The determination of nonylphenol ethylene oxide detergents in wool grease*

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The nonylphenol ethylene oxide nonionic detergent is extracted from wool grease by methanol under reflux and estimated from the infrared absorption at 1510 cm⁻¹. The method estimates between 90 and 100% of the detergent present and is independent of the type of grease. Commercial wool greases recovered from nonionic-detergent wool-scouring liquors contained between 0·5 and 2·4% detergent.

WOOL grease, the raw material for the manufacture of lanolin, is usually recovered by centrifuging wool-scouring liquors. When soap is used for scouring, the main contaminant of the grease is fatty acid, which can be readily determined (Sallee, 1958) and removed during refining. Soap has now largely been replaced by nonylphenol ethylene oxide (NPEO) nonionic detergents which contaminate the grease and adversely affect its emulsifying power. The extent of the contamination in either the crude grease or lanolin has not been previously reported.

We have examined the shortcomings of existing methods for determining the amount of NPEO detergent in the presence of wool grease and we describe a new method based on solvent extraction of the detergent and spectroscopic determination.

Experimental

MATERIALS

The wool greases used were: Sample A, lanolin, B.P. quality, supplied by Lanolin Products Pty. Ltd., Victoria. Sample B, commercial wool grease obtained by extracting Merino wool with white spirit. Sample C, freshly secreted wool grease obtained by extracting the base portion of Merino wool with diethyl ether. Sample D, the diethyl-ether extract of the tip portion of Merino wool. Sample E, obtained by refluxing grease B (25 g) with methanol (100 ml) for 1 hr and recovering the soluble fraction by decantation. All solvents and reagents were Analar grade. The detergent used in the investigation was Lissapol N450(I.C.I.) an NPEO detergent containing an average of 9·5 ethylene oxide units per molecule.

METHODS

For infrared spectroscopic analysis, wool grease samples were dissolved in chloroform (10% w/v). The spectra were measured on a Beckman IR-5 spectrophotometer from 2000–1400 cm⁻¹ against a chloroform blank using 0·2 mm sodium chloride cells. The absorption due to the substituted aromatic nucleus in the detergent was calculated by subtracting

* The term wool grease is used for the lipid material contained in the fleece. In its refined form, wool grease is designated as lanolin.

the background absorption, obtained by means of a tangent connecting the maxima flanking the analytical band, from the absorption at 1510 cm^{-1}. The concentration of detergent was then calculated from the calibration curve shown in Fig. 1.
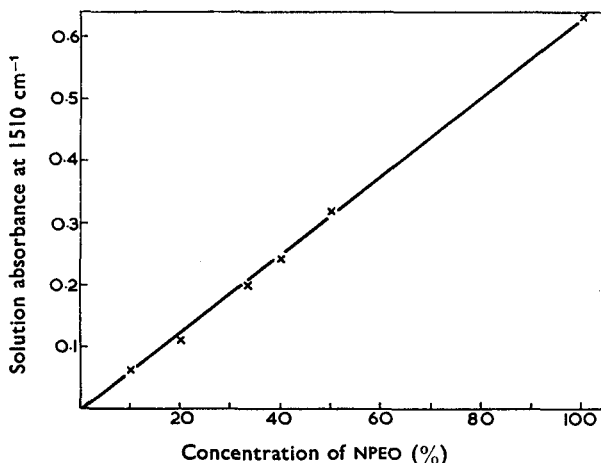

FIG. 1. Calibration curve for determining concentration of nonylphenol ethylene oxide detergent in wool grease (10% w/v solution in chloroform measured against chloroform blank). (Absorbance $= \log_{10}1/\text{Transmittance}$.)

Results and discussion

ESTIMATION OF NONIONIC DETERGENT IN WOOL GREASE BY ESTABLISHED TECHNIQUES

The quantitative determination of NPEO detergents in the presence of other compounds may be made in (i) aqueous solutions, (ii) mixed aqueous–non-aqueous solutions, and (iii) non-aqueous solutions. The methods have been reviewed by Rosen & Goldsmith (1960).

When aqueous solutions alone are used, the wool grease, which is insoluble and difficult to emulsify, is precipitated in the gravimetric methods or interferes in the volumetric and colorimetric methods. Errors are therefore introduced.

The second general technique involves reacting the detergent with ammonium cobaltothiocyanate to form a coloured complex which is extracted from the aqueous solution with chloroform or benzene, and estimated by measuring the absorption at either 620 or 318·5 mμ. The basic method was developed by Gnamm (1941) and modified by Brown & & Hayes (1955), Morgan (1962), Crabb & Persinger (1964) and Greff, Setzkorn & Leslie (1965). In these methods, the detergent is usually present in aqueous solution but preliminary tests indicated that a coloured complex is obtained if an insoluble sample (grease and detergent) and an aqueous ammonium cobaltothiocyanate solution are reacted and then extracted with chloroform or benzene. As the techniques of Crabb &

Persinger (1964) and Greff & others (1965) were the most promising, they were modified to determine NPEO detergent in wool grease.

Analysis by the techique of Crabb & Persinger (1964). In this method. the detergent is extracted from an aqueous test sample with diethyl ether, The ether solution is evaporated to dryness and ammonium cobalto-thiocyanate is added to the residue. As mixtures of detergent and wool grease are not separated completely by solvent extraction, the method will be accurate only if wool grease does not interfere with the colour-forming reaction. Results obtained from various mixtures of detergent (0–5 mg) and grease B (0–500 mg) are shown in Fig. 2. Clearly the method is
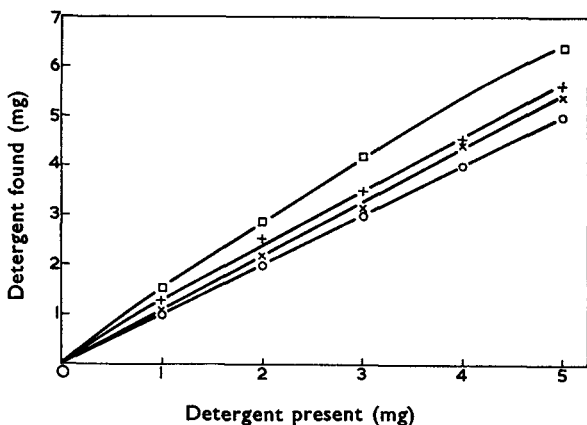

FIG. 2. The effect of wool grease B on the estimation of NPEO detergent by the method of Crabb & Persinger. ○, No added grease; ×, grease:detergent, 0·5:1; +, grease:detergent, 20:1; □, grease:detergent 100:1.
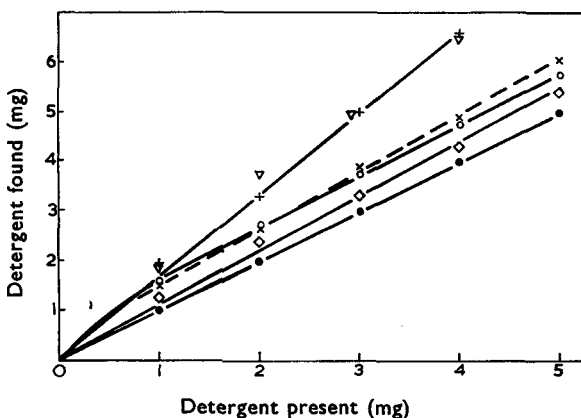

FIG. 3. The effect of various wool greases on the estimation of NPEO detergent by the method of Crabb & Persinger. ●, No added grease; ○, grease C:detergent, 100:1; +, grease D:detergent, 100:1; ▽, grease E:detergent, 100:1; ×, grease D:detergent, 0·5:1; ◇, grease E: detergent, 0·5:1.

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accurate with detergent alone; however, when wool grease is present the experimental value is in error to an extent depending on the grease: detergent ratio. At high ratios (100:1), such as in commercial greases, the error is approx. 28%. Even when the ratio is reduced to 0·5:1 the error is still significant at 8%. The effect also varies with the type of grease present (Fig. 3). Thus, at a ratio of 100:1, the errors are 19, 66 and 62% for greases C, D, and E respectively. It is therefore impossible to apply a correction factor and the method is unsuitable for estimating small amounts of NPEO detergent in commercial wool grease.

   Analysis by the technique of Greff & others (1965). In this method, ammonium cobaltothiocyanate solution is added to an aqueous solution of the detergent and the resulting coloured complex is extracted with benzene. The detergent concentration is then calculated from the extinction coefficient of the complex at 620 or 318·5 mμ. For test solution (100 ml) containing 0–25 mg the method is accurate to 10 $\pm$3%. However, when the test solution contains wool grease also, serious errors occur (Table 1).

TABLE 1.   THE EFFECT OF GREASE* ON THE ESTIMATION OF NPEO DETERGENT BY THE TECHNIQUE OF GREFF & OTHERS (1965)

Detergent present (mg)	Detergent found (mg)	
	at 620 mμ	at 318·5 mμ
24·3	77	97
12·2	34	45
4·9	13·0	19·0
2·4	6·2	9·3
0·49	0·79	1·6

*The ratio of wool grease: detergent in the test solution was 92:1.

   Estimation of NPEO *detergent by ultraviolet spectroscopy.* Griffith's (1957) method in which the detergent-containing solid is dissolved in ethanol and the detergent content estimated from the ultraviolet absorption avoids the difficulties of the preceding methods. However, a prerequisite is that any non-detergent components present should not absorb at the selected wavelength. Measurement of the absorptions of various wool greases at the optimum wavelength for NPEO detergent estimation shows that E (1%, 1 cm) at 275 mμ for detergent and greases A, B, C, D and E are 26, 2·5, 7·0, 1·6, 11·4 and 25 respectively. Therefore even if the grease: detergent ratio could be reduced to 0·5:1, the error in the detergent estimation would be between 12% and 190% depending on the type of grease present.

ESTIMATION OF NONIONIC DETERGENT BY SOLVENT EXTRACTION AND INFRARED SPECTROSCOPY

   A comparison of the infrared spectra of various wool greases and an NPEO detergent (Fig. 4) indicates that the absorption at 1510 cm^{-1}, due to the substituted aromatic nucleus, could be used to estimate the detergent if a suitable preliminary concentration could be effected. As methanol

under reflux extracts the relatively small quantity of polar components from wool grease (Anderson & Wood, 1965), it seemed likely that the detergent might also be extracted. Various parameters of extraction were therefore examined to find the optimum conditions. The findings showed that a maximum recovery of 95% is obtained at a solvent:grease ratio of 4:1 after refluxing for 1 hr. For estimation of detergent, the methanol-soluble fraction was evaporated on a rotary vacuum evaporator and dried *in vacuo* for 30 min. The residue was dissolved in chloroform and the absorption at 1510 cm^{-1} determined.
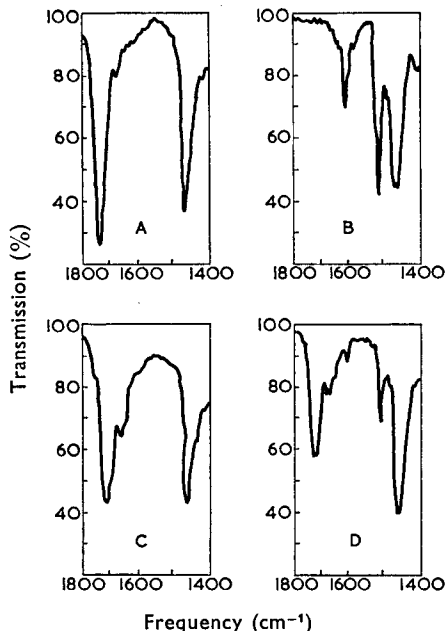

FIG. 4. Infrared spectra of Lissapol N450 and various wool greases: A, commercial centrifuged grease from soap scouring containing no detergent; B, Lissapol N450; C, methanol-soluble fraction of grease used for spectrum A; D, methanol-soluble fraction of commercial centrifuged grease from NPEO scouring. Solutions (5% w/v was used for illustrative purposes) in chloroform were measured against a chloroform blank.

RECOMMENDED PROCEDURE

To anhydrous grease (10·00 g) add methanol (40 ml) and reflux vigorously for 60 min. Cool the mixture to about 20° and then decant the supernatant liquor and flocculent material* into a tared flask. Wash the insoluble grease with cold methanol (2 × 10 ml) and add the washings also to the tared flask. Evaporate the combined methanol solution to dryness. Dissolve the residue in chloroform (10·00% w/v) and determine the absorption at 1510 cm^{-1}, using a 0·2 mm sodium chloride cell. From

* If this is not done about 3% of the detergent will be lost.

the calibration curve (Fig. 1) read off the concentration of detergent in the methanol-soluble (MS) fraction.   Detergent concentration in grease =

$$\frac{\text{Detergent in MS} \times \% \text{ MS}}{100}$$

To establish the accuracy of the method, fourteen mixtures of Lissapol N450 with samples A and B were analysed. The results indicated that the method has an accuracy of $95 \pm 5\%$. Some typical figures are shown in Table 2.

TABLE 2.   DETERMINATION OF DETERGENT CONTENT OF VARIOUS GREASES BY INFRARED SPECTROSCOPY

Detergent conc. (found) (%)	0·55	0·80	1·20	1·95	3·31	4·90
Detergent conc. (actual) (%)	0·55	0·85	1·30	2·03	3·51	5·20

Checks with several NPEO detergents from different manufacturers showed that those normally recommended for wool scouring have 8·5–10 ethylene oxide units in the chain and give virtually the same absorption at 1510 cm^{-1}.

DETERGENT IN COMMERCIAL GREASES

Using the above procedure, the NPEO detergent contents of commercially recovered greases were determined. Twenty samples from 3 different wool-scouring mills contained amounts of detergent varying from 0·55 to 2·4%. It is not known at present whether subsequent refining will remove detergent, but preliminary experiments indicate that water-washing is ineffective.

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