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GAS CHROMATOGRAPHIC DETERMINATION OF ALKYLENE OXIDES IN THEIR COPOLYMERS

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SUMMARY

A simple combined pyrolysis-gas chromatographic method for the determination of the relative alkylene oxide contents of copolymers has been investigated in order to establish relationships for the flame ionization detector response and calibration data and to select appropriate calibration standards. The reliability and accuracy of the results for ethylene oxide and propylene oxide determinations were evaluated statistically. The possible application of this method for the analysis of ethylene oxide adducts is discussed.

INTRODUCTION

Many analytical methods have been applied for the characterization of products based on alkylene oxide polymers because of their technical importance as surfactants, emulsifiers, dispersants, solubilizers, wetting agents, etc. One of their most important characteristics is the content of alkylene oxides [predominantly ethylene oxide (EO) and/or propylene oxide (PO)], often expressed as the number of EO units per mole or the length of the alkylene oxide chain. The EO content can be determined for simple types of products by applying a relationship between their physical properties and the EO content, *e.g.*, by n_D measurement¹ or cloud point evaluation². Another non-destructive approach to this problem is the application of spectral methods such as infrared³ and nuclear magnetic resonance spectroscopy⁴. The direct use of chromatographic methods is aimed rather at the evaluation of the distribution of alkylene oxides in the polymers: although thin-layer (TLC)⁵, gas (GC)⁶ and gel permeation chromatography (GPC)⁷ are sometimes able to give detailed

information of their complex structure, the separation efficiency of these methods cannot be adequate for all of the products concerned.

Several simpler procedures for the evaluation of these polymers have been proposed, based on preliminary cleavage of the ether linkages (in some instances by pyrolysis) using phosphorus pentoxide or orthophosphoric acid⁸, hydrobromic and acetic acids^{9,10}, or toluenesulphonic acid and acetic anhydride¹¹; this is followed by systematic GC analysis of hydrophobic remainder of the original molecules¹²⁻¹⁵. Alternatively, the alkylene oxide chain can be characterized by splitting it with orthophosphoric acid (or phosphorus pentoxide) in a pyrolyzer at high temperatures, and resulting fragments are then separated and determined by GC^{13,16,17}. This technique is especially suitable for the analysis of EO/PO polymers and copolymers¹⁸⁻²²: their EO and/or PO content can be determined either directly (in copolymers) or after the standard addition of the corresponding absent polyalkylene oxide (in polymers). In the last procedure, the sample is mixed with orthophosphoric acid and subjected to short pyrolysis at a high temperature (at least 500°). The ether linkages in the polyalkylene oxide chain are split and acetaldehyde (from EO) and propionaldehyde (from PO) are formed; the formation of smaller amounts of other products (such as dioxan and acetone) from splitting reactions was found by some workers^{13,22,23}. Nevertheless, a correlation between the relative amounts of acetaldehyde and propionaldehyde, separated and determined by GC, and the relative contents of EO and PO in copolymers has been found^{19,22}. The results of such GC determinations of EO and PO have been compared with those of IR measurement^{19,22} and have been found to be more reliable.

Because some limitations have been claimed¹⁹ for the application of pyrolysis GC to the analysis of EO/PO adducts, it is better to rely upon pyrolysis GC for the analysis of EO/PO copolymers based on careful calibration. In addition, certain effects on the results of this method are not yet known. In our laboratories, some tests have been performed on the influence of the response of the GC detector (flame ionization detector, FID) on calibration data and on the influence of the selection of standards on calibration. By the statistical treatment of some of the results obtained in our laboratories, the reliability of the determination of EO and PO has been established; in addition, an attempt has been made to apply this method to the analysis of one type of EO adduct.

EXPERIMENTAL

Products tested, reagents and standards

The products tested (predominantly EO and PO copolymers) were prepared in the Research Department of the W. Pieck Chemical Works, Nováky, Czechoslovakia. Orthophosphoric acid, chloroform and other chemicals were supplied by Labora, Prague, Czechoslovakia. Standards for calibration (series of polyethylene glycols, PEG, and polypropylene glycols, PPG) were prepared in the Research Department of the W. Pieck Chemical Works. Porapak Q was supplied by Carlo Erba, Milan, Italy.

Pyrolyzers

Two types of pyrolyzers were used. The first type was a commercial

pyrolyzer (Carlo Erba) consisting of a pyrolysis chamber with a pyrolyzing helix and a control operating module. The second type was similar to that described by Lew¹² and was constructed of stainless steel in the mechanical workshops of the Chemical Technology Institute, Prague, Czechoslovakia. The first type is characterized by pyrolysis of the sample on a resistor wire helix heated directly by an electric current; pyrolysis of the sample in the second is effected in a stainless-steel cup after it has fallen into the electrically heated zone in the vertical tube of the pyrolyzer.

Gas chromatographic separation

The separation of the main pyrolysis products (acetaldehyde and propionaldehyde) was performed in three laboratories on four different GC instruments fitted with the above two types of pyrolyzers. Table I gives the operating conditions that were found to be suitable for the determination of EO and PO on separate instruments.

TABLE I
OPERATING CONDITIONS FOR PYROLYSIS GC SEPARATION

	A	B	C	D
Instrument	Carlo Erba Fractovap GV	Fractovap GV 200	Chrom 31	Chrom 2
Detector	FID	FID	FID	FID
Column length (cm)	100	60	60	50
Column I.D. (mm)	3	4	6	4
Packing	Porapak Q, 80-100 mesh	Porapak Q, 80-100 mesh	Porapak Q, 80-100 mesh	Porapak Q, 100-120 mesh
Carrier gas and flow-rate (ml/min)	N ₂ , 18	N ₂ , 30	N ₂ , 50	N ₂ at 19.6 kPa, 25
Column temperature (°C)	150	130	100	100
Pyrolysis unit	Carlo Erba with Kanthal wire (0.3 mm)	Carlo Erba with Ni-Cr wire (0.3 mm)	according to Lew ¹²	according to Lew ¹²
Pyrolysis current	2.0 A for 10 sec	2.4 A for 8 sec	—	—
Pyrolysis temperature (°C)	600	600	500	500

Procedure for analysis

A 2.5% solution of the sample in orthophosphoric acid is prepared for direct dosing (0.2–2.0 μ l) on to the pyrolyzer helix or into the pyrolyzer cup; for samples of limited solubility in orthophosphoric acid, 3 g of sample are dissolved in 25 ml of chloroform and 0.2 μ l of this solution is added to one drop of orthophosphoric acid. After closing the pyrolyzer, the GC operating conditions are stabilized and then the pyrolysis is performed followed by the GC separation of acetaldehyde and propionaldehyde. The chromatogram recorded is evaluated by peak area measurements by triangulation and the relative peaks areas are converted into EO and PO contents by using a calibration graph. In order to obtain reliable results, the analyses are repeated 3–5 times and the mean values of the EO and PO contents are calculated.

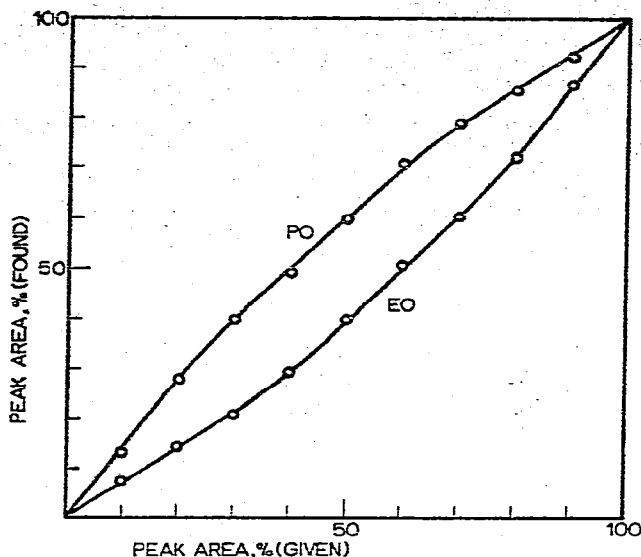


Fig. 1. Calibration graph for evaluation of relative EO and PO contents from relative peak areas.

Calibration and evaluation of results

For calibrations, PEG 600 and PPG 1200 were used as standards. Their solutions in chloroform (3.00 g in 25 ml) were combined in the ratios 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1 so as to produce a sequence of mixtures of various proportions. By repeated analyses of these solutions, chromatograms were obtained and were evaluated by internal normalization. The mean relative peak areas for EO and PO products in these chromatograms as a percentage of their sum were used to plot the calibration graph (Fig. 1). The true EO and PO contents in solutions of PEG plus PPG are affixed to it; for the correct data for calibration carried out under operating conditions A in Table I, see Table II.

RESULTS AND DISCUSSION

The calibration data obtained were compared with data calculated after applying relative FID responses to acetaldehyde and propionaldehyde, taking into account the number of effective carbon atoms in the molecule (*i.e.*, combustible carbon atoms). Thus in a solution of PEG plus PPG containing a certain EO:PO ratio, the recorded peak area ratio of the two aldehydes should be corrected for acetaldehyde, because the ratio of the effective carbon atoms in acetaldehyde and propionaldehyde is 1:2. Taking into account their molecular weights and the percentage content of effective carbon atoms in the aldehyde molecules, conversion factors can be evaluated. In the system EO/PO, the true content of EO should be corrected, for conversion into a relative peak area in the chromatogram, by a factor of 0.659 when the true content of PO is used as a standard for the relative peak areas (conversion factor = 1.000); on the other hand, for the true content of EO as a standard (conversion factor = 1.000), the true PO content should be corrected by a factor of 1.517 for prediction of the relative peak areas. Applying this assumption to

EO/PO ratios in calibration analyses, the ratios of the peak areas of both components could be calculated, and a comparison of them with data measured under operating conditions A in Table I shows very good coincidence (Table II). The theoretical FID response for EO/PO determinations is in agreement with the results obtained. These quasi-ideal calibration results cannot be achieved on each instrument under operating conditions B, C and D, so that separate calibration data and graphs are valid for particular instruments and deviations from the data in Table II must be considered.

TABLE II

COMPARISON OF CALIBRATION DATA FOUND WITH DATA CALCULATED BY APPLYING RELATIVE FID RESPONSES TO CORRESPONDING ALDEHYDES

<i>Proportions by weight</i>		<i>Peak area (%)</i>				<i>Absolute difference</i>
<i>EO (%)</i>	<i>PO (%)</i>	<i>Theory</i>		<i>Found</i>		
		<i>EO</i>	<i>PO</i>	<i>EO</i>	<i>PO</i>	
9.9	90.1	6.7	93.3	7.6	92.4	0.9
19.8	80.2	14.0	86.0	14.7	85.3	0.7
29.7	70.3	21.8	78.2	21.2	78.8	0.6
39.6	60.4	30.2	69.8	29.4	70.6	0.8
49.6	50.4	39.4	60.6	40.3	59.7	0.9
59.6	40.4	49.3	50.7	50.9	49.1	1.6
69.7	30.3	60.2	39.8	60.1	39.9	0.1
79.8	20.2	72.2	27.8	72.0	28.0	0.2
89.9	10.1	85.4	14.6	86.7	13.3	1.3

Because of eventual changes in the chromatographic system owing to the number of analyses performed, the validity of the calibration data should be checked. It is recommended that after 20–30 separate GC runs, several calibration mixtures should be checked in order to control the validity of the data in the calibration graph. After 50 analyses, the inlet part of the Porapak packing should be renewed, and the whole packing should be changed after 200–300 runs. In commercial pyrolyzers, the pyrolysis helix should be cleaned carefully, or preferably it should be changed after several runs. For the vertical pyrolyzer, the stainless-steel cup for the sample should be cleaned by heating. By observing these precautions, reliable results can be achieved. The GC separation of the resulting acetaldehyde and propionaldehyde was performed on Porapak Q without problems and only trace amounts of reaction by-products were noted.

For the investigation of the influence of the choice of calibration standards, various combinations of standards were checked for the determination of EO (DEG, TEG, PEG 600, PEG 1000, PEG 2000 and PEG 3000) and also various standards for the determination of PO (DPG, TPG, PPG 1200 and PPG 4200). The measured relative peak areas as percentages of EO and PO were compared with those calculated from ratios for standards, taking into account the true EO and PO contents in the standards and the relative FID response by means of conversion factors (Tables III and IV). From Table III, it is evident that when lower glycols are used as standards, agreement is achieved only for mixtures that contain low concentrations of EO stan-

TABLE III

COMPARISON OF CALCULATED AND MEASURED DATA FOR EO CONTENT USING LOWER GLYCOLS AS CALIBRATION STANDARDS

Mixture of calibration standards		Using DEG/DPG			Using TEG/TPG		
For EO: DEG or TEG (parts)	For PO: DPG or TPG (parts)	True relative EO content (%)	% of peak area for given EO content		True relative EO content (%)	% of peak area for given EO content	
			Calculated	Found		Calculated	Found
20	80	19.3	13.6	13.5	19.5	13.8	12.8
30	70	29.1	21.3	22.0	29.4	21.5	21.5
40	60	39.0	29.6	28.0	39.3	29.9	28.0
50	50	49.0	38.8	36.5	49.3	39.0	36.8
60	40	59.0	48.7	46.0	59.3	49.0	45.5
70	30	69.1	59.6	56.0	69.4	59.9	55.4
80	20	79.3	71.7	65.5	79.5	71.9	65.0

TABLE IV

COMPARISON OF CALCULATED AND MEASURED DATA FOR COMBINATION OF VARIOUS CALIBRATION STANDARDS

Mixture of standards		Theoretical relative content		% of peak area for given EO content		% of peak area for given PO content	
For EO (30 parts)	For PO (70 parts)	EO (%)	PO (%)	Calculated	Found	Calculated	Found
PEG 600	PPG 1200	29.7	70.3	21.8	21.0	78.2	79.0
PEG 1000	PPG 1200	29.9	70.1	22.0	19.5	78.0	80.5
PEG 3000	PPG 1200	30.2	69.8	22.2	20.5	77.8	79.5
PEG 2000	PPG 4200	29.9	70.1	21.9	20.5	78.1	79.5

dards. Hence the use of lower glycols as standards would cause errors. Better results are shown in Table IV; although various combinations of standards gave acceptable results, the combination of PEG 600 and PPG 1200 gave results nearest to the theoretical values. Similar results were achieved with other PEG and PPG mixtures.

Another problem investigated was concerned with the reproducibility and reliability of the results achieved in one laboratory by one operator, in two laboratories on two different instruments and in one laboratory by one operator on two instruments. The results in Tables V-VII were obtained without special test preparations by the general procedure outlined above, with separate calibrations of the instruments. Statistical evaluation of these data was performed according to simplified procedures for limited numbers of results²⁴; the standard deviation was calculated from the range of results using tabulated coefficients and similarly the relative range of the confidence limits was evaluated. From the results in Table VI, where true values of EO content were known, the relative error of the determination was evaluated. The statistical results are summarized in Table VIII.

The standard deviations found for repeatability (for one operator) and for reproducibility (between laboratories or for two operators) are similar. Nevertheless,

TABLE V

REPEATABILITY OF RESULTS FOR EO CONTENT (%) FOR ONE OPERATOR ON THE SAME INSTRUMENT IN THREE LABORATORIES

GC runs	Sample					
	I	II	III	IV	V	VI
	Instrument					
	A	A	B	B	D	D
1	7.8	27.9	38.3	80.0	14.9	65.8
2	7.3	28.3	38.4	79.5	14.9	64.0
3	6.9	28.6	39.0	79.8	14.5	65.0
4	8.2	30.0	38.5	79.5	14.8	65.4
5	8.5	28.0	38.6	79.5	15.7	64.0
Mean	7.74	28.56	38.56	79.66	14.96	64.84
Standard deviation	0.69	0.90	0.26	0.21	0.52	0.77

TABLE VI

COMPARISON OF MEAN RESULTS IN TWO LABORATORIES ON DIFFERENT INSTRUMENTS WITH TRUE VALUES OF EO CONTENT (%)

	Sample			
	VII	VIII	IX	X
Laboratory A	48.7	30.8	24.7	79.7
Laboratory B	48.4	29.8	23.7	79.5
Mean	48.6	30.3	24.2	79.6
True value	48.8	29.9	24.3	80.0
Standard deviation between laboratories	0.26	0.89	0.89	0.17

TABLE VII

REPRODUCIBILITY OF MEAN RESULTS FOR ONE OPERATOR ON TWO DIFFERENT INSTRUMENTS

The results are percentage EO contents.

Sample	Instrument		Mean	Standard deviation
	B	C		
X	79.7	78.5	79.1	1.06
XI	60.0	58.7	59.4	1.15
XII	27.4	28.8	28.1	1.24

the repeatability was considered generally for three operators; the range of standard deviations for individual operators is likely to be narrow, as indicated by the values in Table V. Hence the different levels of standard deviations for individual operators is the cause of the range of standard deviations between laboratories. This conclusion is supported by values of the relative range of confidence limits expressed as a percentage; these values are substantially higher for results between laboratories than

TABLE VIII
STATISTICAL DATA

	<i>Repeatability of results in 3 laboratories on 6 different samples</i>	<i>Reproducibility of results between 2 laboratories</i>	<i>Reproducibility of results on different instruments</i>
Standard deviation	0.21 to 0.90	0.17 to 0.89	1.06 to 1.24
Relative range of confidence limits (%)	From ± 0.3 to ± 4.1 ; for low values <i>ca.</i> $\pm 10\%$	From ± 3.2 to ± 7.9 ; for low values <i>ca.</i> $\pm 20\%$	—
Relative error (%)	—	Up to 0.8; for low values up to 3%	—

for results of individual operators. For lower values of alkylene oxide content, increased relative ranges of the confidence limits are obtained both for one operator and for two laboratories owing to the poorer repeatability and accuracy in measurements of small peak areas. In general, the relative ranges of the confidence limits found are in agreement with known data from the quantitative evaluation of chromatographic analyses. From a comparison of the mean results in two laboratories and known EO contents (Table VI), it seems that the accuracy of the method is satisfactory: relative errors of up to 0.8% for higher results and up to 3% for lower results. In this instance, however, the same type of instrument was used in both laboratories. When different instruments are used, a higher relative error is to be expected, as indicated by the higher ranges of standard deviations even for operation by the same operator (Table VII). This could be explained by the existence of a systematic error resulting from either the GC operating conditions or the calibration.

An attempt was made to apply this method to the determination of the EO contents, in a series of nonylphenol-EO adducts. The results in Table IX were obtained by modifying the analytical procedure by analyzing a sample added to the same amount of PO standard (PEG 1200): this standard addition was taken into account in calculating the EO contents from the analytical results of relative EO and PO contents.

From the results, it is evident that reliable results can be obtained only for EO adducts that have a high EO content. This is in agreement with published conclusions¹⁹, where the application of pyrolysis GC for analysis of alkylphenol-EO adducts

TABLE IX
ANALYSIS OF NONYLPHENOL-EO ADDUCTS FOR EO CONTENT

<i>Mean content of EO (moles)</i>	<i>EO content (%)</i>	
	<i>Theory</i>	<i>Found</i>
5	50.0	56.3
6	54.6	59.9
10	66.8	72.5
30	85.6	85.2
50	91.0	91.5

was limited to those with EO contents higher than 66%. In addition, the analysis of ethoxylated amines and EO adducts of mixed alcohols was not possible. Considering all of these results, it is evident that the application of pyrolysis GC to the determination of alkylene oxides should be limited mainly to their copolymers.

Satisfactory results of the calibration analyses gave a reliable basis for achieving sufficiently accurate determinations of alkylene oxides. By using the calibration data for particular instruments, comparable results can be obtained within laboratories. Better results were obtained by two operators on an identical type of instrument than by one operator on different instruments, fitted with different types of pyrolyzer. The different natures of the pyrolysis units (directly heated wire or indirectly heated cup) may be the main cause of the higher standard deviation, rather than the influence of differences in the GC operating conditions or the calibration data. For more reliable conclusions, systematic testing would be useful.

CONCLUSIONS

The determination of relative EO and PO contents in their copolymers by pyrolysis is achieved by calibration with suitable PEG and PPG standards. Statistical evaluation of the results achieved in three laboratories showed that this method has adequate reliability and reproducibility if it is limited to the analysis of copolymer rather than alkylene oxide adducts.

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