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Determination of Non-ionic Detergent
in the Cream, Effluent and Sludge from
Wool Scouring Liquors and in
Recovered Wool Grease**

by
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AN IMPROVED METHOD FOR THE RAPID DETERMINATION OF NON-IONIC DETERGENT IN THE CREAM, EFFLUENT AND SLUDGE FROM WOOL SCOURING LIQUORS AND IN RECOVERED WOOL GREASE

by D.W.F. TURPIE and L.T. VAN DER WALT

ABSTRACT

An improved method for the rapid determination of non-ionic detergent in the cream, effluent and sludge from wool scouring liquors and in recovered wool grease was established using dichloromethane as an extraction liquor. By using radio-active techniques it was concluded that under suitable conditions of sample dilution and absorbance the method gave results which in 95 cases out of 100, should be within ± 10 per cent of the true value if three aliquots are tested, or within $\pm 12,5$ per cent of the true value if only one aliquot is tested.

INTRODUCTION

In an attempt to establish a *rapid* method for the determination of non-ionic detergent in wool scouring liquors, some work was carried out at SAWTRI¹ in which a colorimetric method suggested by Milwidsky² for the determination of non-ionic detergent in a mixture of both non-ionic and anionic detergents was adapted and tested. Experiments were carried out on "test solutions" containing known amounts of non-ionic detergents of the ethylene oxide type, either alone or in combination with either wool grease, or wool suint or both. A cobalthiocyanate reagent together with dichloromethane (DCM) was added to the test solutions and, after shaking, two phases separated out. A blue colour developed in the lower dichloromethane phase. Part of this phase was diluted with iso-propanol and the intensity of the colour of this solution was measured at a wave-length of 620 nm. For a specific proportion of iso-propanol the absorbance was found to be primarily dependant on the concentration of the particular non-ionic detergent present, increasing with increasing concentration of detergent.

Although the above procedure could usually be carried out in about 10 minutes it suffered from the disadvantage that the absorbance decreased linearly with an increase in the concentration of suint, and concentrations of over 0,4 per cent suint in the test solution produced difficulties in the separation of the two phases. Excessive dilution of the samples to minimise interference by the suint produced very low absorbance readings, which could give unreliable results when extrapolated. Also, the froth and scum which generally formed in the neck of the volumetric flask used in the preparation of the test solution introduced

another possible source of error in sub-sampling.

A modified procedure for the test method for determining detergent in wool grease was subsequently introduced and was later extended for application to all liquors, cream effluents and sludges. This procedure has been briefly referred to in several publications^{3, 4}. In the case of wool grease, instead of dispersing the sample in *water*, the test solution was prepared using *dichloromethane* as solvent. In the case of cream, effluent, sludge, and liquor samples the water was first evaporated from the sample and the test solution then prepared using dichloromethane as solvent. Evaporation of the water was usually carried out by first evaporating the sample to a syrup on a hot-plate or heating mantle under an airstream, and then drying in a drying oven for three hours at 105°C. The procedure followed after preparation of the test solution was exactly as before excepting that instead of transferring 20 ml of *dichloromethane* to the separating funnel along with 20 ml of the test solution and 20 ml of the cobalthiocyanate reagent, 20 ml of *distilled water* was used. The change in test procedure obviated the formation of froth and scum on the surface of the test solution and the suint, insoluble in dichloromethane, settled at the bottom of the flask. The 20 ml sample of the test solution which was transferred to the separating funnel was then able to react and separate without the interference from the suint and hence more accurate results could be obtained.

On occasion it was evident that erroneous results could still be obtained when using the above modified procedure. In these cases (unreported) it was not clear if the procedure which was followed had in fact extracted all the detergent present, if there had been interference of some kind affecting the expected reaction, *or if perhaps the sample had been decomposed and some detergent destroyed during preparation of the syrup*. It was also not clear if the method was more accurate on certain types of samples, such as grease or cream, than on others, such as effluent or sludge where there could be expected to be major differences in suspended solids, absorbed grease and detergent and in the *type* of grease i.e. oxidised or unoxidised.

In view of the foregoing it was decided to resort to a third method of determining the detergent concentration incorporating the use of a radio-active detergent. Accordingly, a radio-active detergent of known activity was used to scour different raw materials and the detergent contents of the various phases produced by centrifugal treatment of the liquors measured by a suitable technique and compared with the results obtained by the 'aqueous' and 'DCM' methods referred to above. A further motivation for such trials was to establish whether a suitable procedure could be found which would be sufficiently reliable to be able to class the test as "quantitative" for a particular, known detergent.

EXPERIMENTAL

Initially, two series of experiments were carried out on a laboratory scale. In the first series a very dirty liquor was produced by hand-scouring two kg of a blend of greasy wool in four litres of water. This blend comprised 1 000 g of low-yielding short Basutos, 650 g of merino spinners style fleeces and 350 g of low-yielding stained merino locks. In the second series another very dirty liquor was produced by hand-scouring four kg of a blend of greasy mohair in four litres of water. This blend comprised equal parts of four different qualities of hair. The two liquors were made very dirty deliberately so as to test the methods under really adverse conditions.

In the first and second series of experiments 16,01 g and 12,86 g of detergent, respectively, were used. This detergent comprised a mixture of 10 parts by mass of a non-ionic detergent of the ethylene oxide type, known as ©Berol Lanco to 0,1615 parts by mass of C¹⁴-labelled Berol Lanco which was especially manufactured by the detergent manufacturer for this project. The latter, radio-active detergent had a specific activity when despatched of $5,6 \times 10^7$ disintegrations per minute per gram.

During the hand-scouring operations a laboratory stirrer fitted with a heating coil and thermostat was used to keep the liquor hot and to simulate the effects of circulation in the bowl. After scouring had been completed the liquor was heated to 90°C while stirring constantly and then transferred in batches to a laboratory centrifuge and centrifuged for 10 minutes at 3 000 r/min. This produced three phases in the centrifuge tubes. The cream phase was removed into a conical flask with the aid of a spatula, allowing sufficient liquid from the adjacent phase to be removed with it to obtain a cream of a fairly liquid consistency. The middle phase, or 'effluent' phase was decanted into another conical flask, but a little portion just above the sludge phase was left behind, undecanted. Finally the sludge phase, together with the small portion of the middle phase which was left behind, was transferred to a third conical flask, the small portion of the middle phase serving to again produce a fairly liquid consistency of the sludge in accordance with what one might expect to find in practice. The amounts of cream, effluent and sludge were augmented with each successive batch which was centrifuged, until one composite sample (of about 200 to 500 ml) each of cream, effluent and sludge had been collected from the liquor of the first series, and similar composite samples had been collected from the liquor of the second series.

Each of the above composite samples was transferred to a small (500 ml capacity) laboratory scale mixing tank. A small gear pump was connected to the bottom of the tank and continuously circulated the sample by pumping it from the bottom and returning it just below the level of the liquid in the tank. The reticulation included a bleed-off facility which permitted the withdrawal of an

aliquot directly into a graduated flask. This technique of sampling was designed to produce a well-homogenised and reproducible aliquot. About eight aliquots, each of 25 ml, were taken from each of the various composite samples. Some of these were tested by the 'aqueous' method, others by the 'DCM' method and others by the radio-active method. The order of selection of the aliquots for testing was random.

'Aqueous' Method

The 25 ml aliquot to be tested was diluted initially either by a factor of 4 or 10 (depending on circumstance) by transferring to a larger volumetric flask, washing out with de-ionised water and making up to the mark. By withdrawing an appropriately sized aliquot from this diluted test solution, and diluting still further the original aliquot was diluted by factors of up to 62,5. In this manner three test solutions, each at a different dilution, were prepared from each aliquot.

A few preliminary trials had indicated that in some instances, when the original procedure of using 20 ml each of dichloromethane, cobalthiocyanate reagent and test solution was carried out, separation was extremely slow and often incomplete, so that when the lower 15 ml of the dichloromethane layer was withdrawn and transferred to the volumetric flask containing isopropanol the resultant solution was not clear and gave erroneous absorbance values. This was probably due, judging from previous published work, to interference by the suint¹. In spite of the sometimes incomplete separation, however, a small volume of clear blue solution was frequently obtained at the bottom of the funnel, and in order to increase the size of this layer it was decided to increase the portions of dichloromethane, cobalthiocyanate reagent and the test solution to 50 ml each instead of 20 ml.

'DCM' Method

The 25 ml aliquot to be tested was transferred to a round bottomed boiling flask fitted to a rotary evaporator rotating at 20 r/min and evaporated on a water bath at 80°C until all the water had been removed. This normally took 30 minutes or longer. The idea of using a rotary evaporator instead of the normal procedure of evaporating to a syrup on a hot plate or heating mantle was to avoid the possible risk of decomposing the detergent and to reduce the time.

When evaporation of the water from the aliquot had been completed the residue was re-dissolved in dichloromethane and transferred with several washings to a larger volumetric flask. Dilution factors similar to those used for the 'aqueous' method were selected by withdrawing further aliquots from the diluted test solution and diluting still further. These test solutions were all allowed to settle for a few minutes before use.

Equal portions of de-ionised water, cobalthiocyanate reagent and the test solution were transferred to the separating funnel by means of a pipette. (For the sake of consistency 50 ml portions were used). The procedure which was then followed was precisely the same as with the 'aqueous' method.

Calculation of detergent concentration from absorbance results:

Test solutions containing known amounts of detergent in de-ionised water were subjected to the aqueous test procedure and the absorbance recorded. These results were plotted on a graph from which the concentration corresponding to any particular absorbance could be determined.

'Radio-active' method

The 25 ml aliquot to be tested was evaporated on a rotary evaporator as for the 'DCM' method, re-dissolved in 100 ml of dichloromethane and allowed to settle. Different 'cocktails' were prepared in which to disperse aliquots of the latter test solution. It was found that a cocktail prepared by dissolving 5 g PPO (2,5 - Diphenyloxazole) in one litre of toluene gave satisfactory results with regard to the subsequent counting efficiency, and accordingly this cocktail was used in all cases. The procedure involved dispersing 1 ml of the test solution in 20 ml of the cocktail and counting in a Beckman liquid scintillation system for 20 minutes after a stable condition had been reached. In this respect time had to be allowed for chemiluminescence and dark adaptation periods of from 16 to 72 hours were necessary to obtain stable conditions. The number of counts per minute was recorded as T_1 . A known mass of radio-active BeroI Lanco was then added to the dispersion being tested and counting resumed for a further period of 20 minutes after obtaining stable conditions. The number of counts per minute was recorded as T_2 . The following example serves to illustrate how the concentration of detergent in a 25 ml aliquot of cream was calculated:

$$T_1 = 2796$$

$$T_2 = 3306$$

Difference = 510 was the result of introducing a known mass of $1,15 \times 10^{-5}$ g radio-active detergent.

Therefore $T_1 = 2796$ resulted from the presence of

$$\frac{1,15 \times 10^{-5} \times 2796}{510}$$

$$510$$

$$= 6,305 \times 10^{-5} \text{ g radio-active detergent}$$

Thus 100 ml of test solution (representing the whole of the original aliquot) would have contained $6,305 \times 10^{-3}$ g radio-active detergent. The concentration of *radio-active* detergent in the original aliquot was therefore 0,02522 *per cent*. The total concentration of detergent (radio-active plus standard) in the original aliquot was therefore

$$\frac{0,02522 \times 10}{0,1615} = 1,56 \text{ per cent}$$

Detergent content of wool grease

In a third and final series of experiments some grease produced by extraction from a sample of raw wool using dichloromethane, and a known amount of radio-active detergent added. The detergent concentration was then determined by both the 'DCM' and the 'radio-active' methods and compared with the known value.

RESULTS AND DISCUSSION

The grease contents of the three phases produced after centrifuging the liquors from the first and second series are given in Table I. It can be seen that the grease contents varied in a wide range from about 3 to 33 *per cent*.

Results for the concentration of detergent as determined by the 'aqueous', 'DCM' and 'radio-active' methods are given in Tables II to VII. Tables II and III give the results for the *cream phase* from the first and second series, respectively. Tables IV and V give results for the *effluent phase* from the first and second series, respectively. Tables VI and VII give results for the *sludge phase* from the first and second series, respectively. In the discussion which follows the results for the 'aqueous' and 'DCM' methods will be compared with the results for the 'radio-active' method on the supposition that the latter results represent the *true*, or *actual* concentration.

Cream phase It is clear from Table II that the aqueous method gave results which were lower than the true value (about 80 *per cent* of the true value) whereas the DCM method appeared to give results which were fairly close to the true value. In both cases higher dilutions of the aliquot appeared to give slightly higher results. From Table III it is again clear that the DCM method gave the better performance and was close to the true value. When only 20 ml portions of test solution, dichloromethane and cobaltothiocyanate reagent were used in the aqueous test, absorbance values were so high (due to incomplete separation) that the test can be deemed to have failed. When 50 ml portions were used for the aqueous test it was quite obvious that the results were considerably better, and in fact were quite good at the higher dilutions.

TABLE I
GREASE CONTENTS OF THE THREE PHASES PRODUCED
AFTER CENTRIFUGING

PHASE	GREASE CONTENT (% m/v)	
	1st Series	2nd Series
	Wool Scouring liquor	Mohair Scouring liquor
Cream	31,0	32,7
Effluent	2,6	3,8
Sludge	5,0	11,3

Effluent phase It is clear from Table IV that the aqueous method gave results which were over 80 *per cent* of the true value, but again the DCM method gave results which were closer to the true value. Dilution appeared to have a small effect, the results tending to be better at the higher dilutions. From Table V it can be seen that the aqueous test can be deemed to have failed, since even when 50 ml portions had been used no clear blue layer could be produced. It would seem possible that the high proportion of oxidised grease normally associated with mohair played a major rôle in this particular case. The DCM results gave results which were very close to the true value and did not seem affected by the dilution factor.

Sludge phase Table VI shows that both the aqueous method and the DCM method gave results which were almost identical with the true value and which appeared to be completely unaffected by the dilution factor. On the other hand Table VII shows that, while the DCM results were almost identical with the true value and unaffected by the dilution factor, the aqueous results were far from satisfactory. When 20 ml portions of test solution, dichloromethane and cobalthiocyanate reagent were used absorbance values were so high (due to incomplete separation) that the test can again be deemed to have failed. When 50 ml portions were used the result at the highest dilution was fairly accurate, but at lower dilutions it was still obvious that the absorbance values were too high and bore no relation to the true position due to optical interference.

TABLE II

**RESULTS FOR THE CREAM PHASE FROM THE 1ST SERIES
(WOOL SCOURING LIQUOR)**

Method	Aliquot No.	Dilution Factor	Absorbance	Calculated Concentration of Detergent in Undiluted Aliquot (% m/v)	
AQUEOUS	1	10	0,44	0,77 } 0,71 } 0,74 0,74 }	
	2	10	0,40		
	3	10	0,42		
		1	25	0,13	0,79 } 0,82 } 0,80 0,78 }
		2	25	0,14	
		3	25	0,13	
		1	62,5	0,049	0,90 } 0,87 } 0,87 0,84 }
		2	62,5	0,047	
		3	62,5	0,045	
DCM	4	10	0,57	0,95 } 0,98 } 0,95 0,91 }	
	5	10	0,59		
	6	10	0,54		
		4	25	0,20	1,10 } 1,02 } 1,08 1,13 }
		5	25	0,19	
		6	25	0,22	
		4	62,5	0,070	1,20 } 1,15 } 1,15 1,10 }
		5	62,5	0,066	
		6	62,5	0,062	
RADIO-ACTIVE	7	4	<p align="center">COUNTS PER MINUTE $T_1 = 1500$ $T_2 = 2580$ Mass of radio-active detergent added $= 3,0 \times 10^{-5} \text{ g}$</p>	1,03	

TABLE III
RESULTS FOR THE CREAM PHASE FROM THE 2ND SERIES
(MOHAIR SCOURING LIQUOR)

Method	Aliquot No.	Dilution Factor	Absorbance	Calculated Concentration of Detergent in Undiluted Aliquot (% m/v)
AQUEOUS	8	10*	2,0	Test failed
		10	0,60	0,99
		25*	1,8	Test failed
		25	0,25	1,24
		62,5*	1,8	Test failed
		62,5	0,07	1,20
DCM	9	10	0,79	1,25
		25	0,255	1,25
		62,5	0,075	1,38
RADIO-ACTIVE	10	4	<p style="text-align: center;">COUNTS PER MINUTE $T_1 = 2177$ $T_2 = 3709$</p> <p>(Mass of radio-active detergent added = $3,7 \times 10^{-5}$ g)</p>	1,30

* Only 20 ml portion of test solution, dichloromethane and cobalthiocyanate reagent transferred to separating funnel.

TABLE IV
RESULTS FOR THE EFFLUENT PHASE FROM THE 1ST SERIES
(WOOL SCOURING LIQUOR)

Method	Aliquot No.	Dilution Factor	Absorbance	Calculated Concentration of Detergent in Undiluted Aliquot (% m/v)	
AQUEOUS	11	10	0,065	0,18 } 0,19 0,19 } 0,20 }	
	12	10	0,070		
	13	10	0,072		
	DCM	14	4	0,28	0,20 } 0,21 0,22 } 0,21 }
		15	4	0,30	
		16	4	0,30	
DCM	14	10	0,098	0,25 } 0,25 0,24 } 0,25 }	
	15	10	0,095		
	16	10	0,100		
	DCM	14	25	0,030	0,24 } 0,24 0,25 } 0,24 }
		15	25	0,032	
		16	25	0,030	
RADIO-ACTIVE	17	2	<p style="text-align: center;">COUNTS PER MINUTE $T_1 = 720$ $T_2 = 2220$</p> <p>(Mass of radio-active detergent added $= 3,87 \times 10^{-5}$ g)</p>	0,23	

TABLE V

**RESULTS FOR THE EFFLUENT PHASE FROM THE
2ND SERIES
(MOHAIR SCOURING LIQUOR)**

Method	Aliquot No.	Dilution Factor	Absorbance	Calculated Concentration of Detergent in Undiluted Aliquot (% m/v)
AQUEOUS	18	10 25 62,5	2,0 1,8 1,8	Test failed
DCM	19 20	4 4	0,335 0,340	0,24 } 0,24 } 0,24
	19 20	10 10	0,10 0,10	0,25 } 0,25 } 0,25
	19 20	25 25	0,028 0,030	0,22 } 0,24 } 0,23
RADIO-ACTIVE	21	4	<p>COUNTS PER MINUTE $T_1 = 435$ $T_2 = 891$</p> <p>(Mass of radio-active detergent added $= 1,10 \times 10^{-5} \text{ g}$)</p>	0,26

TABLE VI

**RESULTS FOR THE SLUDGE PHASE FROM THE 1ST SERIES
(WOOL SCOURING LIQUID)**

Method	Aliquot No.	Dilution Factor	Absorbance	Calculated Concentration of Detergent in Undiluted Aliquot (% m/v)	
AQUEOUS	22	10	0,185	0,40 0,38 0,39 } 0,39	
	23	10	0,175		
	24	10	0,180		
		22	25	0,052	0,38 0,41 0,42 } 0,40
		23	25	0,057	
		24	25	0,060	
		22	62,5	0,020	0,42 0,38 0,37 } 0,39
		23	62,5	0,018	
		24	62,5	0,017	
DCM	25	10	0,190	0,41 0,40 0,41 } 0,41	
	26	10	0,185		
	27	10	0,190		
		25	25	0,055	0,40 0,41 0,40 } 0,40
		26	25	0,057	
		27	25	0,055	
RADIO-ACTIVE	28	4	<p>COUNTS PER MINUTE $T_1 = 640$ $T_2 = 1712$ (Mass of radio-active detergent added = $2,73 \times 10^{-5}$ g)</p>	0,40	

Statistical analysis

Repeat tests using different aliquots at the same dilution were carried out in many instances, and the results are shown in various tables. The within-sample variation in the results for the detergent concentration (within-sample coefficient of variation, *per cent*) was found to be 6,1 *per cent* for the aqueous method and 4,8 *per cent* for the DCM method. These results are given in Table VIII together with other statistical data. Repeat tests were obviously not carried out on those tests which were deemed to have failed, and the statistical analysis only applies to those cases where a clear blue layer had separated out.

From the pooled results for the aqueous method given in Table VIII it can be seen that a between-sample variation of 4 *per cent* was obtained. This meant that, taking *all the data* into consideration, the 95 *per cent* confidence limits of a mean value determined by testing *three* separate aliquots were within 11 *per cent* of that mean, or by making a *single* test were within 15 *per cent* of that mean. Unfortunately, however, the mean value was itself some 14 *per cent* below the true value. Considering the results for the aqueous method more closely it is clear that at low dilution the between-sample variation was highest, and the mean value was furthest away from the true value. At a dilution factor of 10 the mean result of three tests could, in fact, be 40 *per cent* below the true value. The accuracy of the determination improved as the dilution increased but even at a dilution factor of 62,5 the mean was still 10 *per cent* below the true value. Obviously the suint was responsible for this trend, as previously reported¹, and higher dilutions reduced the interference.

From the pooled results for the DCM method given in Table VIII it can be seen that a between-sample variation of 1,5 *per cent* was obtained. This was considerably better than the respective value for the aqueous method and meant that, taking *all the data* into consideration, the 95 *per cent* confidence limits of a mean value determined by testing *three* separate aliquots were within 6 *per cent* of that mean, or by making a *single* test were within 10 *per cent* of that mean. The mean itself was within 0,1 *per cent* of the true value. Looking more closely at the results, however, it can be seen that a certain drift in the mean values was apparent with both dilution and absorbance. At low dilution or high absorbance the mean values appeared to be up to 8 *per cent* too low. At high dilution the values appeared to be about 5 *per cent* too high. It is possible that these trends may be purely an artifact of the lower number of results available at low and high dilution and high absorbance. Nevertheless it would seem expedient to carry out the test at a dilution factor of not less than 10 and preferably in the range from 10 to 25, and in an absorbance range from 0,02 to say 0,4. Under these conditions the 95 *per cent* confidence limits of a mean value determined by testing *three* separate aliquots could be expected to be within about 7,5 *per cent* of that mean, or by making a *single* test to within about 10 *per cent* of that mean. The mean itself should be within about 2,5 *per cent* of the true value. The result should,

TABLE VII
RESULTS FOR SLUDGE PHASE FROM THE 2ND SERIES
(MOHAIR SCOURING LIQUOR)

Method	Aliquot No.	Dilution Factor	Absorbance	Calculated Concentration of Detergent in Undiluted Aliquot (% m/v)
AQUEOUS	29	10*	2,0	Test failed
		10	0,51	0,87
		25*	1,8	Test failed
		25	0,145	0,84
		62,5*	1,7	Test failed
		62,5	0,024	0,50
DCM	30 31	10	0,218	0,45 } 0,45
			0,218	
	30 31	25	0,070	0,48 } 0,48
			0,071	
	30 31	62,5	0,024	0,50 } 0,48
			0,023	
RADIO-ACTIVE	32	4	<p style="text-align: center;">COUNTS PER MINUTE $T_1 = 913$ $T_2 = 1850$</p> <p>(Mass of radio-active detergent added $= 2,0 \times 10^{-5} \text{ g}$)</p>	0,48

* Only 20 ml portions of test solution, dichloromethane and cobalthiocyanate reagent transferred to separating funnel.

Therefore, in 95 cases out of 100 be within ± 10 per cent of the true value if three aliquots are tested, or within $\pm 12,5$ per cent of the true value if only one aliquot is tested.

TABLE VIII

VALUES FOR WITHIN SAMPLE AND BETWEEN SAMPLE VARIANCE FOR THE AQUEOUS AND DCM METHODS

	AQUEOUS METHOD*				DCM METHOD				All Results Pooled		
	Dilution Factor		All Results Pooled	Dilution Factor		Absorbance Range		0.5 to 0.8			
	10	25		4	10	25	62,5				
No. of Results	3	3	2	8	2	6	3	6	6	2	17
σ_w (%)	←			6,1	←			4,8			→
σ_b (%)	10	9	5	4	0	3,2	1,6	3,6	2,2	2,9	2,8
\bar{x} (%)	-18	-13	-10	-14	-8,0	-1,5	+1,1	+5,3	+1,8	+4,2	-3,2
95% Confidence Limits (3 aliquots)	±22	±19	±12	±11	±5,5	±8,5	±6,5	±9,0	±7,0	±8,0	±7,5
95% Confidence Limits for a single test				±15	±10	±11	±10	±12	±10	±11	±11

* Provided test not invalidated by incomplete separation.

\bar{x} Average deviation of mean value from 'true' value

TABLE IX
DETERGENT CONTENT OF WOOL GREASE

EXPERIMENTAL DETAIL

Mass of grease	3,752 g
Mass of detergent added	0,058 g
	3,810

• • Concentration of detergent = 1,52% (m/m)

DCM METHOD

Dissolved in DCM and made up to 250 ml

Absorbance = 0,083

• • Concentration of detergent
(Assuming a specific gravity of 0,95 for grease)
= 1,52% (m/m)

RADIO-ACTIVE METHOD

Counts per minute (T_1) obtained on aliquot of above DCM solution
= 300

Counts per minute (T_2) after adding $1,59 \times 10^{-5}$ g of radio-active detergent
= 930

• • Concentration of detergent = 1,52% (m/m)

Wool grease itself

Results for the concentration of detergent in wool grease itself are given in Table IX. It is clear that the DCM method gave a result which was in perfect agreement with the radio-active method and that the result given in the latter case was in fact the true value, since it in turn was in perfect agreement with the specific quantity of detergent added to the grease.

SUMMARY AND CONCLUSIONS

Using a radio-active detergent of known activity the accuracy of the rapid determination of non-ionic detergent in the cream, effluent and sludge from wool scouring liquors and in recovered wool grease was determined for the *aqueous method* originally adapted and modified from the work of Milwidsky, and for the more recent 'DCM' method developed at SAWTRI. Very dirty liquors were produced from both wool and mohair to test the methods under really adverse conditions.

Due to interference by the suint it was found that the aqueous method gave results which were sensitive to the dilution of the sample. For a sample diluted by a factor of 62,5 the 95 *per cent* confidence limits were at best within 12 *per cent* of the mean value, but the mean value itself was 14 *per cent* below the true value. For a sample diluted by a factor of 10 the mean result of three tests could be as much as 40 *per cent* below the true value. In some cases, the aqueous test was invalidated due to incomplete separation of the phases during the carrying out of the test procedure and was deemed to have failed.

The DCM method gave results which were, on balance, fairly accurate. A certain drift in the values was apparent with both dilution and absorbance, but may have been an artifact of the smaller number of tests carried out at extremes of dilution and absorbance.

The following test procedure is recommended for routine testing:

Test Procedure

The sample to be tested should be warmed up in a water bath and well homogenised before testing. Then test solutions should be prepared as follows: (Note that dilutions of the test solutions are given only as a guide):

- (a) Wool grease: Weigh off about 4 g . Dissolve in DCM. Transfer to a 250 ml graduated flask making up to the mark with DCM.
- (b) Thick cream, thick liquor or thick sludge: Weigh off about 10 g into a 50 ml conical flask.
- (c) liquors, effluents, ultrafiltrates, thin creams, thin sludges: Transfer 10 ml into a 50 ml conical flask by pipette.

In the case of (b) and (c) evaporate to dryness on an oil bath at 125 to 130°C. This should take about 30 minutes. In the case of (b) re-dissolve in DCM, transfer to a 250 ml graduated flask, making up to the mark with DCM. In the case of (c) re-dissolve in DCM, transfer to a 100 ml graduated flask, making up to the mark with DCM.

After allowing any suspended matter to settle, proceed in all cases (a), (b) and (c) as follows:

Pipette equal portions (preferably about 25 ml) of the test solution, cobalthiocyanate reagent and de-ionised water into a clean separating funnel of suitable capacity. Shake vigorously for about one minute. Allow a little time for the phases to separate. Transfer 10 ml of iso-propanol to a 25 ml graduated flask and make up to the mark with 15 ml of the lower phase. Gently shake to homogenise the solution and test its absorbance in a suitable colorimeter. Compare this value with values already plotted from known concentrations of that specific non-ionic detergent, and calculate the answer in accordance with the volume or mass of the sample taken and the dilution of the test solutions. (It would probably be advisable to check the plotted values from time to time to see that values for successive batches of the same detergent are more or less constant).

It will be noted that an oil bath has been suggested for evaporating the samples to dryness. This has been suggested to avoid the risk of decomposing the detergent (which may have been responsible for certain erroneous results observed previously), is very convenient and quick. (About 30 minutes is required to evaporate a 10 ml sample of liquor). As an alternative a rotary evaporator can be used, and evaporation achieved in a similar time, but only one sample can be done at a time.

Under conditions whereby the dilution factor was not less than 10 (and preferably from 10 to 25) and the absorbance in the range 0,02 to 0,4 the results indicated that the above DCM method should provide an answer which, in 95 cases out of 100 would be within ± 10 per cent of the true value if three aliquots are tested, or within $\pm 12,5$ per cent of the true value if only one aliquot is tested.

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