

Estimation of Flame-Ionization Detector Relative Response Factors for Oligomers of Alkyl and Aryl Ether Polyethoxylates using the Effective Carbon Number Concept

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Abstract

The decreasing molar flame ionization detector response with the increasing length of the polyethylene oxide chain of three series of alkyl- and aryl-polyoxyethylene-trimethylsilyl ethers and a series of bis-trimethylsilylpolyoxyethylene ethers is described in terms of the effective carbon number (ECN) of each oligomer. When the ECN contribution of the $-\text{CH}_2-\text{O}-\text{Si}(\text{CH}_3)_3$ group is assumed to be equivalent to 3.69 carbon atoms, the presence of each oxygen atom in the ethylene oxide chain is found to be equivalent to -0.41 ± 0.05 carbon atoms.

Introduction

Commercial alkyl or aryl polyethoxylate surfactants ($\text{R}[\text{OCH}_2\text{CH}_2]_n\text{OH}$) generally contain a wide range of oligomers. With the advent of high-temperature gas chromatography (GC) capillary columns, the individual oligomers in many of these mixtures can be resolved. The flame-ionization detector (FID) is often the detector of choice for this class of compounds because of its high sensitivity and broad linear range. The response of an FID is generally considered to be proportional to the carbon content of the analyte, and although the exact flame chemistry of the FID is not completely understood, there is general agreement (1–3) that the most important ionization reaction is:



This ionization reaction is inhibited to various degrees by electronegative atoms present in functional groups of the analyte resulting in a decrease in the detector response. Accordingly, the FID response to the individual oligomers of an alkyl or aryl polyethoxylate decreases with the increasing amounts of oxygen in the higher oligomers. Therefore, unless external standards with oligomer contributions closely matching the sample are available, accurate quantitation of polyoxyethylene derivatives by FID cannot simply be achieved.

In an attempt to quantitate this reduction in detector response by electronegative atoms, the concept of "effective carbon number" (ECN) has been formulated. Sternberg (1) and others (4–6) have tabulated the effect of various functional groups on the measured ECN of a range of simple compounds. They concluded that the effect of oxygen on the ECN of a molecule was dependent on the nature of the functional group and proposed that the presence of an ether or carbonyl oxygen reduced the ECN by 1, whereas a primary alcohol oxygen decreased the ECN by 0.6 carbons. Edwards (7) applied the ECN concept to 31 different oxygenated steroids containing various combinations of hydroxyl, keto, and ester groups and concluded that in all cases, the presence of an oxygen atom contributed a net value of -0.5 to the total ECN of the steroid regardless of the nature of the functional group.

McClure (8) reported the FID quantitation of the acetate esters of the oligomers of a commercial dodecanol polyethoxylate separated by high-performance liquid chromatography (HPLC) using the two monodisperse external standards, dodecyl-tri-oxyethylene ether acetate and dodecyl-octa-oxyethylene ether acetate. He did not use the ECN concept but determined response factors for the external standards with respect to dodecanol acetate and concluded that the response factors for the individual oligomers increased linearly by 0.04 per ethylene oxide unit. This value was then used to extrapolate the response factors for oligomers with up to 26 ethylene oxide units.

The first application of the ECN concept to the GC–FID analysis of trimethylsilyl ethers of alkyl polyethoxylates was reported in a method for the analysis of ethoxylated fatty alcohols by Milwidsky and Gabriel (9). They proposed the following formula:

$$\text{ECN} = x + 0.4y + 3.5 \quad \text{Eq 2}$$

where x is the number of carbons in the hydrophobe, y is the number of ethylene oxide units, and 0.4 and 3.5 are the ECN contributions of the oxyethylene ether group and the trimethylsilyl group, respectively. No supporting evidence or references for this formula were given.

Scanlon and Willis (10) determined the FID response of the trimethylsilyl (TMS) ethers of a range of six alcohols and eight polyols and reported the average value of 3.69 for the contribution

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for the $-\text{CH}_2\text{O}-\text{Si}(\text{CH}_3)_3$ group. By using the value of -1 for the ECN contribution of an ether oxygen, they postulated that the ECN of the oligomers of dodecyl-polyoxyethylene-trimethylsilyl ethers could be predicted by the following formula:

$$\text{ECN} = 14.69 + n$$

where n is the number of ethylene oxide units. This can be expressed by the general formula:

$$\text{ECN} = \{(\text{C}_{\text{hydrophobe}} - 1 + \text{ECN}_{\text{TMS}}) + n(2 + \text{ECN}_{\text{ether}})\} \quad \text{Eq 3}$$

where ECN_{TMS} and $\text{ECN}_{\text{ether}}$ are the ECN contributions of the $-\text{CH}_2\text{O}-\text{Si}(\text{CH}_3)_3$ group and the ether oxygen, respectively.

These formulas produce significantly different response factors, particularly for the higher oligomers. The aim of the present work was to establish the correct ECN formula required to allow the accurate quantitation of the oligomers of alkyl or aryl polyethoxylates by GC-FID.

Experimental

Polyethoxylates

A range of nonylphenol ethoxylates (TERIC N series) and octylphenol ethoxylates (TERIC X series) were obtained from ICI (Melbourne, Australia). Samples of dodecanol ethoxylates (Brij 30 and Brij 35) and polyethylene glycol (PEG 400) were obtained from Sigma (Sidney, Australia).

Polyethoxylate preparation

The various polyethoxylates were fractionated by gel permeation chromatography (GPC) to produce samples with a narrow range of oligomer distributions. The appropriate polyethoxylate, dissolved in an equal volume of dichloromethane, was loaded via a 1-mL sample loop onto a $250 \times 22\text{-mm-i.d.}$ stainless steel column slurry-packed with Bio-Beads SX-3 resin (34 g, 200–400

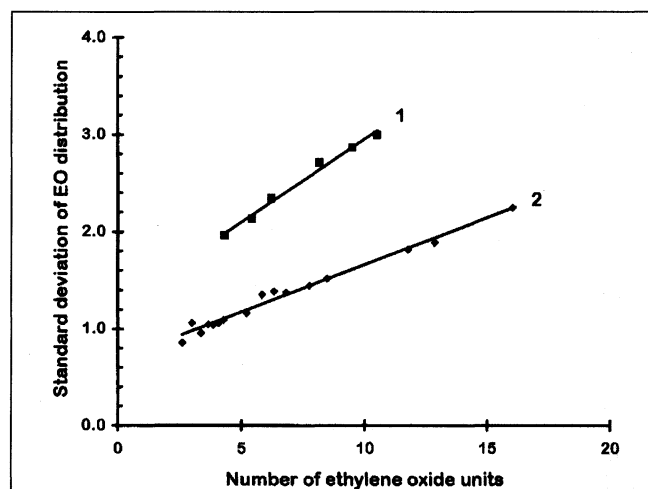


Figure 1. Polydispersity of ethylene oxide oligomers in octylphenol polyethoxylates expressed as their standard deviation. 1, Commercial Teric X series; 2, narrow distribution range octylphenol ethoxylates produced by GPC fractionation.

mesh) (Bio-Rad Laboratories, Sydney, Australia), which was swollen in hexane-dichloromethane (1:1). The eluting solvent, hexane-dichloromethane (1:1), was pumped at a rate of 4 mL/min by a model 2350 pump (ISCO, Lincoln, NE), and 1-mL fractions of the eluting polyethoxylate were collected using a Foxy Jr fraction collector (ISCO). Up to 10 replicate injections were made to obtain about 100 mg of sample for GC analysis.

All samples were dried under a stream of N_2 at 120°C for 40 min and cooled in a desiccator, and an 80 mg aliquot was accurately weighed and dissolved in ethyl acetate (10 mL) containing either hexadecane or heptadecane (≈ 400 ppm) as an internal standard. Duplicate 1-mL aliquots were trimethylsilylated by 150 mL of BSA (Pierce, Rockford, IL) at 80°C for 30 min and analyzed by GC.

GC

A Varian 3400 GC (Varian, Harbor City, CA) fitted with an FID, a 1093 septum purge programmable injector, and a BX-5 capillary column ($7.5 \text{ m} \times 0.32\text{-mm i.d.}$, 0.25-mm film , SGE, Melbourne, Australia) was used. The injector was programmed from 60 to 360°C at $100^\circ\text{C}/\text{min}$ and held at 360°C for 20 min. The column oven was programmed from 80 to 390°C at $15^\circ\text{C}/\text{min}$ and held at 390°C for 5 min. The detector was set at 400°C and used the gas flows for air, hydrogen, and nitrogen makeup specified by the manufacturer. Helium was used as the carrier gas with a flow rate of 50 cm/s . The injection volume was 0.5 mL . The output data was collected and processed using DAPA software (DAPA Scientific, Kalamunda, WA, Australia).

Results and Discussion

Commercial alcohol-polyethoxylates have wide oligomer distributions that are generally dependent on the degree of condensation. In this work, these commercial products were fractionated by GPC to produce samples with a much narrower range of oligomers, as shown by the standard deviations of the oligomer distributions in Figure 1. However, the numbers of oligomers present in each sample increased significantly with the degree of condensation. It was not possible to produce essentially monodisperse samples for analysis, so the average ethylene oxide content of each sample was determined from the measured peak areas without correction for the different ECN contributions. These values were then used to calculate the average molecular weight of the polyethoxylates in the sample, and the results were plotted as the total relative peak area per mole against the average ethylene oxide content, as shown in Figure 2.

The linear plots are consistent with the ECN concept described in Equation 3 in which the ordinate intercept is proportional to the contributions of the carbons in the hydrophobe and trimethylsilyl ether and the slope is proportional to the contribution of the ethoxylate ether group.

If the value 3.69 is assumed for the ECN of the $-\text{CH}_2\text{O}-\text{Si}(\text{CH}_3)_3$ group (determined by previous workers [10]), the ECN contribution of the ether oxygens could readily be estimated. As shown in Figures 1 and 2, the samples of polyethoxylates contained a number of oligomers. To take this into account, the first estimated ether value was used to derive the appropriate response factors relative to the

major oligomer present in each sample according to Equation 4 (10), and the detector response of the minor oligomers was adjusted.

$$F_w = \frac{MW_{\text{compound}} \times ECN_{\text{ref.}}}{MW_{\text{ref.}} \times ECN_{\text{compound}}} \quad \text{Eq 4}$$

where F_w is the relative weight response factor.

The ECN contribution of the ether oxygen was then reiteratively calculated. As shown in Table I, this produced only minor changes in the ECN contribution value of the ether oxygen, which were well within the experimental error of ± 0.05 .

Table I. Parameters From Least Squares Fit of Relative Area per Mole Versus Ethylene Oxide Number Used to Calculate the ECN Contribution of the Ether Oxygen in Various Polyethoxylates

Ethoxylate series	First estimate				Final iteration			
	Slope*	Intercept†	r^2	ECN -O-‡	Slope*	Intercept†	r^2	ECN -O-‡
Nonylphenol	0.1859	2.0364	0.992	-0.385	0.1831	2.0410	0.991	-0.413
Octylphenol	0.1841	1.9499	0.986	-0.404	0.1801	1.8399	0.993	-0.366
Dodecanol	0.1813	1.6749	0.980	-0.410	0.1798	1.6505	0.977	-0.400
PEG	0.1825	0.6749	0.982	-0.429	0.1812	0.6785	0.982	-0.445
Average				-0.41				-0.41

* Relative area \times mole⁻¹ \times ethylene-oxide number⁻¹.

† Relative area \times mole⁻¹.

‡ ECN contribution of the ether oxygen.

The average value of -0.41 was significantly less than the value of -1 reported by earlier workers (1,4,6) and the more recent average value of -0.78 reported by Jorgensen et al. (11) for three mono ethers and two furans but was consistent with the values calculated from the data reported for the FID response of other polyethoxylates. Calzolari et al. (12) provided data in the form of area percent and mole percent of the bis-trimethylsilyl ethers of the oligomers of three polyethylene oxide samples. When the relative area per mole was plotted against the number of ethylene oxide units (Figure 3), the contribution of the ether oxygen could be calculated according to the following formula:

$$ECN = 2 \times ECN_{\text{TMS}} + (n-1)(2 + ECN_{\text{ether}}) \quad \text{Eq 5}$$

This gave an average value of -0.44 ± 0.02 . It is difficult to place too much reliance on this set of data, however, because the authors did not disclose how the mole percentages of these mixtures were determined. McClure (8) determined the relative response factors for acetate esters of dodecyl-tri-oxethylene ether and dodecyl-octa-oxethylene ether with respect to dodecanol acetate. By assuming an ECN contribution of -1.27 for the ester group $-\text{CO}_2-$ (11) and using the formula given in Equation 6 (10), the ECN contribution of the ether oxygen was calculated to be -0.38 ± 0.12 .

$$ECN_{\text{compound}} = \frac{MW_{\text{compound}} \times ECN_{\text{ref.}}}{MW_{\text{ref.}} \times F_w} \quad \text{Eq 6}$$

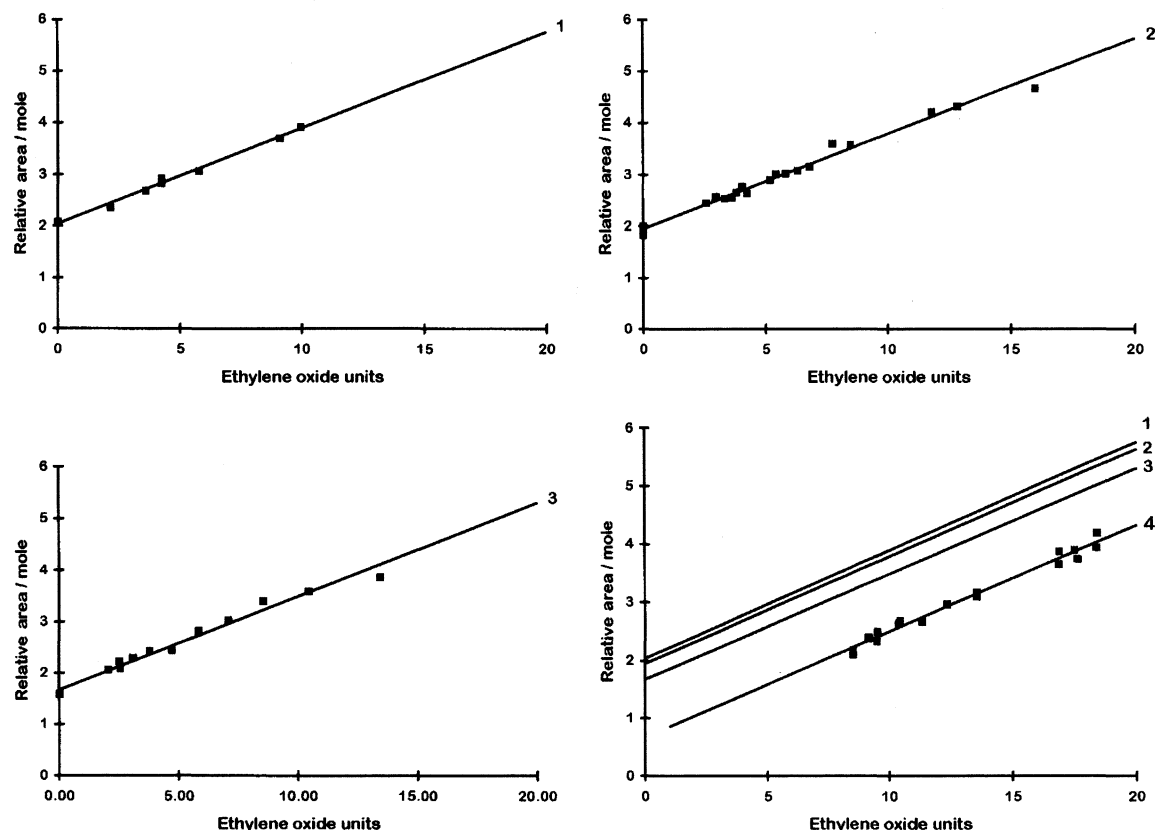


Figure 2. Variation in detector response with oxyethylene chain length for trimethylsilyl derivatives of mono-alkyl-ether ethoxylates and polyethylene glycols. 1, nonylphenol ethoxylates; 2, octylphenol ethoxylates; 3, dodecanol ethoxylates; 4, polyethylene glycols.

Although these values obtained from the studies of various workers represent a considerable variation in the ECN contribution of the ether oxygen, it should be noted that much of the early work was based on only a few small compounds. For example, Jorgensen et al. (11) reported a range of values from -0.59 to -0.99 for five different compounds containing a single ether group. In the present study, the individual polyethoxylates contained between three and 18 ether groups, and each plot in Figure 2 contained between eight and 20 different individual polyethoxylates. This weight of ether linkages provided a high degree of confidence in the correctness of the -0.41 value reported here for the ECN contribution of an ether linkage in a polyethoxylate. Accordingly, the most suitable formula for predicting the ECN of an alkyl or aryl ether polyethoxylate may be obtained by substituting in Equation 3 the values of 3.69 for the ECN contribution of the TMS group and -0.41 for the ECN contribution of the ether group.

Conclusion

Accurate analysis of polyethoxylate oligomers will always be best achieved by the use of closely matching standards and samples, but where the appropriate standard is not available, the use of the ECN concept will allow the accurate prediction of outlying oligomers only if the correct values for the contribution of the ether oxygen is used. This is highlighted in Figure 4 where the effect on the calculated response factor for dodecyl-polyoxyethylene-trimethylsilyl ethers relative to dodecyl-trimethylsilyl ether using various conflicting ECN values predicted by different workers has been plotted.

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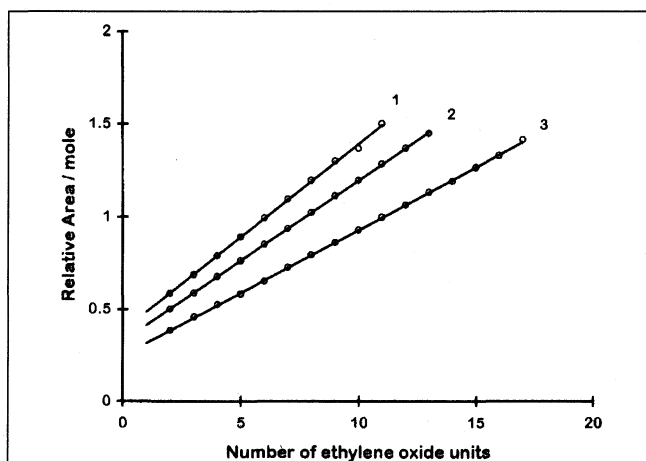


Figure 3. Variation in detector response with oxyethylene chain length for trimethylsilyl derivatives of polyethylene glycols according to Calzolari et al. (12). 1, PEG 300; 2, PEG 400; 3, PEG 600.

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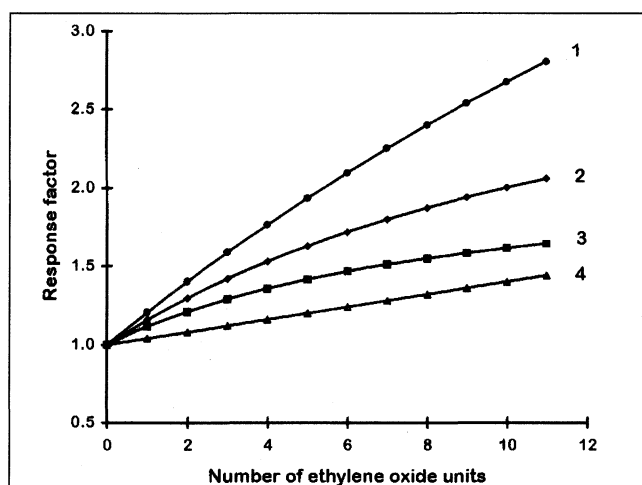


Figure 4. Response factors for individual oligomers of dodecyl-polyoxyethylene-trimethylsilyl ethers relative to dodecyl-trimethylsilyl ether calculated according to different formulas: 1, $ECN = 12 + 0.4n + 3.5$ (9); 2, $ECN = 14.69 + n$ (10); 3, $ECN = 14.69 + 1.59n$ (based on Equation 3 and ECN values used in the present work); 4, response factor = $1 + 0.04n$ (8) where n is the number of ethylene oxide units.