

The determination of ethoxylated non-ionic surfactants in wool grease

J. R. CHRISTOE* AND D. J. EVANS

CSIRO Division of Textile Industry, Geelong, Victoria, Australia

Surfactants in grease can be identified by dissolving the grease (5 g) in hexane-ethyl acetate (1:1 v/v) and adding to silica gel (100-200 mesh), eluting first with solvent and then with 50% v/v aqueous ethanol, evaporating and extracting with acetone. After evaporation, the residue is heated at 130 °C for 2 h with the mixed anhydride of acetic acid and 4-toluene sulphonic acids (cleavage reagent) (3 ml) to give ethyleneglycol diacetate (EGD) and the corresponding acetate or phenolic derivatives of the hydrophobic portion of the surfactant. When cool, the mixture is diluted with water, added to Na₂SO₄ (anhyd.) neutralized with Na₂CO₃, extracted with ether, dried (Na₂SO₄), concentrated and a sample (3 μl) gas chromatographed (glass column 1 m × 3 mm i.d., packed with 15% Carbowax 20M on Gas-Chrom Q, oven temp. 170 °C, inlet/outlet 210 °C, N₂ carrier 30 ml min⁻¹) and compared with g.c.s of known surfactants. Quantitatively, the grease (0.1-1.0g) is refluxed with cleavage reagent as above, cooled to 60 °C, distilled water (15 ml) added and the separated liquor centrifuged (3000 rev min⁻¹, 5 min). The clarified liquor is added to Na₂SO₄ (anhyd.), neutralized and extracted with ethyl acetate and a sample (3 μl) chromatographed as above with oven temp. 150 °C. The concentration of surfactant can be determined from comparison of the height of the EGD peak (Rt 2.5 min) with heights from known amounts of the surfactant treated concurrently. The type of grease (commercial, lanolin B.P., and a methanol-soluble fraction of a commercial grease were examined) has no effect on the method.

Non-ionic surfactants are extensively used for scouring greasy wool. Wool grease, which is normally recovered by centrifuging the scouring liquors, is contaminated by the surfactant used for scouring, and lanolin, the refined form of wool grease, may contain traces of the surfactant. Non-ionic surfactants can affect the emulsifying properties of lanolin and cause dermatitis (Clark 1977).

The four types of non-ionic surfactant used in wool scouring are products formed by the ethoxylation of nonylphenols, octylphenols, primary alcohols (C12-15) or secondary alcohols (C11-15), the average ethoxylate chain length being between 7 and 10.

A number of methods have been used for determining non-ionic surfactants in wool grease (Table 1). These methods are not entirely satisfactory for the following reasons:

- (i) None can be used for identifying the type of surfactant.
- (ii) The spectroscopic methods can only be used for determining surfactants with aromatic groups and interference is possible.
- (iii) Wool grease interferes with the colorimetric method using ammonium cobalthiocyanate (Anderson et al 1966; Christoe unpublished findings).

(iv) The gravimetric method is tedious.

One method for determining non-ionic surfactants is to cleave them with suitable reagents and then to analyse the reaction products by gas chromatography (see Longman 1975). By using the mixed anhydride of acetic and 4-toluene sulphonic acids, Tsuji & Konishi (1974) claimed to have overcome the difficulties encountered with cleavage reagents such as hydriodic, hydrobromic or phosphoric acids. With ethoxylated non-ionic surfactants, the hydrophilic chain is cleaved to form ethylene glycol diacetate (EGD) and the hydrophobic portion gives the corresponding acetate or phenol.

In this paper the use of the above method for identifying and determining non-ionic surfactants that are likely to be found in wool grease is discussed.

MATERIALS AND METHODS

Materials

The surfactants used were Teric X10 (an ethoxylated octylphenol, ICI), Teric N9 (an ethoxylated nonylphenol, ICI), Teric G12A8 (an ethoxylated primary alcohol, ICI) and Nonion E (an ethoxylated secondary alcohol, Albright & Wilson).

The wool greases used were: Sample A, commercial wool grease obtained by extracting wool with hexane, supplied by Solvent Belge S.A., Verviers, Belgium; Sample B, commercial wool grease ob-

* Correspondence.

Table 1. Methods for determining surfactants in wool grease.

Method	Principle	References
U.v. spectroscopy	Aromatic peak at 275 nm	Griffith (1957) see Anderson et al (1966)
I.r. spectroscopy	Aromatic peak at 1510 cm^{-1}	Anderson et al (1966)
Gravimetry/ Colorimetry	Molybdenum complex at $\sim 650 \text{ nm}$	Clark (1971)
Colorimetry	Ammonium cobaltothiocyanate complex at 620 nm	Anderson, et al (1966) Turpie & Van der Walt (1977)

tained by centrifuging scouring liquors in which soap was the scouring agent, supplied by Coates Paton, Launceston, Tasmania; Sample C, commercial wool grease obtained by centrifuging scouring liquors in which a non-ionic surfactant was the scouring agent, supplied by Dodd & Co., Melbourne; Sample D, lanolin, B.P. quality (refined from grease recovered from soap-scouring liquors), supplied by Croda Chemicals Group (Victoria), Melbourne; Sample E, lanolin, B.P. quality (refined from grease recovered from non-ionic surfactant scouring liquors), supplied by Croda Chemicals Group (Victoria), Melbourne; Sample F, the methanol-soluble fraction of sample B.

Solvents and reagents were Analar grade unless otherwise stated.

Analysis

A Bendix Series 2500 Gas Chromatograph was equipped with a flame ionization detector. The glass column (1 m \times 3 mm i.d.) was packed with 15% (w/w) Carbowax 20M on Gas-Chrom Q and the oven temperature was maintained at 170°C unless specified otherwise. The inlet and outlet temperatures were maintained at 210°C and the rate of flow of carrier gas (N_2) was 30 ml min^{-1} .

Methods

Preparation of cleavage reagent. The cleavage reagent was prepared according to the method of Tsuji & Konishi (1974).

Identification of non-ionic surfactants in wool grease. Wool grease (5 g) was dissolved in hexane-ethyl acetate (1:1 v/v) and the solution was transferred to a column of silica gel (100–200 mesh). The column was eluted successively with the solvent mixture and 50% (v/v) aqueous ethanol. The alcohol fraction was

evaporated to dryness under vacuum and the residue was extracted with acetone. The extracts were poured into a 20 ml pear-shaped flask and evaporated to dryness. Cleavage reagent (3 ml) was added to the flask and the mixture was refluxed at 130°C for 2 h. When the flask had cooled to room temperature, the contents were diluted with water and poured into a conical flask containing anhydrous sodium sulphate. After neutralization with a saturated solution of sodium carbonate (using bromophenol blue as indicator) the mixture was extracted with diethyl ether (4 \times 20 ml). The combined ether extracts, after drying over anhydrous sodium sulphate, were concentrated on a water bath and a portion (3 μl) was injected into the gas chromatograph. The surfactant was characterized by comparing its chromatogram with those of known surfactants.

Quantitative determination of ethoxylated non-ionic surfactants in wool grease. Wool grease (0.1–1.0 g depending upon the estimated concentration of surfactant) was accurately weighed into a 25 ml pear-shaped flask and cleavage reagent (3 ml) was added. The mixture was refluxed at 130°C for 2 h. After the flask had been cooled to 60–80°C, distilled water (15 ml) was added and the flask was shaken for several minutes. The liquor that separated was decanted into a centrifuge tube and centrifuged at 3000 rev min^{-1} for 5 min. After the grease layer had been removed with a spatula, the clarified liquor was poured into a conical flask containing 5 g anhydrous sodium sulphate and neutralized with a saturated solution of sodium carbonate (using bromophenol blue as indicator). The mixture was extracted with ethyl acetate (5 ml) and a portion of the solvent layer (3 μl) was injected into the gas chromatograph (the oven temperature was 150°C). The concentration of the surfactant was determined by comparing the height of the EGD peak (retention time = 2.5 min) with the heights obtained for known amounts of the surfactant that had been treated, concurrently, in the same way.

RESULTS AND DISCUSSION

Identification of typical non-ionic surfactants in wool grease

Teric X10, Teric N9, Teric G12A8 and Nonion E were chosen to represent each type of surfactant likely to be found in wool grease. The gas chromatograms of their cleavage products are shown in Fig. 1(a). The chromatograms are sufficiently different for each to be used as a 'fingerprint' for the particular type of surfactant. That the chromatograms were characteristic for the particular type in question was

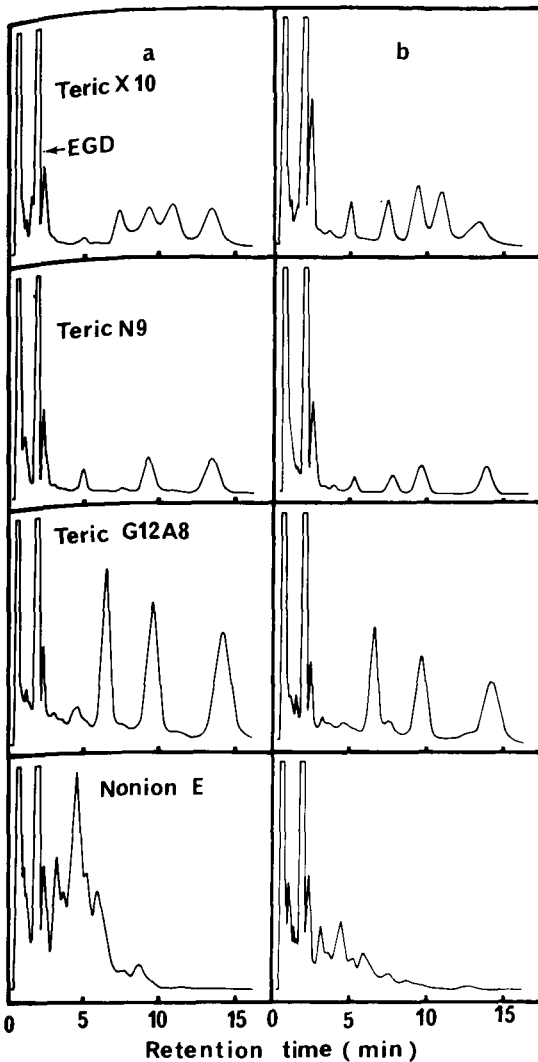


FIG. 1. Gas chromatograms of the cleavage products of typical ethoxylated nonionic surfactants used for scouring wool: (a) original surfactants (b) the same surfactants after recovery from wool grease.

confirmed by running chromatograms of the cleavage products of a number of surfactants having the same hydrophobic portion.

When samples of wool grease containing different surfactants were analysed in the same way, peaks from the wool grease interfered with those from the cleavage products of the hydrophobic portion of the surfactant. Consequently, a method was sought to separate surfactants from wool grease before analysis. The method that was finally adopted was a modification of that used by Green et al (1955) for separating an ethoxylated non-ionic surfactant from lanolin by adsorption chromatography. Silica gel

was found to be a better adsorbant for ethoxylated non-ionic surfactants than ion-exchange resins.

This method was used to separate the four model surfactants from samples of wool grease containing about 1% (w/w) of each surfactant. The gas chromatograms of the cleavage products of the recovered surfactants are shown in Fig. 1(b). These chromatograms are sufficiently similar to those of the original surfactants (Fig. 1(a)) to enable the hydrophobic portion of the surfactant to be identified.

Although it is possible to estimate the average ethoxylate chain length of a surfactant by comparing the ratio of the areas of the peaks of EGD and those of the hydrophobic portion with the ratios obtained for a series of homologous surfactants, this step is usually unnecessary because the chain lengths (average) in a given series of surfactants suitable for scouring wool are small. For example, the optimum average chain length of nonylphenol surfactants is 9–10 for jet-scouring (Anderson et al 1965). Thus, once the hydrophobic portion of the surfactant is identified, the ethoxylate chain length can be estimated with a reasonable degree of certainty.

Quantitative determination of ethoxylated non-ionic surfactants in wool grease

EGD is the most suitable cleavage-reaction product for gas chromatographic analysis because it is formed when any ethoxylated non-ionic surfactant is reacted with the cleavage reagent. It also elutes rapidly giving a sharp, well-defined peak.

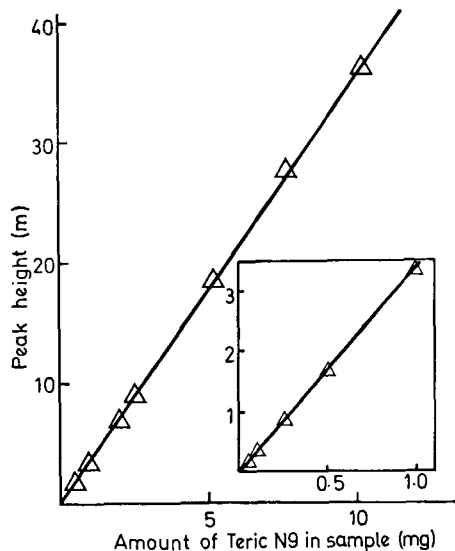


FIG. 2. Determination of EGD by gas chromatography using different amounts of Teric N9.

The calibration graph for the analysis of EGD formed when different amounts of Teric N9 (0.05–10 mg) were cleaved is shown in Fig. 2. Peak heights (actual peak height multiplied by the attenuation factor) were more satisfactory than the integrator (mechanical) data.

Although wool grease, itself, did not interfere with the analysis of EGD, the comparatively large amounts of grease that were injected into the gas chromatograph with each sample led to a gradual deterioration in the performance of the column.

When the cleavage mixture was diluted with water before neutralization, the homogeneous emulsion, which formed initially, rapidly destabilized into a dark grease phase and a yellow aqueous phase that could be clarified by centrifuging. Analysis of the two phases (after centrifuging) showed that an insignificant amount of EGD remained in the grease when 15 ml water was used for dilution. Grease was thus separated by this method for the quantitative analysis.

Samples of grease D containing known amounts of Teric N9 or Nonion E were analysed for their surfactant contents (Table 2). Linear regression analyses of the results gave lines that passed through the origin and had slopes of 0.96 and 1.00 and regression coefficients of 0.99 and 1.00 for the Teric N9 and Nonion E determinations, respectively. The difference between the slope of the theoretical line (1.0) and the regression line for Teric N9 is not statistically significant (95% confidence level) using a test of the confidence limits for the regression coefficient.

If the average ethoxylate chain length of the surfactant being analysed is estimated from a knowledge of its hydrophobic group, the error in the quantitative determination of the surfactant should be small because of the narrow range of homologous surfactants likely to be present. For example, if the average ethoxylate chain length of the nonylphenol surfactant mentioned in Table 2 were 8 or 10, the concentrations of surfactant in the grease would be increased or decreased by 7%, respectively and if the surfactant were assumed to have an average chain length of 9,

Table 2. Determination of Teric N9 and Nonion E in wool grease by gas chromatography.

		Concn % Teric N9					
Found	0.05	0.11	0.44	1.09	1.92	3.78	
Actual	0.04	0.13	0.45	1.09	2.12	3.89	
		Concn % Nonion E					
Found	0.06	0.08	0.41	0.88	1.72	3.91	
Actual	0.05	0.06	0.43	0.88	1.82	3.89	

the linear regression lines would have slopes of 0.90 and 1.03 for the 8 and 10 ethoxylates respectively. The differences between these slopes and the theoretical slope are still not statistically significant (95% confidence limit).

When samples of grease D, containing a known concentration of Teric N9 (0.45% w/w), were analysed on five different occasions, a mean of 0.45% was obtained with a standard deviation of 0.01% thus suggesting that the method gives consistent results.

Different weights of grease D (0.182–1.110 g) containing the same concentration of Teric N9 (0.45% w/w), were analysed for their surfactant contents (Fig. 3). Although linear regression analysis shows that the concentration of surfactant (as measured) depends slightly upon the amount of grease in the sample, the difference between the slopes of the line of no dependence and the regression line is not statistically significant (95% confidence level), at least within the weights of grease studied.

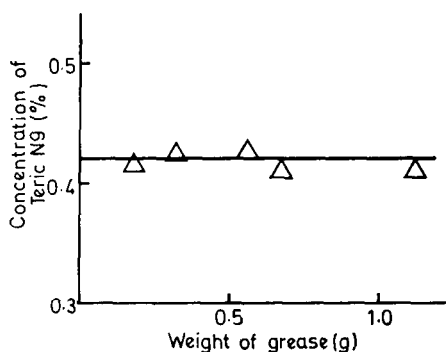


FIG. 3. Effect of wool grease on the analysis of Teric N9.

Samples of a number of different wool greases (A to F), representing the types likely to be encountered in practice, were analysed for their surfactant contents and only grease C (0.59% expressed as Teric N9) and grease E to a small extent (0.05%), gave a positive result. One can conclude that the type of grease had no effect on the analytical method.

Conclusion

Gas-chromatographic analysis is a convenient method for accurately determining the concentrations of ethoxylated non-ionic surfactants in wool grease. The method can also be used to identify the hydrophobic portion of an unknown surfactant and

therefore characterize it with a reasonable degree of confidence. Wool grease interferes with both the qualitative and the quantitative analytical procedures, but methods have been devised which enable the grease to be easily separated before analysis.

Acknowledgements

The authors wish to thank ICI (Australia) and Albright and Wilson (Australia) for samples of surfactants; Croda Chemicals Group (Victoria), Solvent Belge S.A., Verviers, Belgium, Coates Paton, Launceston, Tasmania and Dodd & Co., Melbourne for samples of wool grease; Jenny Jennings and Rhonda Hill for their technical assistance.

REFERENCES

- Anderson, C. A., Lipson, M., Wood, G. F. (1965) *J. Text. Ind.* 56 (5): T280-T286
- Anderson, C. A., Ganly, R. G., Wood, G. F. (1966) *J. Pharm. Pharmacol.* 18: 809-814
- Clark, E. W. (1971) *J. Soc. Cosmet. Chem.* 22: 421-37
- Clark, E. W., Cronin, E., Wilkinson, D. S. (1977) *Contact Dermatitis* 3: 69-74
- Green, T., Harker, R. P., Howitt, F. O. (1955) *Analyst* 80: 470-475
- Griffith, J. C. (1957) *Chem. Ind. (New York)* 1041-1042
- Longman, G. (1975) *The Analysis of Detergents and Detergent Products*. London: Wiley-Interscience
- Tsuji, K. T., Konishi, K. (1974). *J. Am. Oil Chem. Soc.* 51(3): 55-60
- Turpie, D. W. F., Van der Walt, L. T. (1977) SAWTRI Technical Report No. 353