5. Cumene hydroperoxide — a sample kindly supplied by Professor M. S. KHARASCH, University of Chicago, via Dr H. P. KOCH, had b.p. 65°/0.18 mm. n_D^{20} 1.5237. (Found: C, 71.3; H, 7.95. Calc. for $C_9H_{12}O_2$: C, 71.1; H, 7.90 %).

6. Cyclohexene hydroperoxide— highly purified cyclohexene (b.p. 82.7°/755 mm), free from peroxide and conjugated diene, was shaken in oxygen at 760 mm pressure at 55° for 24 hours when about 0.5 % extent of oxygen by weight had been absorbed. The cyclohexene was removed under reduced pressure and the residue molecularly distilled at 20°/10^{-4} mm on to a condenser at 0°. The product then had n_D^{20} 1.4896 and a purity estimated by the method described in this paper of 94 %. (Found: C, 63.05; H, 8.8. Calc. for $C_6H_{10}O_2$: C, 63.20; H, 8.8 %). The use of chemical methods for further purification was prevented by the sensitivity of the peroxide to both acid and alkali and chromatographic methods using silica gel as adsorbent were ineffective. Some of the impurities were removed by repeated steam distillation at 20 mm pressure, the residual peroxide being fractionally distilled (b.p. 35°/10^{-2}mm) after each operation. The increasing difficulty of purification and the losses involved limited the final purity obtained in this way to 97 % (estimated as before). The product had an elemental analysis of C, 63.2; H, 8.8 %. The peroxide was found to be stable under these experimental conditions and could be stored without change for long periods in pyrex tubes at -10°.

It is of interest to note here that samples prepared by photochemical oxidation of cyclohexene to the same extent and isolated by molecular distillation as described above, were much less pure (82-85 % based on stannous chloride estimation; C, 64.6; H, 9.0 %) and repeated fractional distillation gave a limiting purity of approximately 90 %.

Recommended Procedure

The sample containing 0.75-1.0 milliequivalents of peroxide is dissolved in acetic acid (10 ml) in a 250 ml Erlenmeyer flask which is then evacuated to 20 mm and filled with nitrogen. 15 ml of 0.1 *N* stannous chloride solution are added from a pipette and the flask immediately re-evacuated and filled with nitrogen, this latter procedure being twice repeated. After leaving for one hour at room temperature, a boiling solution consisting of 5 ml stock ferric solution, 1 g ammonium chloride and 45 ml water is added. The mixture is kept at 75° for 30 seconds, rapidly cooled and 10 ml phosphoric acid solution added. The ferrous iron is titrated with 0.05 *N* potassium dichromate solution using 6 drops of indicator solution, the end point being a sharp transition from green to violet. Blank determinations are carried out in a similar manner.

$$\%\ \text{peroxide estimated} = \frac{(\text{Blank - titre}) \cdot \text{dichromate normality} \cdot \text{Mol.Wt. of peroxide} \cdot 100}{2000 \cdot \text{sample weight}}$$

References p. 487/488.

Under these conditions the method has been shown to yield theoretical results by standardisation against several peroxides. The precision obtainable is shown in Table I. The same order of precision has been found in many routine analyses on autoxidised olefins and excellent correlation obtained between the hydroperoxide estimated and that calculated from the oxygen absorbed. In common with the ferrous and iodometric techniques, the stannous chloride method cannot be used to estimate dialkyl peroxides, no reduction of di-*tert.*-butyl peroxide being observed either at room temperature or at 80°.

TABLE I

STANDARDISATION OF THE STANNOUS CHLORIDE METHOD

Peroxide	% estimated {mean of 5 determinations}	Standard Deviation
tert.-Butyl hydroperoxide	99.9	0.30
Cumene hydroperoxide	99.0	0.40
Tetralin hydroperoxide	99.4	0.25
Hydrogen peroxide	100.3	0.25
Benzoyl peroxide*	99.7	0.50
Cyclohexene hydroperoxide	96.7	0.30

* determination carried out at 80° as reduction incomplete after 1 hour at room temperature.

DISCUSSION OF THE METHOD

The development of the standard procedure and the effect of variations in the experimental conditions are conveniently summarised point by point.

1. *The estimation of excess stannous chloride*

The methods previously used for this estimation have been titration with ferric or iodine solutions. Both involve the necessity of titrating in an inert atmosphere and the latter is not suitable in the presence of organic sulphur compounds. We have adopted a standard analytical procedure of adding excess ferric and titrating the resulting ferrous iron with potassium dichromate solution. To ensure complete stannous - ferric reaction at the particular acidities involved ammonium chloride as catalyst[48] and a minimum standing time of 30 seconds at 75° have been found necessary.

Blank determinations, carried out as under the recommended procedure, were found precise to ± 0.10 ml and accurate to within 0.10 ml of the stannous chloride titre when standardised directly. In practice the mean of several blanks for any given solvent was used with occasional control determinations.

2. *Reaction time*

The reaction between stannous chloride and the hydroperoxides examined is rapid in homogeneous solution at room temperature, being complete in all cases after 30 minutes. Further increase in the reaction time did not alter the results obtained as illustrated for a typical peroxide in Table II. The reduction of benzoyl peroxide, a typical acyl peroxide, was found to proceed appreciably more slowly but was complete after 30 minutes at 80°.

TABLE II

INFLUENCE OF REACTION TIME ON THE ESTIMATION OF *tert.*-BUTYL HYDROPEROXIDE IN ACETIC ACID

Reaction time	% estimated
0.5 hours at room temp.	99.7
1.0 ,, ,, ,, ,,	99.9
4.0 ,, ,, ,, ,,	99.7
6.0 ,, ,, ,, ,,	100.0

3. *Effect of acidity*

Owing to the extreme sensitivity of many organic hydroperoxides to mineral acids the optimum acidity at which to carry out the reduction was determined using cyclohexene hydroperoxide as a typical example. This peroxide in aqueous acetic acid solution, 0.5 N with respect to hydrochloric acid, was completely decomposed in a few minutes. However, as shown in Table III, no significant change was observed in the values estimated when the peroxide was reduced in solutions varying from 0.2N in hydrochloric acid. The recommended final acidity, 0.5N, is considered to leave a sufficient margin of safety for all peroxides.

TABLE III

EFFECT OF ACIDITY ON THE ESTIMATION OF CYCLOHEXENE HYDROPEROXIDE (93.5 % PURE) IN ACETIC ACID

Normality of reaction mixture with respect to mineral acid	% estimated
0	93.5
0.36	93.7
1.0	93.5
1.5	93.7
2.0	92.9
3.0	92.1
4.0	90.5

4. *Solvent*

An ideal solvent should have the following properties: — (a) water-miscibility to give a homogeneous reaction medium; (b) stability to potassium dichromate solution; (c) low volatility to facilitate the evacuation procedure. Acetic acid fulfilled these requirements satisfactorily but in certain kinetic investigations for which these techniques have been employed it was found necessary to use a non-acidic solvent. *tert.*-Butanol was used in these cases and found to give results of the same precision as acetic acid. However, an absolute error of 2-3 %, was always encountered, this being thought to arise from a reaction of the type

$$R_3COH + R'OOH \rightarrow R_3COOR' + H_2O$$

Such reactions are known to occur between tertiary alcohols and hydroperoxides in the presence of mineral acid. Attempts to obviate this error by replacing the mineral acid in the stannous chloride solution with acetic acid were successful in some cases.

Estimations often need to be carried out on peroxides present in water-immiscible solvents such as hydrocarbons. The use of benzene as a solvent was therefore investigated and found to be satisfactory. Agitation for two hours either by shaking or by a magnetic stirrer was necessary for the more water-insoluble peroxides.

These various features of the estimation as brought out by the use of different solvents are illustrated for typical examples in Table IV.

TABLE IV

THE INFLUENCE OF THE SOLVENT ON THE ESTIMATION

Peroxide	Solvent	Reduction conditions at room temperature	% estimated
Tetralin hydroperoxide	Acetic acid	Standing for 1 hr.	99.4
,,	Benzene	Agitation for 2 hrs.	99.9
,,	*tert.*-Butanol	Standing for 1 hr.	97.8
Cumene hydroperoxide	Acetic acid	Standing for 1 hr.	99.0
,,	Benzene	Agitation for 2 hrs.	99.0
,,	*tert.*-Butanol	Standing for 1 hr.	97.3
Cyclohexene hydroperoxide*	Acetic acid	Standing for 1 hr.	93.7
,,	Benzene	Agitation for 2 hrs.	92.3
,,	*tert.*-Butanol	Standing for 1 hr.	91.1

* The sample of *cyclo*hexene hydroperoxide used was 93.5 % pure.

5. *Influence of the alcohol derived from the peroxide*

It will be observed in the recommended procedure that after the addition of the hot ferric solution to the reaction mixture a standard time of 30 seconds heating at 75° is allowed. There seems no reason at first sight why this temperature and excess ferric iron concentration should not be exceeded since an increase in either would ensure the more certain completion of the ferric-stannous reaction. With some peroxides, however, such increases gave rise to serious discrepancies in the form of low results. These peroxides were those producing β-γ unsaturated secondary alcohols on reduction and the discrepancies have been traced to the production of ferrous iron from the oxidation of these alcohols by ferric iron. Table V shows the extent of this reaction with Δ^2-cyclohexenol under conditions corresponding in all respects, except for the variables shown, with those of the excess stannous chloride determination in a typical peroxide analysis.

TABLE V

THE REACTION OF FERRIC IRON WITH Δ^2-CYCLOHEXENOL

Amount of Δ^2-cyclohexenol	Ferric concentration	Acidity of final mixture with respect to HCl	Time of heating	Ferrous iron produced in ml. 0.05 N $K_2Cr_2O_7$
a. 0.0005 moles	As R.P.* × 2	0.50 N	1 min. *a* 95°	0.35
,,	,,	,,	2 ,, ,, ,,	1.05
,,	,,	,,	3 ,, ,, ,,	2.65
b. ,,	As R.P. × 2	0.50 N	2 min. *a* 95°	1.05
,,	,,	0.65 N	,, ,, ,, ,,	1.86
,,	,,	1.00 N	,, ,, ,, ,,	3.05
,,	,,	1.40 N	,, ,, ,, ,,	3.90
c. ,,	As R.P.	0.30 N	½ min. *a* 75°	0.00
,,	,,	,,	1 ,, ,, ,,	0.10
,,	,,	,,	2 ,, ,, ,,	0.10
,,	,,	,,	4 ,, ,, ,,	0.22
d. ,,	As R.P.	0.50 N	½ min. *a* 75°	0.14
,,	,,	0.80 N	,, ,, ,, ,,	0.18
,,	,,	1.20 N	,, ,, ,, ,,	0.20
,,	,,	1.60 N	,, ,, ,, ,,	0.18

* R.P. refers to the ferric iron concentration used in the recommended procedure, *viz.*, 5 ml of the stock ferric solution made up to 50 ml with ammonium chloride solution and added to the reaction mixture. 'As R.P. × 2' then indicates 10 ml of stock ferric solution made up to 50 ml and added to the reaction mixture.

Sections (a) and (b) in Table V show that the errors introduced by increasing the temperature can be serious, representing in the examples given between 2-25 % of a normal peroxide titre. It is also evident that the alcohol oxidation is favoured by an increase in the acidity of the medium. Sections (c) and (d) show that the error introduced under the recommended procedure is zero and still negligible over a considerable range of heating time and acidity.

The oxidation of Δ^2-cyclohexenol by ferric iron was examined also on a macro scale and found to proceed quite readily. The nature of the product is still in doubt but unexpectedly is not Δ^2-cyclohexenone.

6. *Effect of temperature*

The results are independent of reaction temperature over the range 0-80° except for those hydroperoxides giving rise to β-γ unsaturated secondary alcohols on reduction. Thus for tetralin and cyclohexene hydroperoxides in acetic acid the estimations at 80° were lower than those at room temperature by 4-5 %. That these differences were not due to an initial decomposition at the higher temperature was shown by the fact that cyclohexene hydroperoxide, reduced at room temperature and then heated at 80° for 1 hour before the estimation procedure, still showed the same decrease. The effect is derived from an alcohol oxidation analogous to that described above, in this case by stannic ion to regenerate some of the stannous ion previously oxidised by the peroxide.

Investigations again using Δ^2-cyclohexenol showed, as might be expected, that the oxidation with stannic ion is much less rapid than with ferric ion and moreover is suppressed almost entirely when *tert.*-butanol is used as solvent. Table VI illustrates these features as they affect the peroxide determinations under the various conditions. It can be seen with cyclohexene hydroperoxide for instance, that although the results in *tert.*-butanol at room temperature are lower than those in acetic acid due to the solvent effect discussed above, they show no significant variation with temperature because of the suppression of the stannic oxidation of the Δ^2-cyclohexenol.

TABLE VI

EFFECT OF INCREASING THE REACTION TEMPERATURE

Peroxide	Solvent	Temperature	% Estimated
Cyclohexene hydroperoxide	Acetic acid	Room temp.	93.8
,,	,,	80°	89.7
,,	*tert.*-butanol	Room temp.	91.0
,,	,,	80°	90.9
Tetralin hydroperoxide	Acetic acid	Room temp.	99.4
,,	,,	80°	95.7
Cumene hydroperoxide	Acetic acid	Room temp.	99.0
,,	,,	80°	99.4

7. *Sample size*

It was found convenient in some cases to reduce the sample size of peroxide below the range (0.75-1.0 milliequivalents) which gives the optimum accuracy under the standard conditions. Determinations carried out with the same experimental technique as before using 0.25-0.3 milliequivalents peroxide, 5 ml 0.1 *N* stannous chloride solution, 5 ml solvent, 0.15*M* stock ferric alum solution and 0.0167 *N* potassium dichromate gave satisfactory results for all the standard peroxides in Table I, with however a slightly lower precision than that found under the recommended procedure. The standard deviation of results expressed in percentage purity was of the order 1.0 on the reduced scale as compared with 0.3 on the normal scale.

The reduction of up to 30 g of peroxide has been carried out using 0.5 *N* stannous chloride solution. The results obtained by the titration of aliquot portions correspond closely with normal estimations on the same sample.

8. *Interfering substances*

In most experimental applications of the analytical method other substances, besides pure peroxide and solvent, will be present. Interference by such substances can occur either through their reduction with stannous chloride or their oxidation by potassium dichromate. The former would lead to high, the latter to low, results.

Substances investigated included aldehydes, ketones, primary, secondary and tertiary alcohols, carboxylic acids, olefins, thioethers, sulphoxides and sulphones.

Of these only aldehydes were found to be reduced at room temperature by the dilute stannous chloride solution employed. In amounts up to twice the molarity of a normal peroxide sample, typical aliphatic and aromatic aldehydes gave rise to errors corresponding to 0.2-0.3 ml 0.05 *N* potassium dichromate solution, *i.e.*, 1-2 % of the usual peroxide titre.

Substances liable to oxidative attack by potassium dichromate solution were limited to thioethers and primary alcohols. By shaking the solution with carbon tetrachloride immediately before titration thioethers passed into the organic layer and caused no interference in the resulting two-phase mixture even when present in 8 molar excess over the peroxide. Primary alcohols in equimolar amounts were oxidised to a negligible extent but gave rise to seriously low results in higher concentrations. In such cases one must resort to the iodometric titration of the excess stannous chloride.

The remaining substances could be present in large amounts without interference.

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SUMMARY

A method employing stannous chloride as reductant has been developed for the analysis of organic peroxides and standardised against several peroxides of high purity. A detailed survey of the factors influencing the accuracy and the precision of the method has been made and a recommended procedure established.

RÉSUMÉ

Une méthode, utilisant le chlorure d'étain(II) comme réducteur, a été appliquée à l'analyse de peroxydes organiques et standardisée pour de nombreux peroxydes très purs. Les auteurs proposent une méthode appropriée, après avoir examiné en détail les facteurs influençant la précision du dosage.

ZUSAMMENFASSUNG

Eine Methode, welche Zinn(II)-Chlorid als Reduktionsmittel verwendet, wurde zur Analyse von organischen Peroxyden entwickelt und mit verschiedenen Peroxyden von hohem Reinheitsgrade standardisiert. Eine ausführliche Übersicht über die Faktoren, welche die Genauigkeit der Methode beeinflussen, wurde zusammengestellt und eine geeignete Arbeitsweise ausgearbeitet.

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