Selective analytical reactions of epoxide groups in the presence of unsaturated carboxylic acids, aromatic amines, and isocyanates

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INTRODUCTION

To analyse epoxide groups, use is most often made of the reaction of the addition of hydrogen halides (HBr, HCl) [1]. The reaction proceeds fairly rapidly and, in glacial acetic acid, the direct titration of epoxide groups by HBr occurs. Difficulties in carrying out the chemical-analytical reaction arise in the presence of other functional groups capable of reacting with hydrohalic acids.

Epoxy–acrylate copolymers are used as dipping compositions in electrical engineering [2]. The reaction of cocondensation is monitored from the mass fraction of epoxide groups and the acid number (mg KOH/g), which are determined by two independent methods [3]. This makes practical technological monitoring of the reaction very difficult, particularly at its final stage. Therefore, an urgent task is to develop a rapid method for determining the ratio of epoxide and acid groups in the epoxy–acrylate copolymer during its synthesis.

Aromatic amines are widely used as curing agents for epoxy resins [4]. In particular, combined systems of epoxy and aniline–phenol–formaldehyde resins are used to produce prepregs in the production of lamellar plastics. It is obvious that the nature of curing and the properties of the cured system depend considerably on the effective concentrations of epoxide and amine groups, for the determination of which it is necessary to use a selective analytical reaction.

Epoxy–isocyanate systems are widely used as binders in the production of different composite materials [5]. To determine epoxide groups in the presence of isocyanate groups, it has been proposed to preblock the latter with lower aliphatic alcohols, which increases considerably the time needed for analysis [6]. Determination of isocyanate groups in the presence of epoxide groups by treating a sample with excess amine is impossible on account of possible reaction of the epoxide groups with the amine. In connection with the above, an important task is to develop selective procedures for determining epoxide and isocyanate groups when they are both present.

EXPERIMENTAL

Materials investigated

In the present work an investigation was made of the cocondensation of epoxy resin ED-16 (GOST 10587–84) and methacrylic acid (TU 6-02-59–89). Epoxide groups were determined by direct titration with HBr in glacial acetic acid [7], and the acid number was determined by titration of an acetone solution of the sample with an alcoholic solution of alkali [3].

To determine epoxide and amine groups when both present, use was made of combined systems of epoxy–triphenolic resin ETF (TU 2225-316-09201208–94) and aniline–phenol–formaldehyde resin SF-340A (GOST 18694–80).
To investigate procedures for determining epoxide and isocyanate groups when both present, use was made of models based on combined systems of phenol-blocked 2,4-toluylene diisocyanate (monophenylurethane, TU 113-38-99–90) and epoxy resin ED-22 (GOST 10587–84). The content of isocyanate groups in monophenylurethane was determined by the procedure described in [8], and the mass fraction of epoxide groups in the epoxy resin was determined according to GOST 12497–78, section 3.

Solvents and reagents
Use was made of chemically pure glacial acetic acid, twice distilled methyl ethyl ketone, acetone, and piperidine (chemically pure), HCl, HBr, and HClO₄ (chemically pure), analytical-grade diethylamine, and pure tetraethylammonium bromide.

Apparatus
Potentiometric titration was carried out on a Mettler DL 40 RC automatic titrator with glass and calomel electrodes. IR spectra of solutions were recorded in 0.2 mm liquid cells of KBr on a Perkin Elmer 983 G instrument.

RESULTS AND DISCUSSION

Determination of epoxide and carboxyl groups
For the titration of mixtures of acids, it is recommended to use amphiprotic solvents — alcohols, ketones, nitriles, esters [9]. The most convenient solvents for epoxy resins are ketones, and therefore, in the present case, acetone was selected. The selection of a solvent for the titrant (ethanol) was governed by the fact that the acidity scale of ethanol lies within the acidity scale of acetone and has little effect on the extent of the acidity scale of the mixed solvent during titration.

Preparation of the specimen for titration reduces to the epoxy resin solution with excess hydrogen halide. When HBr is used, three potential jumps are present on the potentiometric titration curves of a mixture of epoxy resin and methacrylic acid. The first potential jump relates to titration of the excess HBr, as the strongest (semineutralisation potential ∆E = 500 mV). It is well known [10] that hydrogen halides can add by double bonds, contrary to Markovnikov’s rule. As a result of the given reaction, the formation of 2-methylbromoacetic acid is possible (∆E = −980 mV), the magnitude of pKₐ of which should be considerably lower than that of methacrylic acid. On the basis of the Henderson equation, the difference between the values of pKₐ of methacrylic and 2-methylbromoacetic acid was calculated and turned out to be equal to 2.88. The corresponding difference for acrylic and bromoacetic acids amounts to 1.89. Consequently, as a result of the addition of HBr, methacrylic acid (pKₐ = 4.66) forms strong 2-methylbromoacetic acid, and the use of hydrobromic acid for the determination of epoxide groups in epoxy resin in the presence of methacrylic acid leads to the appearance of an additional potential jump on the potentiometric titration curve. A third potential jump on the potentiometric titration curve corresponds to the titration of methacrylic acid (∆E = 1150 mV).

When excess HCl is used as the reagent, only two potential jumps are present on the potentiometric titration curve, which indicates the absence of addition of hydrogen halide by the double bond of methacrylic acid. The first potential jump corresponds to the titration of HCl, and the second to the titration of methacrylic acid.

To assess the possibility of visual recording of points of equivalence on the corresponding potential jumps, a number of indicators were tested. The criteria of their applicability are: the presence of a contrast change of light in the region of the point of equivalence, and the absence of mutual masking of colour when they are added successively to the titrated solution. The indicators alizarin red and bromothymol blue satisfy these criteria. It was established that, during titration with an alkali, in the region of the point of equivalence of the first potential jump, alizarin red changes the colour from yellow to light-pink, and bromothymol blue (the second potential jump) changes it from a dull grey to a stable light-blue colour.

In the indicator titration of the analysed specimen in acetone with an ethanol solution of alkali, the colour of the indicators in the region of the potential jumps changes monotonically, and therefore the recording of the points of equivalence is difficult. The use of a double solvent of acetone and ethanol, in the present authors’ view, increases considerably the contrast of the change in colour of the indicators, and therefore, before titration, it is expedient to dilute the titrated acetone solution with ethanol in a 1:1 ratio.

DETERMINATION OF THE MASS FRACTIONS OF METHACRYLIC ACID AND EPOXIDE GROUPS IN EPOXY RESIN WHEN BOTH ARE PRESENT

A model system consisting of 0.0824 g of methacrylic acid and 0.2208 g of epoxy resin ED-16 (mass fraction of epoxy groups 16.75%) is dissolved in 20 ml of acetone, and 25 ml of 0.1M HCl in acetone is added. After 2 min, 20 ml of ethanol and three drops of alizarin red are added, and titration with a 0.1M solution of alkali in ethanol is carried out until a light-pink colour appears; three drops of indicator bromothymol blue are added, and titration is carried out until the appearance of a stable
light-blue colour of the solution. The volume of alkali that is added before the change in colour from yellow to light-pink, \( V_1 \), corresponds to the titration of excess HCl; the volume of alkali added before the change to a light-blue colour, \( V_2 \), corresponds to titration of the total HCl and methacrylic acid. A control experiment without a specimen, \( V' \), is carried out in parallel.

The mass fractions of methacrylic acid, \( X_1 \), and epoxide groups, \( X_2 \), in the analysed specimen are calculated by means of the formulae

\[
X_1 = \left( \frac{V_2 - V_1}{m} \right) \times 8.6 \times M, \quad X_2 = \left( \frac{V - V_1}{m} \right) \times 4.3 \times M
\]

where 8.6 and 4.3 are conversion factors in the calculation of the mass fractions of methacrylic acid and epoxide groups respectively, \( M \) is the concentration of ethanol solution of alkali (mol), and \( m \) is the weight of the specimen, g.

The results of determining the mass fractions of methacrylic acid and epoxide groups in the model system are given in Table 1.

The mass fractions of methacrylic acid and epoxide groups during copolymerisation of the acid and epoxide resin were determined. Copolymerisation was carried out at a temperature of 135˚C with an epoxy resin/methacrylic acid ratio of 3:1.

A sample of 5 g of reaction mixture is taken and dissolved in 30 ml of acetone, and 10 ml of 0.1 M HCl in acetone is added. After 2 min, 30 ml of ethanol is added, and titration with a 0.1 M solution of alkali in ethanol is carried out. The first point of equivalence is recorded from the change in colour of alizarin red, and the second point from the change in colour of bromothymol blue. A control experiment is carried out in parallel.

The sought quantities are calculated in a similar manner to that given above for model systems. The results of determining the volume fractions of methacrylic acid and epoxide groups in the copolymer by the proposed method and by the well-known method are given in Table 2. The conversion of methacrylic acid and epoxide groups in the copolymer during the reaction is presented in Table 3.

An important advantage of the proposed procedure is the possibility of obtaining the sought results on the basis of data of single titration, whereas separate determination of methacrylic acid and the epoxide number is fairly lengthy. This fact plays a key role in the technological monitoring of reactions occurring at high speed. The rapidity of the procedure can be increased considerably by using an automatic titrator, when analysis is carried out for 1.5–2 min. It must be stressed that the developed procedure can also be used in the production of epoxy resins modified with vegetable oil fatty acids.

### Table 1 Results of determining mass fractions of methacrylic acid and epoxide groups (%) in model system (\( n = 5; P = 0.95 \))

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Found  ( X \pm \Delta Y )</th>
<th>( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methacrylic</td>
<td>27.18</td>
<td>27.80 ± 0.16</td>
<td>0.003</td>
</tr>
<tr>
<td>Epoxide groups</td>
<td>12.21</td>
<td>12.05 ± 0.07</td>
<td>0.003</td>
</tr>
</tbody>
</table>

### Table 2 Results of determining acid number and mass fraction of epoxide groups in copolymer by proposed and known methods (\( n = 5; P = 0.95 \))

<table>
<thead>
<tr>
<th></th>
<th>Proposed method</th>
<th>Known method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid number, mg KOH/1 g</td>
<td>( X \pm \Delta Y )</td>
<td>( X \pm \Delta Y )</td>
</tr>
<tr>
<td></td>
<td>( s )</td>
<td>( s )</td>
</tr>
<tr>
<td>Epoxide groups, %</td>
<td>0.060 ± 0.001</td>
<td>0.062 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>0.004</td>
<td>0.003</td>
</tr>
</tbody>
</table>

### Table 3 Results of determining mass fraction of epoxide groups (\( X_1 \), %) and acid number (\( X_2 \), mg KOH/1 g) in epoxy-acrylate copolymer by proposed and known methods

<table>
<thead>
<tr>
<th>Specimen</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proposed</td>
<td>0.95</td>
<td>33.0</td>
<td>0.84</td>
<td>24.6</td>
<td>0.69</td>
</tr>
<tr>
<td>Known</td>
<td>1.03</td>
<td>29.7</td>
<td>0.81</td>
<td>24.2</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Determination of epoxide and amine groups

There is a well-known procedure for determining epoxide groups using halides of quaternary ammonium [11]. The latter generates hydrogen halide in an acetate medium, which adds to the epoxide groups. The base precipitating as a result of the addition of hydrogen halide can be
titrated back with perchloric acid in glacial acetic acid. Since, under these conditions, aromatic amines are also titrated, the given procedure can be used to determine epoxide and amine groups from data of titration of the sample and a control experiment.

As follows from procedures for determining epoxide and amine groups, in both cases titration is carried out in glacial acetic acid with an HClO₄ solution in the presence of crystalline violet. Consequently, the volume of titrant expended on titration of the sample without the addition of tetraethylammonium bromide is equivalent to the amine group content in the sample. The volume of titrant expended on titration of the sample with the addition of tetraethylammonium bromide (taken in excess in relation to epoxide groups) is equivalent to the sum of the amine and epoxide groups. The difference in volumes of the titrant between the second and first titrations is equivalent to the epoxide group content.

To assess the applicability of the procedure, model solutions of epoxy–triphenolic and aniline–phenol–formaldehyde resins were prepared with a known content of epoxide and amine groups respectively. On the basis of known ratios of the epoxy and aniline–phenol–formaldehyde resins and the content of the functional groups analysed in the initial components, their theoretical values in the blend were calculated. The results of determining the content of amine and epoxide groups in comparison with the theoretical values are given in Table 4.

As follows from data in Table 4, calculated values of the mass fractions of amine groups in the blend of analysed resins are in good agreement with experimentally obtained results. It must be pointed out that the interaction of primary amines with epoxide groups in the general case proceeds successively with the formation of secondary and then tertiary amines. Taking into account that, by the titration of perchloric acid in glacial acetic acid, the sum of primary, secondary, and tertiary amines is determined, it can be concluded that, during the interaction of epoxy resin with amine groups, the total mass fraction of the latter does not change.

Thus, the kinetics of the reaction can be judged only from the change in the content of epoxide groups. Since no significant reduction is observed in the content of epoxide groups in the combined product, and overestimated results are obtained in the second experiment, it can be concluded that, in the cold, the epoxide groups hardly react with the amine groups. Consequently, the procedure developed can be used to monitor the content of components in the combined product.

**Determination procedure.** A sample of solution of combined epoxy and aniline–phenol–formaldehyde resins (~0.3–0.5 g) is dissolved in 10 ml of glacial acetic acid, 10 ml of a 0.1 M solution of tetraethylammonium bromide in glacial acetic acid is added, and, after 5 min, 0.1 M HClO₄ is titrated in glacial acetic acid until change in the colour of crystalline violet. A control experiment is carried out in parallel without adding tetraethylammonium bromide. The mass fraction of amine nitrogen is determined on the basis of the titration of the control experiment; the mass fraction of epoxide groups is determined from the difference between two analyses in terms of epoxide groups.

The procedure was used to establish the optimum ratio of epoxy and aniline–phenol–formaldehyde resins in combined products in the production of prepregs (semiproducts for the manufacture of glass fibre laminates), since, with a shortage of epoxy component or excess aniline–phenol–formaldehyde resin, prepregs with low elasticity are produced. It was found that the optimum contents of epoxide and amine (content of amine nitrogen) groups in the combined product should amount to 9.5–11.5 and 0.55–0.75% respectively.

**Determination of epoxide and isocyanate groups when both are present**

The properties of combined epoxide–isocyanate systems both in the initial and in the cured state are determined in many ways by the ratio of mass fractions of epoxide and isocyanate (free and “hidden”, or phenol-blocked) groups. Isocyanate groups are determined from the reaction with aliphatic amines (dibutylamine [11], diethylamine [8], piperidine [12]), and here, in most cases, reverse titration of excess amine is used. It is known that epoxide groups react readily with amines, and therefore the given type of reaction cannot be used to determine isocyanate groups when both are present.

<table>
<thead>
<tr>
<th>No.</th>
<th>Epoxide groups in ETP</th>
<th>Amine nitrogen in APF</th>
<th>Combined product, %</th>
<th>Epoxide groups</th>
<th>Amine groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td>1</td>
<td>23.75 ± 0.08</td>
<td>4.82 ± 0.01</td>
<td>9.24</td>
<td>9.04 ± 0.18</td>
<td>0.58</td>
</tr>
<tr>
<td>2</td>
<td>23.92 ± 0.12</td>
<td>5.25 ± 0.02</td>
<td>9.12</td>
<td>9.38 ± 0.11</td>
<td>0.63</td>
</tr>
<tr>
<td>3</td>
<td>24.01 ± 0.10</td>
<td>5.47 ± 0.04</td>
<td>9.49</td>
<td>9.42 ± 0.12</td>
<td>0.77</td>
</tr>
</tbody>
</table>

*Table 4* Results of determining mass fraction of epoxide groups and amine nitrogen in combined product based on epoxy–triphenolic (ETP) and aniline–phenol–formaldehyde (APF) resins (n = 5; P = 0.95)
Direct titration of isocyanate groups by amines [12, 13] makes it possible to differentiate the reactions of aliphatic amines with isocyanate and epoxide groups, and to use the method of potentiometric titration for determination of isocyanate groups.

To determine epoxide groups, as indicated above, use is made of reactions of addition of hydrogen halides (HBr, HCl) in glacial acetic acid. The rate of the reaction of HBr with epoxide groups is so high that it makes it possible directly to titrate epoxide groups in glacial acetic acid with potentiometric and indicator (crystalline violet) recording of the point of equivalence. It is well known [14] that the interaction of isocyanate groups with carboxylic acids proceeds in accordance with the scheme

\[
R\equiv C\equiv O + R'\text{ COOH} \rightarrow R\text{ NHCOR} + R'\text{ COOH}
\]

\[
\rightarrow R\text{ NH}_2 + R'\text{ COC} = R' + \text{ CO}_2
\]

The amines formed react readily with anhydrides and isocyanates. It must be assumed that, during the titration of epoxide groups by HBr in glacial acetic acid in the presence of isocyanate groups, the latter may form compounds with acetic acid, thus masking isocyanate groups during the titration of epoxide groups.

IR spectroscopy (Figure 1) established that the intensity of the absorption band of isocyanate groups of monophenylurethane (MPU) at 2276 cm\(^{-1}\) (4.393 µm) in the presence of a double molar excess of acetic acid in chloroform (MPU concentration 1%) decreases in time, and a narrow intense absorption band appears in the region 2340 cm\(^{-1}\) (4.273 µm). Earlier, in investigation of the interaction of isocyanate groups with N-methylpyrrolidone, we suggested that similar shift of the absorption band of isocyanate groups is due to the possibility of forming a molecular complex [14].

High-frequency shift of the absorption band of isocyanate groups is due to the acceptor effect of carbonyl groups of a number of compounds on cumulated double bonds [15]. In particular, for N-methylpyrrolidone, the given effect is confirmed by the appearance of absorption bands in the UV and visible region of the spectrum at 345 and 435 nm [14]. It was shown that high-frequency shift of the absorption band of isocyanate groups in cyclohexanone and dimethyl formamide is not accompanied with the appearance of absorption bands in the visible part of the spectrum. This indicates change in the resonance structure of the isocyanate group during interaction with carbonyl-containing compounds, which, under certain conditions, may lead to the formation of a charge transfer complex.

The given data make it possible to assume that acetic acid may also interact with isocyanate groups. The curve of the time dependence of the intensity of the absorption band at 2340 cm\(^{-1}\) is S-shaped (Figure 2), which suggests the formation of intermediates for the realisation of subsequent reactions. It is obvious that, in acetic acid, the given reactions proceed with an incomparably higher rate than in weak solutions in chloroform. The experimental data presented indicate that, at the initial stage of the reaction, intermediates are formed that play a kinetically significant role in the complex chain of subsequent transformations of the reacting substances.

To study the effect of isocyanate groups in the determination of epoxide groups, a number of model systems were prepared by the dissolution in acetic acid of resin ED-22 (mass fraction of epoxide groups 22.38 ± 0.31%) and monophenylurethane (mass fraction of free isocyanate groups 6.48 ± 0.16%, mass fraction of phenol-blocked isocyanate groups 22.04 ± 0.14%) in an epoxide groups/free isocyanate groups equivalent ratio of 5:1–5:5. Model systems of the given composition were selected for the following reasons. The rate of interaction of the isocyanate groups with epoxide groups at normal temperature is low, and it proceeds only at elevated temperatures in the absence of a catalyst [5]. The content
of hydroxyl groups in the epoxy resin increases with increase in its molecular weight, and therefore the low molecular weight epoxy resin contains a minimum amount of secondary hydroxyl groups capable of reacting with the isocyanate groups [1].

It was established that, within the range of given ratios of functional groups that are most often used in practice, the results of determining epoxide groups by potentiometric titration with 0.1M HBr in glacial acetic acid (Figure 3) are characterised by correctness, fairly high accuracy, and reproducibility (Table 5). The conditions of potentiometric titration were $E_{1/2} = 530$ mV and $\Delta E = 50$ mV, where $E_{1/2}$ is the semineutralisation potential, and $\Delta E$ is the range of potentials that characterises the curve of potentiometric titration from value $E_{1/2}$ to the potential corresponding to 100% excess reagent.

It must be pointed out that the correctness of the results depends considerably on the titration rate. With a titration rate of more than 5 ml/min, the results of determination proved to be slightly overestimated, which indicates partial interaction of HBr with phenol-blocked isocyanate groups, since the mass fraction of free isocyanate groups hardly changed in this case. Evidently, the rate of the reaction of epoxide groups with HBr in glacial acetic acid is lower than what for phenol-blocked isocyanate groups. The latter readily interact with compounds containing mobile protons, for example, with primary and secondary amines [16]. The process is accelerated significantly in the presence of catalysts of ionic or zwitterionic nature [17]. Taking into account the nature of the solvent and titrant, all the preconditions are in place for the occurrence of the given reaction under conditions of excess titrant, when the rate of its addition is greater than the rate of the reaction with epoxide groups.

On the other hand, the reactivity of the free isocyanate groups in position 6 of monophenylurethane is considerably lower than that for the isocyanate groups in position 4 during interaction with amines, which is explained by steric hindrances. When the given groups interact with water, this order changes [16]. Thus, the rate of the reaction evidently depends on the size of the nucleophile. Thus, by the titration of epoxide groups in the presence of 4,4′-diphenylmethane diisocyanate (MDI) in a wide range of epoxy resin/MDI ratios, mass fractions of the epoxide groups that correlated well with theoretical values were obtained with a rate of addition of the titrant up to 5 ml/min. On the basis of the experimental data obtained it can be concluded that, in the general case, the optimum titration rate should not exceed 2 ml/min.

To determine isocyanate groups in the presence of epoxide groups, a study was made of the procedure of direct titration with piperidine in methyl ethyl ketone. In contrast to the procedure developed earlier for determination from the reaction with diethylamine [8], the latter was replaced with piperidine to reduce the steric hindrances during interaction with the isocyanate group, which increases considerably the rate of the nucleophilic reaction [18]. The reverse titration of excess amine under these conditions gives considerably underestimated results of determining isocyanate groups, which indicates partial interaction of the amine with the epoxide groups.

The conditions of direct potentiometric titration of isocyanate groups with piperidine in methyl ethyl ketone in the presence of epoxide groups (Figure 4, curve 1) were $E_{1/2} = -160$ mV and $\Delta E = 60$ mV. The results of determining the mass fraction of isocyanate groups in model systems are given in Table 6. With a greater than 25-fold excess of epoxide groups in relation to isocyanate groups, a reduction is observed in the value of $\Delta E$, and the error of determination increases.

In determination of the mass fraction of isocyanate groups in epoxy–isocyanate systems containing MDI and other highly reactive isocyanates, titration is best carried out in the presence of aprotic non-polar solvents (toluene, xylene) to avoid the effect of keto-enol tautomerism of methyl ethyl ketone on the results of analysis. Here, the nature of the potentiometric titration curves hardly changes (Figure 4, curve 2).

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**Table 5** Results of determining mass fraction of epoxide groups (%) in presence of isocyanate groups ($n = 5, P = 0.95$). Theoretical content of epoxide groups $22.38 \pm 0.31%$

<table>
<thead>
<tr>
<th>Ratio of epoxide and isocyanate groups, equ</th>
<th>Found $X \pm \Delta X$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>22.63 ± 0.43</td>
<td>0.006</td>
</tr>
<tr>
<td>1:2</td>
<td>22.89 ± 0.32</td>
<td>0.005</td>
</tr>
<tr>
<td>1:3</td>
<td>22.23 ± 0.27</td>
<td>0.005</td>
</tr>
<tr>
<td>1:4</td>
<td>22.27 ± 0.36</td>
<td>0.006</td>
</tr>
<tr>
<td>1:5</td>
<td>22.32 ± 0.40</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Procedure for determining epoxide groups in the presence of isocyanate groups. A sample of the analysed specimen containing 0.2–0.6 mequ epoxide groups is dissolved in 50 ml of glacial acetic acid and titrated potentiometrically with a 0.1M solution of HBr in glacial acetic acid with glass and calomel electrodes. The feed rate of the titrant is no more than 2 ml/min. Titration can be carried out in the presence of crystalline violet with visual recording of the point of equivalence. No more than a sixfold excess of isocyanate groups in relation to the epoxide groups is permitted.

Procedure for determining isocyanate groups in the presence of epoxide groups. A sample of the analysed specimen containing 0.2–0.6 mequ isocyanate groups is dissolved in 40 ml of methyl ethyl ketone, 20 ml of toluene is added, and it is titrated with a 0.1M solution of piperidine in methyl ethyl ketone potentiometrically with glass and calomel electrodes. The feed rate of the titrant is no more than 5 ml/min. No more than a 25-fold excess of epoxide groups in relation to the isocyanate groups is permitted.

Table 6 Results of determining mass fraction of isocyanate groups (%) in presence of epoxide groups \( (n = 5; P = 0.95) \). Theoretical content of isocyanate groups \( 6.48 \pm 0.16\% \)

<table>
<thead>
<tr>
<th>Ratio of epoxide and isocyanate groups, equ</th>
<th>Found</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( X \pm \Delta X )</td>
<td>( s )</td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>6.23 ± 0.31</td>
<td>0.026</td>
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<tr>
<td>1:2</td>
<td>6.49 ± 0.32</td>
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<tr>
<td>1:3</td>
<td>6.26 ± 0.27</td>
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<tr>
<td>1:4</td>
<td>6.27 ± 0.36</td>
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<tr>
<td>1:5</td>
<td>6.52 ± 0.40</td>
<td>0.036</td>
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REFERENCES

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