

Development of a Measure for Rinse Performance in Washing Machines

Report on Stage 1 Tests Conducted By Macquarie
Research Ltd

Report Prepared By
Energy Efficient Strategies

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1 Introduction

In 2002 a working group of EL15/4 was formed to progress the development of a rinse performance test for clothes washers. Late in 2002 a preliminary test program was developed to test three alternative methods of measurement:

- Conductivity
- Alkalinity
- UV spectrophotometry

The main focus of the work was to be on UV spectrophotometry. This test uses UV spectrophotometry measurement of the concentration of sodium dodecylbenzene sulfonate (SDBS) in the aqueous liquor held in the wet load on completion of the program. SDBS is the surfactant in the AS/NZS 2040.1 wash performance reference detergent.

Two specialist laboratories were approached to conduct the preliminary testing. Following a tender process, Macquarie Research Ltd was awarded the contract. The scope of works undertaken by Macquarie Research is reproduced in Appendix A. The list of samples tested is included as Appendix B.

The report prepared by Macquarie Research Ltd is included as Appendix C of this report. This report draws on the most critical data from the Macquarie report and provides additional analysis and comment. For detailed descriptions of test methods reference should be made to the report in Appendix C.

The test program contained 5 main components as follows:

1. Development of a test procedure for measuring SDBS concentrations.
2. Verification tests on principal supplied samples.
3. Trial rinse performance tests.
4. Comparative tests using conductivity and alkalinity measurements.
5. Review of available equipment for measuring SDBS concentration.

Each of these components (except item 5) is examined in detail in this report. Details of available equipment is covered in detail in section 1 of the report from Macquarie Research.

1.1 Acknowledgements

A number of organisations provided assistance to this project. Their efforts are gratefully acknowledged as follows (in alphabetical order):

- *Australian Greenhouse Office* for funding the administrative costs of this project.
- *Colgate Palmolive (Spiro Vamvouklis)* for preparing the pre-mixed test samples.
- *Electrolux* for conducting preliminary tests, the top loader tests and for providing a spin extractor for the testing.

- *Environment Australia* for providing funding to cover Testing and development costs.
- *Richard Brown* for providing valuable feedback during the development phase of the testing program
- *Test Research* for procuring, preparing and delivering samples, with financial assistance from Environment Australia.
- *VIPAC Engineers and Scientists* for conducting the front load tests and conditioned load tests with financial assistance from Environment Australia.

2 Main Findings

1. The concentration of SDBS in the wash water was found to be in the order of 150-200 mg/L and in the rinse liquor (average rinse) in the order of 30-50 mg/L. This was at variance with figures provided from a previous study (Pailthorpe) which now appears to be out by a magnitude of 100. This meant that the target range for measurement was found to be 10-100 mg/L rather than 0.1-1 mg/L as first thought.
2. Repeatability of the SBDS measurement was found to be very good at approximately $\pm 1\%$ (at a 95% confidence level).
3. Reproducibility of the SBDS measurement was found to be reasonably good at approximately $\pm 4\%$ to 5% (at a 95% confidence level).
4. Blind verification tests support Macquarie's claims for the precision of the measurement.
5. Storage of test samples in either plastic (HDPE) or glass for up to 21 days was found to have no effect on the measured values. Off site measurements of SDBS (if required) or batch processing from a number of tests is therefore likely to be practical.
6. In testing of the various ions present in the detergent and the chemicals within the swatches, none of these materials were found to have a significant impact on the test result.
7. Different supply waters were found to have similar levels of "background" SDBS (approx. 2mg/L) with a standard deviation of only 0.37 (which includes poor quality and hard water supplies).
8. The background level of SDBS in the supply water (2 mg/L) was found to be small when compared to the target measurement range (50mg/L) and could potentially be ignored or easily corrected. This is in contrast to alkalinity and especially conductivity where background levels vary considerably with different water sources and the correction can be large.
9. Trial rinse performance tests demonstrated a useful range for SDBS concentration for different levels of rinsing:
 - Excellent Rinsing = Approximately 20 mg/L
 - Average Rinsing = Approximately 40 mg/L
 - Poor rinsing = Approximately 100 mg/L
10. Trial rinse performance tests demonstrated a useful range for SDBS mass per kg load washed for different levels of rinsing:
 - Excellent Rinsing = Approximately 10 mg/kg load
 - Average Rinsing = Approximately 20 mg/kg load
 - Poor rinsing = Approximately 60 mg/kg load

11. Rinse performance results were comparable for the two types of washers examined – a top loader and a front loader. Note that the relevant reference detergent for front loaders and top loaders was used for these tests (the active ingredient in the IEC reference detergent A is also a form of SDBS).
12. Levels of SDBS found to be retained in the load between washes did not vary greatly according to the age of the load ie the age of the load is unlikely to significantly affect the test result.
13. It has been suggested that a small amount of chemical marker could be used as an alternative to measuring SDBS concentrations – the marker would be unaffected by contaminants in the supply water and would provide more accurate measurements from less expensive equipment. Furthermore, the marker would be immune to possible future changes in the detergent composition but there are a range of other issues (and potential problems) that need to be considered with this approach¹.
14. Test results showed that conductivity and alkalinity measurements provided very good linear correlation with SDBS measurements for prepared laboratory samples on known concentrations (where reference detergent components were all mixed in known concentrations in conditioned water samples).
15. However, the correlation between conductivity and alkalinity and SDBS were all fairly poor when the results from a range of real rinse tests using reference detergents was examined. It appears that the interactions of the other components in the detergent with the load, soil swatches and variations in detergent concentrations may have a non linear impact on the readings obtained for conductivity and alkalinity. All evidence so far indicates that conductivity and alkalinity become unreliable when used on reference detergent samples in real wash performance tests.
16. Real tests showed that about 25% of the SDBS is taken up during the wash operation (absorbed by the load, converted in the reaction with soil).
17. Theoretical analysis has shown that the method of SDBS measurements is likely to be unaffected by other components in the reference detergents, swatches or tap water (see section 3.4).
18. The spin extraction process had no trouble in recovering more than sufficient quantities of rinse liquor from machines with WEI of 0.55 to 0.6.

3 Development Of The Test Procedure (SDBS measurement)

Macquarie research undertook a number of tests to develop a test procedure suitable for measuring SDBS in rinse liquor. These tests included:

- Development of sampling and sample treatment methods.
- Assessment of potential sources of interference.
- Determination of accuracy and precision of the test method.

¹ If a marker were to be used, tests would need to be undertaken to establish that the marker does not affect wash performance results. Using a separate marker may produce significant problems of contamination of the load or residuals between rinse performance runs if the tracer is not used in every wash load.

3.1 The test method

The developed test procedure uses ultra violet spectrophotometry of the sample water at the absorbance maxima for SDBS (224nm) and at a background point of 280nm. The procedure is described in detail in Appendix A of Macquarie's Report (see Appendix C of this report which includes a full copy of the report).

3.2 Test Precision

The developed test procedure was found by Macquarie Research to have a precision of approximately $\pm 1\%$ (at 95% confidence level) and a standard deviation of better than 0.3 for repeat tests ie same spectrophotometer and same analyst. Tests using three different spectrophotometers and two different analysts (total of 6 measurements) (ie a reproducibility test) found that the results had a standard deviation of 2% or better. Based on these results, the calculated inter-laboratory precision was approximately $\pm 4-5\%$ (at a 95% confidence level).

3.3 Sample Storage

A number of different storage methods were trialed including both glass and HDPE bottles with and without air purging. Bottled solutions were tested at 1 day, 7 days, 14 days and 21 days. No loss of SDBS was measured over the 21 day period.

3.4 Assessment of Potential Sources of Interference

For the test protocol to be effective, materials other than SDBS that possess strong ultraviolet absorbances must be absent from the rinse water. Tests were conducted to determine possible interference from ions present in the detergent or from chemicals present in the soiled AS9 swatches. None of these materials were found to have a significant impact.

4 Verification Tests On Supplied Samples

4.1 Measurements of the Background Levels of SDBS

In order that accurate measurements of SDBS concentrations could be made, it was considered necessary to take account of the background readings associated with the water used to make the sample. In the case of wash tests this is the water fed into the washing machine (basically tap water conditioned to a specified hardness of 45 ppm of Ca CO₃ equivalent – AS/NZS 2040.1 – Appendix A, Clause A5). In addition, each participating laboratory was asked to fill a sample bottle with distilled water. This was done to assess the background level associated with chemicals associated with the sample bottles (and probably associated with the distilled water containers).

The main finding from these tests is that the background SDBS reading associated with conditioned water supplies (from 3 states) is relatively consistent (approx. 2.0 mg/L) and more importantly, relatively small compared to the target range for measurement of rinse performance (30 to 100 mg/L) (see Table 1 and Table 2). This is a unique feature of SDBS measurement, as background levels associated with alkalinity and conductivity measurements were found to be as high as 50% and 90% respectively when compared to the target range for measurement (for particular water supplies these values are likely to be higher still).

Table 1: Background “SDBS” levels associated with conditioned water supplies

Sample Source	Sample Code	mg/L
Test Research (Sydney)	7	2.566
SGS (Melbourne - Blackburn)	18	1.72
VIPAC (Melbourne - Port Melbourne)	6	1.967
Electrolux (Adelaide)	12	1.85
F&P (Auckland)	23	N/A
	Average	2.03
	Std Dev	0.37

Table 2: Background “SDBS” Levels associated with sample containers / distilled water

Sample Source	Sample Code	mg/L
Test Research (Sydney)	A	0.9
SGS (Melbourne - Blackburn)	B	0.7
VIPAC (Melbourne - Port Melbourne)	C	0.254
Electrolux (Adelaide)	D	0.135
F&P (Auckland)	E	N/A
Colgate Palmolive	F	0.212
	Average	0.44
	Std Dev	0.34

For SDBS measurement, adjustments for background levels in water supplies could potentially be avoided (ie only a measurement of the SDBS level in the rinse water would be required). For Alkalinity and Conductivity measurements, background levels would always need to be taken into account for any rinse performance measurement.

4.2 Verification Tests on Principal Supplied Samples

As noted in section 3.2, Macquarie University carried out a number of tests to determine the precision of the test method. In order that we could satisfy ourselves of the accuracy of the test method, a number of premixed samples with known concentrations of SDBS were prepared at the laboratories of Colgate Palmolive. It is important to note that these samples used commercial grade SDBS as a separate component and mixed in the appropriate quantities of other materials in the reference detergent according to the relevant specifications so that the concentration of SDBS was known exactly in each sample. These samples were sent to Macquarie Research for measurement. This round of tests were blind tests; ie Macquarie Research were not advised of the concentrations in each sample. Results are presented in Table 3 and Table 4 below. A second set of verification tests were conducted where samples from various tests were taken in duplicate (Macquarie Research were not advised which of the samples provided were duplicates, therefore this test represents a blind repeat test). The results are presented below in Table 5.

The results indicate that the measured values were within $\pm 3.4\%$ of the expected value (usually much better). For the duplicate tests the measured values for the duplicate samples varied by less than 1% except for concentrations of less than 10 mg/L. At these lower concentrations the variation increased up to 2.4%. However this represents an absolute difference of less than 0.2 mg/L!

Table 3: Verification Tests – SDBS samples mixed with distilled water

Samples mixed with Distilled Water	Sample Code	As Mixed Concentration mg/L	Measured Concentration mg/L	Absolute Difference mg/L	% Difference %
10ppm sample in distilled Water	26	10	9.999	0.001	0.0%
20ppm sample in distilled Water	29	20	19.7	0.3	1.5%
30ppm sample in distilled Water	10	30	30.16	0.16	0.5%
300ppm sample in distilled Water	15	300	299	1	0.3%
			Max	1	1.5%

Note: The mixed concentration is made from reference detergent with known concentration of SDBS

Table 4: Verification Tests – samples mixed with conditioned water

Samples mixed with Conditioned Water	Sample Code	As Mixed Concentration mg/L	Measured Concentration mg/L	Absolute Difference mg/L	% Difference %
10ppm sample in conditioned Water	20	10	9.858	0.142	1.4%
20ppm sample in conditioned Water	27	20	19.47	0.53	2.7%
30ppm sample in conditioned Water	28	30	30.46	0.46	1.5%
300ppm sample in conditioned Water	21	300	289.8	10.2	3.4%
			Max	10.2	3.4%

Note: The mixed concentration is made from reference detergent with known concentration of SDBS

Table 5: Verification Tests – tests on duplicate samples

Duplicate Tests	Sample Codes	Duplicate Sample 1 SDBS (mg/L)	Duplicate Sample 2 SDBS (mg/L)	Difference (mg/L)	Difference %
Conditioned Water Used by Test Research	7 & 5*	2.566	2.628	0.062	2.4%
Conditioned Load Samples – Supplied by VIPAC	2 & 8	9.284	9.113	0.171	1.8%
Top Loader Poor Rinse Sample – Electrolux	25 & 13	112.6	111.8	0.8	0.7%
20ppm sample in distilled Water – Colgate Palmolive	29 & 4	19.7	19.7	0	0.0%
300ppm sample in distilled Water - Colgate Palmolive	15 & 16	299	299.8	0.8	0.3%
20ppm sample in conditioned Water - Colgate Palmolive	27 & 22	19.47	19.58	0.11	0.6%
300ppm sample in conditioned Water - Colgate Palmolive	21 & 24	289.8	290.2	0.4	0.1%
			Max	0.8	2.4%

* Note: The result for sample 5 reported by Macquarie Research was 0.062, however Macquarie Research had been advised that sample 5 was obtained using conditioned water from sample 7. Therefore they deducted the sample 7 result from the sample 5 reading and obtained almost zero, which is to be expected as they are in fact the same water. The figure reported above is the measurement without adjustment for background levels.

Note 1: In this report all results for SDBS measurement have been adjusted for background levels associated with the water supply (see Table 1) unless noted otherwise.

Note 2: The samples of known mixed concentration of SDBS (in distilled water) were also measured for conductivity and alkalinity (see section 5)

4.3 Trial Rinse Performance Tests

4.3.1 Tests undertaken to produce rinse samples

The developed test method was trialed on rinse water recovered from tests conducted on two washing machines, one 5.5 kg top loading machine tested at Electrolux in South Australia and one 5 kg front loading machine tested at VIPAC in Victoria.

Each laboratory conducted a set of three wash tests on each machine. The tests were conducted in accordance with AS/NZS 2040.1:1998. At the end of the program the load was removed from the machine and placed (in parts) into a spin extractor that complied with the requirements of IEC 60456-1994-01 and the extractor was operated at 2800 rpm until the flow of water had reduced to a minimum. At the end of each test both the washing machine and spin extractor were thoroughly cleaned with water.

The three tests that were conducted were as follows:

- **An Average Rinse** – In this test each machine was operated on its regular program.
- **A Poor Rinse** – A single rinse only was used (single spray rinse in the case of the top loader) before the program was switched to final spin.
- **An Excellent Rinse** – In this test each machine was operated on its regular program followed by another complete set of rinse cycles. In the case of the front loader the complete program was re-run without the addition of detergent.

Details of the setup for the two machines are shown in Table 6.

All samples were supplied to Macquarie Research without identification as to the type of rinsing regime performed.

Table 6: Details of trial rinse performance tests

Machine	Average volume of Water in initial fill (l)	Mass of detergent added (g)	Calculated Mass of SDBS added (g)	Calculated Concentration of SDBS in Wash Water (mg/L)	Average Mass of Moisture retained in the load (g)	Average Mass of Liquor extracted (g)
Front Loader	20 ¹	62.5	4.75	237.5	2750 ¹	N/R ¹
Top Loader	61.8	104	13.5	218.9	3300	1300

1. Value based on previous test results

2. N/R – Value not recorded

4.3.2 Measured levels of SDBS in wash water

Testing laboratories were asked to take a sample of the wash water from one of the three tests. This sample was taken from the first pump out ie after the wash cycle had been completed. The results are presented below in Table 7.

Electrolux (top loader) decided to take a sample from all three tests, surprisingly the result for the third test showed some variation from the first two (approximately 7.5% lower concentration). The cause of this variation is unknown and may warrant some further investigation.

The measured concentration levels were found to be approximately 75%–80% of the calculated concentration at the commencement of the wash (see 5th column in Table 6). This reduction is believed to be a result of a number of factors including:

- Absorption of SDBS by the load.
- Chemical conversion of SDBS when combined with the soils in the swatch.
- Possible adhesion of SDBS to the drum.

Table 7: Measured levels of SDBS in the wash water

Rinse Type	Top Loader		Front Loader	
	Sample code	SDBS Concentration (mg/L)	Sample code	SDBS Concentration (mg/L)
Poor Rinse	19A	173.4	9	191.3
Average Rinse	19B	173.7	N/R	N/R
Excellent Rinse	19C	160.4	N/R	N/R
Average		169.2		191.3

NR = Not Recorded

4.3.3 Measured levels of SDBS in Rinse Liquor

Testing laboratories were asked to take a sample of the rinse liquor for each of the three tests performed. The sample was taken following high speed spin extraction and was then promptly forwarded to Macquarie Research for SDBS measurement. The results are presented below in Table 8. For each machine tested the tests returned reasonably similar SDBS concentrations for each rinse type examined.. Two other forms of comparison were also undertaken, SDBS concentrations as a percentage of the wash water concentration (Table 9) and calculated mass of retained SDBS per kg of load (Table 10).

The mass of the retained SDBS per kg of load was calculated by multiplying the concentration of SDBS (Table 6) by the mass of moisture retained in the load (Table 6) then dividing by the rated capacity of the machine.

For each of the sets of results presented below the measured values for top and front loaders are comparable with ranges for poor, average and excellent washes showing good differentiation.

Table 8: Measured concentrations of SDBS in the rinse liquor

Rinse Type	Top Loader		Front Loader	
	Sample code	SDBS Concentration (mg/L)	Sample code	SDBS Concentration (mg/L)
Poor Rinse	25	114.45	11	103.92
Average Rinse	17	44.27	1	35.40
Excellent Rinse	3	20.21	14	15.11

Table 9: Measured levels of SDBS in the rinse liquor as a % of wash water concentration

Rinse Type	Top Loader		Front Loader	
	Sample code	SDBS Concentration (mg/L)	Sample code	SDBS Concentration (mg/L)
Poor Rinse	25	65%	11	53%
Average Rinse	17	24%	1	17%
Excellent Rinse	3	11%	14	7%

Table 10: Calculated mass of SDBS retained per kg of load

Rinse Type	Top Loader		Front Loader	
	Sample code	SDBS Mass (mg/kg load)	Sample code	SDBS Mass (mg/kg load)
Poor Rinse	25	64.4	11	56
Average Rinse	17	26	1	18.4
Excellent Rinse	3	11.1	14	7.2

4.3.4 Measured Levels of SDBS retained in the load (between washes)

VIPAC conducted tests to determine the level of SDBS retained in the wash load following conditioning. In this test two 5kg conditioned loads were tested, one that was relatively new and one that was relatively old. Note that the loads were not run through the same machine before they were tested below (ie the background SDBS level is partially random depending on the last machine in which each load was tested, which is not known). Each load was immersed in a container of distilled water (approximately 30 litres) for one hour. The load was then removed and spun “dry” in a conventional washing machine. Following this the load was placed in a spin extractor and a sample extracted for measurement at Macquarie Research.

The results from these measurements are presented below in Table 11. Based on the limited results it can be concluded that during the initial fill and wash cycle the conditioned load will retain between about 0.3 and 0.45 grams of SDBS. It would appear that an increase in the age of the load may decrease the background SDBS concentration slightly (noting that the machine and program last used on each load was not controlled for this particular test). The extent to which the amount of retained SDBS in the conditioned load affects the wash result is difficult to assess from these limited tests, however based on these results and those from the excellent rinse (which returned comparable concentrations) it is expected that the conditioned load typically

retains an SDBS equivalent of between 10 and 20 mg/L and that this persists as a background level in the clothes load and represents the upper limit for rinse performance.

Table 11: Measured concentration of SDBS retained in the conditioned load

Load Type	Sample Code	mg/L
New Load	30	14.8
Old Load	2	9.3

5 Comparative Tests Using Conductivity and Alkalinity Measurements

For comparative purposes some test solutions as well as the trial rinse performance samples were tested for both conductivity and alkalinity.

Total alkalinity was determined using potentiometric titration as per ISO Standard 9961-1:1994. Conductivity was determined using a TPS model LC-84 conductivity meter. All tests were done in triplicate.

The results are presented in Table 12 (premixed test solutions), Table 13 (top loader results) and Table 14 (front loader results).

Table 12: SDBS readings – reference detergent made up to known SDBS concentrations

Sample Description	SDBS (mg/L)	Conductivity mS/m	Alkalinity mmol/L
Macquarie Research 10mg/L pre-mix		19.5	0.658
Macquarie Research 50mg/L pre-mix		49.0	1.339
Macquarie Research 200mg/L pre-mix		158.4	3.995
Conditioned water (used to make up sample)		14.4	0.273

Note: Readings are raw readings, samples are made up with conditioned water.

Table 13: Top Loader – SDBS, conductivity and alkalinity measurements

Top Loader		Measurements					
		Raw Readings			Adjusted Readings²		
Sample	Sample Code	SDBS (mg/L)	Cond. mS/m	Alkalinity mmol/L	SDBS (mg/L)	Cond. mS/m	Alkalinity mmol/L
Conditioned Water (Tap) (Adelaide)	12	1.85	73.9	1.521	0	0	0
Wash Water	19 ¹	171.05	234.5	6.697	169.2	160.6	5.176
Poor Rinse	25	114.45	198.4	6.787	112.6	124.5	5.266
Average Rinse	17	44.27	99.9	3.065	42.42	26	1.544
Excellent Rinse	3	20.21	87.7	2.338	18.36	13.8	0.817

1. For the wash water SDBS measurement the average of Samples 19A, 19B and 19C was used
2. Adjusted readings are adjusted for the background levels found in the conditioned (tap) water – tap readings are subtracted from the total reading.

Table 14: Front Loader – SDBS, conductivity and alkalinity measurements

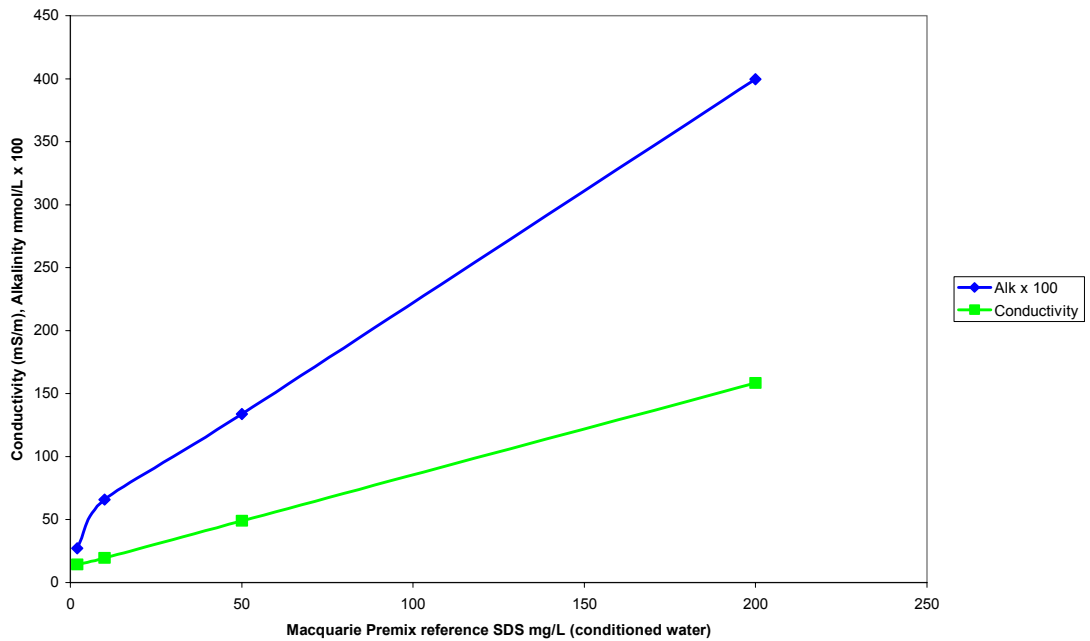
Front Loader		Measurements					
		Raw Readings			Adjusted Readings¹		
Sample	Sample Code	SDBS (mg/L)	Cond. mS/m	Alkalinity mmol/L	SDBS (mg/L)	Cond. mS/m	Alkalinity mmol/L
Conditioned Water (Tap) (Melbourne)	6	1.967	14.5	0.278	0	0	0
Wash Water	9	193.27	230.5	9.443	191.30	216	9.165
Poor Rinse	11	103.92	154.4	7.287	101.95	139.9	7.009
Average Rinse	1	35.40	44.1	2.406	33.43	29.6	2.128
Excellent Rinse	14	15.11	28.5	1.402	13.14	14	1.124

1. Adjusted readings are adjusted for the background levels found in the conditioned (tap) water – tap readings are subtracted from the total reading.

In order to assess the relative readings from these three methods, Macquarie Research mixed up their own samples of reference detergent using laboratory grade raw components as specified in the standard. The three samples were made up in conditioned water at three SDBS concentration levels (10 mg/L, 50 mg/L and 200 mg/L). The results are shown below.

The readings for conductivity and alkalinity showed a remarkable linear correlation with the SDBS concentration for the laboratory samples as mixed by Macquarie Research. This tends to suggest that in a laboratory situation, any of the three methods could be used as the basis for a rinse performance assessment. The results from Table 12 are illustrated in Figure 1 below.

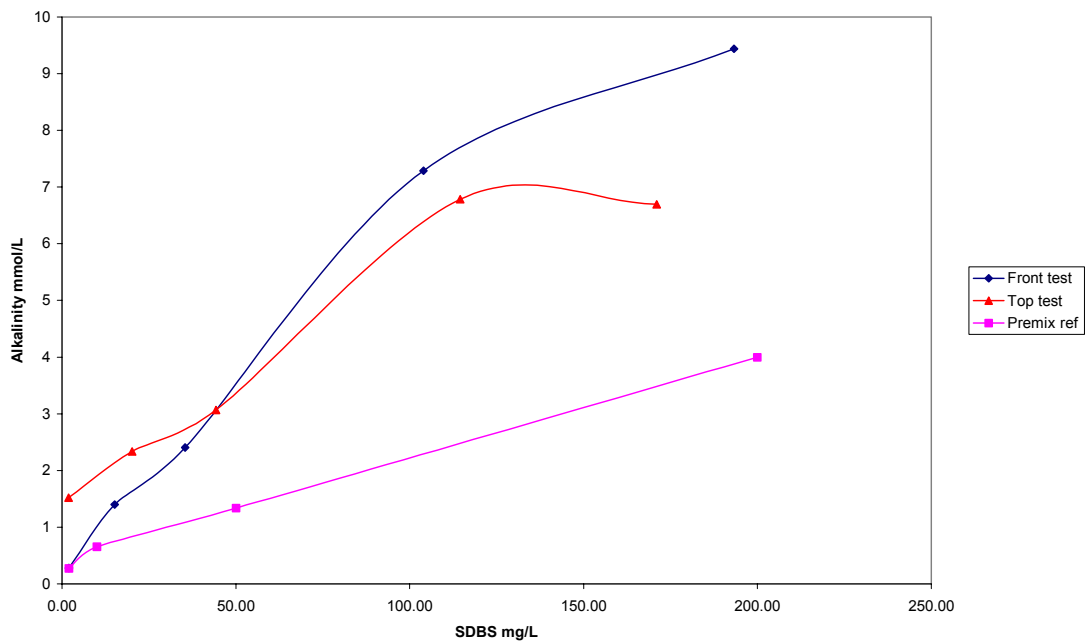
Figure 1: Relationship between SDBS, conductivity and alkalinity – laboratory samples



Note: Alkalinity readings have been multiplied by 100 for illustrative purposes.

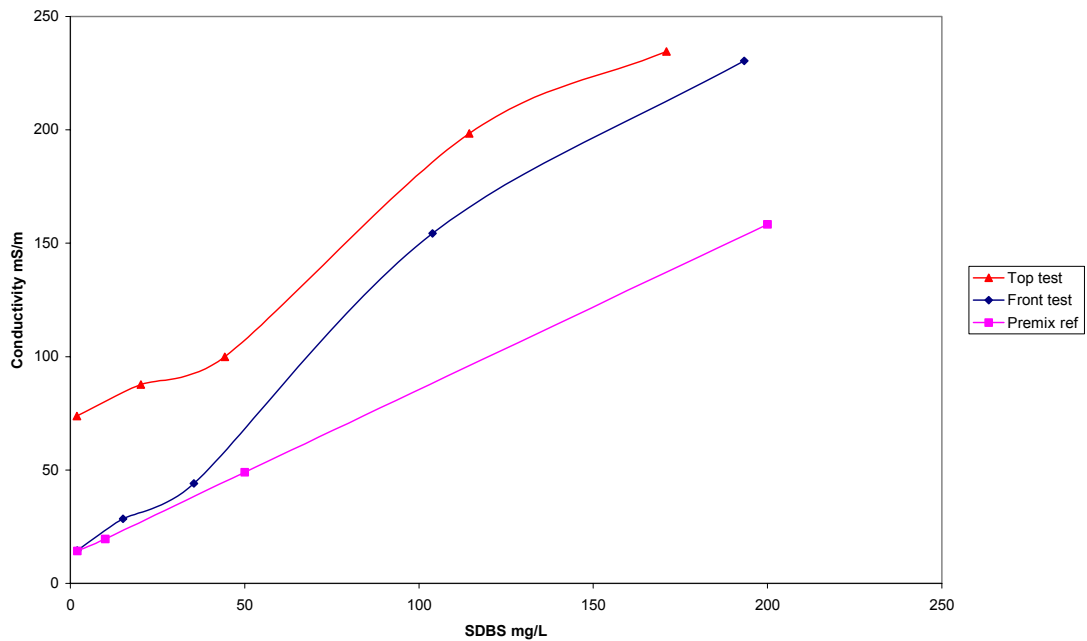
However, when data using laboratory pre-mixed samples is compared against real wash samples from top and front loader tests, the conductivity and alkalinity results become quite erratic when compared to the SDBS readings. These are illustrated below in Figure 2 and Figure 3.

Figure 2: SDBS versus alkalinity for a range of tests



Note: These are raw readings that have not been corrected for source water readings.

Figure 3: SDBS versus conductivity for a range of tests



Note: These are raw readings that have not been corrected for source water readings.

Not only are the effects of the source water evident (the readings for an SDBS value of about 2 mg/L are conditioned water for Sydney (premix), Melbourne (front) and Adelaide (top)), but the effects of the machine, load and swatches for varying detergent concentrations appear to be non-linear in nature, indicating that both conductivity and alkalinity, while giving a very broad indication of rinse performance, are not reliable enough indicators to be used as a rinse performance measure.

Using this data, comparisons were made between the measurements of SDBS and those for conductivity and then alkalinity. These comparisons are presented in graphical form in Figure 4 (Conductivity vs SDBS) and Figure 5 (Alkalinity vs SDBS).

For each of the comparisons a linear trend line was superimposed over the data points. These trend lines were set such that they would pass through the origin. The correlation between the two sets of measurements can be assessed by the comparing the closeness of fit of the data points to the trend line.

Of most concern is the fact that the correlation between the SDBS reading and the conductivity and the alkalinity appears to differ significantly between the front and top load tests.

Figure 4: Conductivity vs SDBS

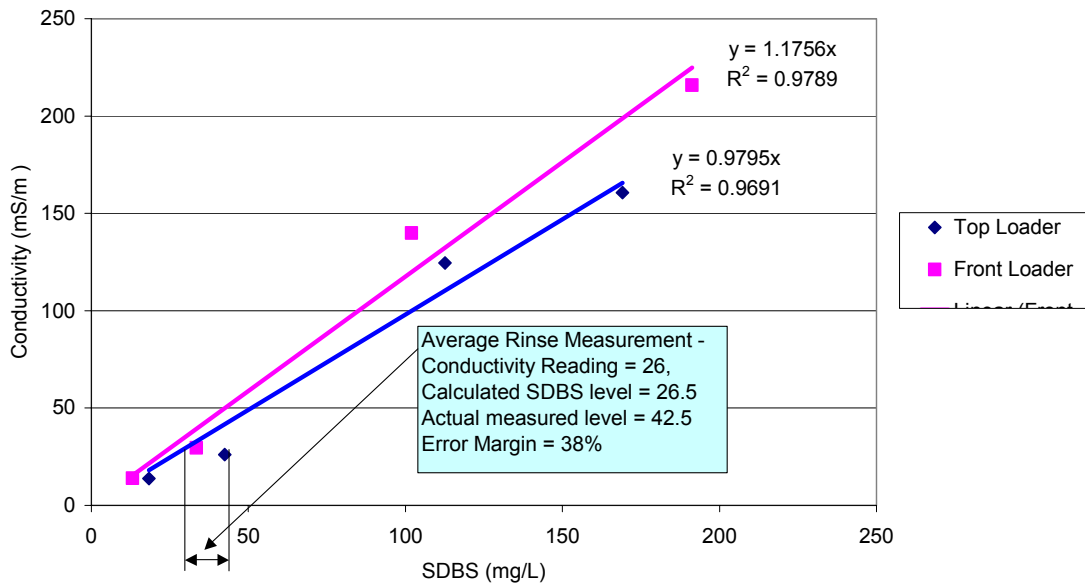
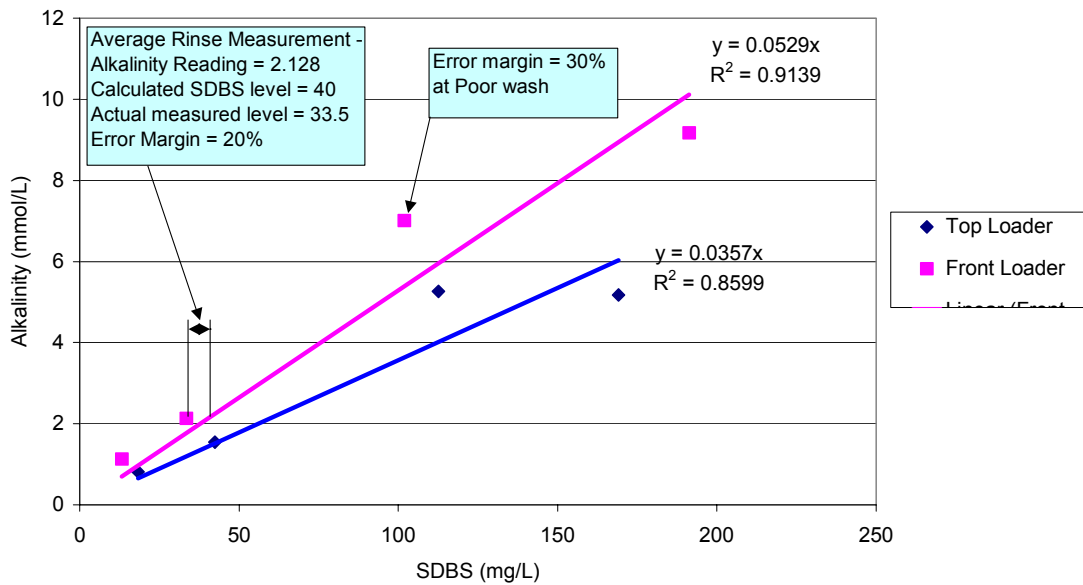


Figure 5: Alkalinity vs SDBS



The exact reasons for the non-linear nature of both alkalinity and conductivity with variations in SDBS concentration under different circumstances (laboratory sample versus top loader versus front loader) is unclear at this stage. It may be useful to gain a better understanding of the key factors which influence these measures, even if just to provide added weight to the recommendation to use SDBS as the primary measure for rinse performance. It would appear that factors such as interactions with the load, soil swatches and interaction with the machine itself appear to have significant impact on the alkalinity and conductivity readings.

The “loss” of a significant proportion of the SDBS during a normal wash operation is yet to be accounted for. It will also be important to understand the factors that are influencing this loss to see whether SDBS concentration remains a valid indicator of “detergent” concentration in the load at the end of the rinse cycle.

6 Recommendations For Further Testing

The following sets out proposals and rationale for limited additional testing associated with the development of a rinse performance requirement in AS/NZS 2040.1.

Stage 1 – gain better understanding of washing processes

It is important to better understand the washing process so that we can account for and understand the changes in the concentration of detergent components during washing. Anecdotal evidence suggests that some SDBS is converted when reacting with soil and that some SDBS may adhere to the load or machine at certain stages during a washing test. Being able to account for SDBS and other detergent components during washing is critical in ensuring that the measure used for rinse performance is indeed a valid parameter.

Initially, discussions with detergent chemists are proposed to gain an improved understanding. One set of tests may be required to track SDBS and other detergent components through the wash and rinse operations. This would involve measuring volume of water into the machine for each operation and taking a sample out for each operation (as well as a volume measurement from the machine at the end of each operation). It is recommended that segmented samples be taken from the final rinse and a separate extraction process be undertaken to ascertain whether there is any change in the concentration of SDBS with reducing levels of water flow from the machine.

Stage 2 – assessing the impact of key parameters

A range of tests are proposed to examine the robustness of the measurement methodology and the impact of various external and internal parameters on the rinse performance result. The key areas to be investigated are:

- Test machine repeatability (are typical machines likely to vary significantly from run to run under an equilibrium test condition?);
- Assess the impact of initial background detergent concentrations in the load on the final rinse performance measure for a particular machine (ie is the

- condition of the load at the start of the test an important parameter to be controlled for consistent results?);
- Does the initial detergent concentration in the wash liquor and the presence of a soil load in the wash have a marked influence on the final rinse performance result?

To assess these issues, a couple of fairly simple tests can be developed.

Machine repeatability and impact of initial SDBS level in the load: A load is washed 10 times in a row with the same program, load, detergent dose and soil swatches to ensure that it is in equilibrium. The final SDBS is determined after each run (this also gives a measure of machine repeatability). A program with a poor rinse performance (say spray rinse) is then run on the machine (the load will be left with a relatively high SDBS level). It is then washed again on the standard program used to establish equilibrium and rinse liquor SDBS concentrations measured. The load is then washed 3 times without soil or detergent (the load will be left with a relatively low SDBS level). It is then washed again on the standard program used to establish equilibrium and rinse liquor SDBS concentrations again measured. Equilibrium results are then compared to the results from the runs with initial high and initial low SDBS levels. The results of these initial tests will have some bearing on how the loads are prepared for the subsequent tests (whether pre-conditioning has a significant impact on rinse performance).

Impact of swatches on rinse performance: To gauge the impact of the soil swatches on the rinse performance measurement, two tests should be conducted using a standard program and detergent dose with and without swatches. A sample of the wash water, the rinse water and extracted water should then be measured for SDBS concentration.

Impact of spin speed on rinse performance: To gauge the impact of spin speed on the rinse performance a series of tests should be undertaken on a single machine. Three identical runs should be conducted except that for each run a different spin speed should be used (say 400rpm, 800rpm and 1500rpm or relevant relative speeds, depending on the machines' size and settings). The concentration and the total mass of SDBS in the rinse liquor and the extracted water should be assessed.

Impact of detergent concentration on rinse performance: To gauge the impact of detergent concentration on the rinse performance a series of tests should be undertaken on a single machine. Three identical runs should be conducted except that for each run a different detergent dose should be used (say 50%, 100% and 150% of the standard dose). Both the concentration and the total mass of SDBS in the rinse liquor should be assessed.

Stage 3 – setting a minimum rinse performance requirement

To make a judgement about a suitable minimum rinse performance requirement, results using the preferred test method will be required on a wide range of clothes washers. This could be achieved by making the rinse performance test a mandatory reportable test for energy labelling applications. Whilst the reporting of the test results would be mandatory, minimum performance levels would not be applied until

sufficient data had been gathered to establish an appropriate level. This could be done in about 2 years from publication of the test method (allowing some time for transition).

Alternatively, a range of representative machines could be tested in a laboratory and the results used to set a rinse performance limit in the short term.

Appendix A – Project Brief

Development of a measure for Rinse Performance in Washing Machines covered by AS 2040.1:1998

OVERVIEW

Standards Australia (working group EL 15/4) is seeking to develop a reliable test method for measuring the rinse performance of washing machines. Such an indicator of machine rinse effectiveness is required for incorporation into AS/NZS 2040. It is needed so existing voluntary and any future mandatory water efficiency rating schemes can be based on pertinent, accurate and reproducible test results.

Existing measures used for measuring rinse performance (eg ANSI/AHAM and IEC) have all depended on measuring concentrations of alkali. All have fallen into disuse because of doubts of their accuracy. At a meeting of the EL 15/4 standards committee in October 2002 it was agreed that an alternative method should be trailed

The recommended method relates to detergent dissolved in the retained water in a wet load (That is at the end of the spin cycle). It depends upon UV spectrophotometry measurement of the concentration of sodium dodecylbenzene sulfonate (SDS) in the aqueous liquor held in the wet load on completion of the program. SDS is the surfactant in AS/NZS wash performance test.

It is believed that tests based on SDS measurement will be significantly more accurate and reproducible than tests based upon measurement of alkalinity. UV spectrophotometry measurement of SDS concentration is more accurate than pH measurement of alkalinity.

To facilitate a measure of rinse performance three factors will need to be determined. These are:

1. The conditioned dry mass of the load.
2. The mass of water retained in the load at the end of a program,
3. The concentration of SDS dissolved in the water retained in a load at the end of a program,

Test Labs currently engaged in wash performance testing to AS 2040.1:1998 already have procedures for determining the first two factors. It is the focus of this contract to develop an acceptable method for determining the third factor

In developing an acceptable method for determining the concentration of SDS the contractor must have regard to the following considerations:

-
- The test should be relatively simple to perform. It should be capable of being performed by laboratory technicians currently engaged in conducting tests to AS 2040.1:1998.
 - The test should not involve hazardous materials such as chloroform. Test labs currently engaged in conducting tests to AS 2040.1:1998 do not have facilities for handling such materials.
 - Test equipment such as the UV spectrophotometer must be reasonably affordable (at least less than \$10,000 but ideally less than \$5,000 AU)
 - It is expected that a resolution of 0.1 ppm in the rinse liquor would be required.
 - Limitations on rinse liquor extraction techniques mean that the quantity of available liquor may be quite small (possibly as low as 20ml in some cases). The developed technique must be capable of providing accurate readings from samples of this size

TESTING REQUIREMENTS

There are two main steps involved in the testing requirements, both these steps are included in the scope of these works.

Step 1 – Development Phase

The contractor shall undertake testing and development as necessary to establish a reliable method for determining the concentration of SDS dissolved in the water retained in a load at the end of a program

The required accuracy of the measurement technique will need to be 0.1 ppm or better within the range 0 to 1 ppm. (Note: Samples of Wash water (see step 2) are likely to have a concentration in the range 1 – 10 ppm, for these samples dilution with 10 parts of distilled water may be required)

Such development would be expected to include (but not necessarily limited to the following:

- Review of available UV spectrophotometry equipment and any modifications that may be required.
- Prepare samples for testing using analytical grade SDS diluted to various levels within the range 0 to 1 ppm¹. As part of the contract, the contractor is to supply the principal with a sealed container with 50g of analytical grade SDS.

¹ Samples should be prepared using conditioned water typically used by test laboratories for conducting rinse performance tests. This water should be tested first to determine if the UV spectrophotometer picks up any background levels of SDS. This water will be supplied upon request from the laboratories of Test Research in Sydney

-
- Conduct tests on prepared samples as a means of refining and verifying the measurement technique. It is expected that the characteristic SDS UV absorption at 223.1nm shall be used to quantify the amount of SDS present using Beer's Law
 - Conduct comparative tests using the following techniques:
 - Alkalinity test in accordance with ISO standard 9963-1 : 1994 Water Quality Determination – Alkalinity – Part 1
 - conductivity
 - ICP Analysis (subject to cost – this is to be separately costed in the tender)

The contractor shall provide advice on suitable extraction techniques for the removal of rinse liquor from washed and spun clothes loads. Advice shall also be provided on suitable methods for sampling, handling, storing and transporting samples to MacQuarie University (for the purposes of completing step 2).

As part of Step 1 the contractor shall conduct tests as necessary to determine if aging of the sample presents any problems in terms of possible degradation of SDS content over time. A sample of water to be supplied from the conditioned water supply of Test Research laboratories in Sydney should be mixed with a sample of the top load detergent (also to be supplied by Test Research in Sydney). The concentration of the SDS should then be measured at the following intervals:

- Within 1 hour
- The following day
- At one week
- At two weeks

Step 2 – Initial Verification Phase

To gauge the accuracy, repeatability and usefulness of the developed measurement technique the contractor shall be supplied with a set of 22 samples (min. 20ml each) to be measured for SDS concentration. The samples to be supplied shall include the following:

1. 5 Samples of supply water (Sydney, Melbourne x 2, Auckland, Adelaide)
2. 2 Samples of water extracted from a reconditioned load soaked in distilled water
3. 2 samples of wash water recovered from actual tests to AS 2040.1 – one from a top loader and one from a front loader (if possible)
4. 2 samples of rinse liquor extracted from an actual test to AS 2040.1 using a cycle designed to give a poor rinse, one from a top loader and one from a front loader

-
5. 2 samples of rinse liquor extracted from an actual test to AS 2040.1 using a cycle designed to give an average rinse, one from a top loader and one from a front loader
 6. 2 samples of rinse liquor extracted from an actual test to AS 2040.1 using a cycle designed to give a good rinse, one from a top loader and one from a front loader
 7. 5 laboratory mixed samples of known concentrations - mixed using distilled water
 8. 5 laboratory mixed samples of known concentration – mixed using conditioned test laboratory water
 9. 5 samples that are duplicate of one or more of the above samples (to test repeatability)

The 30 samples will be identified only by alpha numeric characters (ie a blind test) and results are to be supplied to the project manager using these identifiers.

REPORTING REQUIREMENTS

Two reports are required to be prepared:

A brief report at the end of Step 1 detailing

- the options for equipment to be used and their cost.
- the test procedure developed.
- the accuracy of the measurement.

A complete report at the end of step 2 detailing

- all items covered in the report from step 1.
- the test results from the 30 blind tests conducted.

Appendix B – Sample Schedule

**SCHEDULE OF SAMPLES REQUIRED FOR RINSE PERFORMANCE TEST
DEVELOPMENT – Revision – 05**

Sample Type	Sample No.	Description	Code	Supplied By
Supply Water Samples	1	Conditioned Water as used by Test Research	7	Test Research
	2	Divide the sample into 2 for duplicate testing	5	Test Research
	2a	Distilled Water – Test Research	A	Test Research
	3	Conditioned Water as used by SGS	18	SGS
	3a	Distilled Water - SGS	B	SGS
	4	Conditioned Water as used by VIPAC	6	VIPAC
	4a	Distilled Water - VIPAC	C	VIPAC
	5	Conditioned Water as used by Electrolux	12	Electrolux
	5a	Distilled Water - Electrolux	D	Electrolux
	6	Conditioned Water as used by F & P	23	F & P
	6a	Distilled Water - F & P	E	F & P
Conditioned Load samples	7	Using a conditioned clothes load (5kg) that is relatively new, immerse the load in a container of distilled water for one hour. Remove the wet load and spin dry. Remove the spun load and place in a centrifuge to extract a sample of the remaining liquor	30	VIPAC
	8	Using a conditioned clothes load (5kg) that is relatively old, immerse the load in a container of distilled water for one hour. Remove the wet load and spin dry. Remove the spun load and place in a centrifuge to extract a sample of the remaining liquor.	2	
	9	Divide the sample into 2 for duplicate testing	8	
Samples from a Top loading Machine. A series of wash performance tests to AS/NZS 2040.1 shall be performed on a selected machine and the following samples taken Please record the quantity of wash water and the quantity of detergent added	10	A sample taken from the wash cycle	19	Electrolux
	11	<i>Poor Rinse Sample (using only a spray rinse)</i> A sample of rise liquor extracted using a centrifuge	25	
	12	Divide the sample into 2 for duplicate testing	13	
	13	<i>Average Rinse Sample (using a normal set of spray and deep rinses)</i> A sample of rise liquor extracted using a centrifuge	17	
	14	<i>Excellent Rinse Sample (using a normal set of spray and deep rinses followed by a repeat of the entire set of rinse cycles)</i> A sample of rise liquor extracted using a centrifuge	3	
Samples from a Front loading Machine. (Wascator?) A series of wash performance tests to AS/NZS 2040.1 shall be performed on a selected machine and the following samples taken Please record the quantity of wash water and the quantity of detergent added	15	A sample taken from the wash cycle	9	VIPAC
	16	<i>Poor Rinse Sample (using only a single rinse)</i> A sample of rise liquor extracted using a centrifuge	11	
	17	<i>Average Rinse Sample (using 3 rinse cycles)</i> A sample of rise liquor extracted using a centrifuge	1	
	18	<i>Excellent Rinse Sample (using 6 rinse cycles)</i> A sample of rise liquor extracted using a centrifuge	14	

Sample Type	Sample No.	Description	Code	Supplied By
Prepared - Reference Samples (Distilled Water) To be prepared in a laboratory using distilled water and analytical grade SDS (to be provided)	19	Sample with a concentration of 10 ppm	26	ColgatePalmolive
	20	Sample with a concentration of 20 ppm	29	ColgatePalmolive
	21	Divide the sample into 2 for duplicate testing	4	ColgatePalmolive
	22	Sample with a concentration of 30 ppm	10	ColgatePalmolive
	23	Sample with a concentration of 300 ppm	15	ColgatePalmolive
	24	Divide the sample into 2 for duplicate testing	16	ColgatePalmolive
Prepared - Reference Samples (Lab Water) To be prepared in a laboratory using conditioned test water and analytical grade SDS (to be provided)	25	Sample with a concentration of 10 ppm	20	ColgatePalmolive
	26	Sample with a concentration of 20 ppm	27	ColgatePalmolive
	27	Divide the sample into 2 for duplicate testing	22	ColgatePalmolive
	28	Sample with a concentration of 30ppm	28	ColgatePalmolive
	29	Sample with a concentration of 300 ppm	21	ColgatePalmolive
	30	Divide the sample into 2 for duplicate testing	24	ColgatePalmolive
Distilled Water Sample	30a	Distilled Water – Colgate Palmolive	F	ColgatePalmolive
Conditioned Water Sample	30b	Conditioned Water - Colgate Palmolive	G	ColgatePalmolive

Instructions for taking samples

1. Do not use any PVC products in the sample taking process
2. Sample bottles shall be supplied pre cleaned. Do not re clean
3. Bottles should be filled as close as possible to the top, and the bottle capped (while squeezing the bottle) so as to exclude air at the top. Ideally samples should fill the 125ml bottles supplied. If the sample will not fill the 125ml bottle (applies to samples 7 to 18 only) then a 50ml bottle should be used.
4. Samples should be taken as close to the delivery date (17 June 2003) as possible. If storage is required then this should be in a cool place –preferably a refrigerator.
5. No special packing requirements apply to the samples. Each bottle should be marked with the number (or letter) noted in the schedule under Code.
6. For samples 7 to 18 a spin extractor will need to be used (VIPAC and Electrolux only). For these tests the load should be transferred to the spin extractor and spun until no more liquor can be extracted (say down to less than one drop per minute). If the sample exceeds 125ml use the larger bottle (125ml) if not use the smaller 50ml bottle. Loads should be rinsed and dried as per AS2040.1 between tests.

Samples should be delivered to the following address:

Attn: Dr Christopher McRae
 Building F7B, Room 328
 Department of Chemistry
 Macquarie University, NSW, 2109

Appendix C – Macquarie Research Report

FINAL REPORT

**PREPARED FOR:
ENERGY EFFICIENT STRATEGIES**

**DEVELOPMENT OF A MEASURE
FOR RINSE PERFORMANCE IN
WASHING MACHINES COVERED
BY AS/NZS 2040.1:1998**

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June 2003



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APPENDICES

Appendix A – Test Protocol AM No.03A

Appendix B – UV Spectrophotometer Suppliers, Contact Details

Appendix C – Energy Efficient Strategies Document: Development of a Measure for Rinse Performance in Washing Machines covered by AS 2040.1:1998

1 – REVIEW OF AVAILABLE UV SPECTROPHOTOMETRY EQUIPMENT

To expedite the review of available UV spectrophotometric equipment a request for quotation (RFQ) was made to *www.1800quotes.com.au*. The specifications requested were as per the initial requirements for test instrumentation suggested in the Scope of Works document prepared by Energy Efficient Strategies (see Appendix C), i.e. “Test equipment such as the UV spectrophotometer must be reasonably affordable (at least less than \$10,000 but ideally less than \$5,000)”. Eight responses were obtained, the results of which are summarised in Table 1.

Table 1 - Summary of available UV spectrophotometric equipment available, arranged in order of increasing price (See Appendix B for contact details for the various suppliers).

Manufacturer/Distributor	Model	Price
Rowe Scientific	Labomed Spectro UV-VIS RS	\$ 5,925 ex GST
Biolab	Helios Gamma	\$ 7,098 ex GST
Shimadzu	UV-mini 1240	\$ 7,200 ex GST
Edwards Instruments	Metertech SP-8001	\$ 7,500 ex GST
Radiometer Pacific	Lightwave S2000	\$ 7,999 ex GST
Varian	Cary 50	\$ 11,000 ex GST
Biolab	Helios Beta	\$ 11,191 ex GST
Perkin Elmer	EZ301	\$ 13,500 ex GST
TSE	Cecil 1000 & 2000 series	\$ TBA

A summary of the capabilities of the above instruments and their applicability to the test protocol can be found in Table 2.

Requests were made to each manufacturer/distributors for demonstration machines to enable evaluation of the developed method on their respective instruments. Only Shimadzu and Edwards Instruments supplied instruments and Test Protocol AM No.03A (see Appendix A) was evaluated on both. Section 3.1 of the test protocol (see Appendix A) includes the minimal specifications required of the spectrophotometer to perform the determination. These minimal specifications need to be adhered to if the precision levels stated in section 5.5 of the protocol are to be realised. Both the Shimadzu and Edwards Instruments machines meet the requirements for the test protocol. Of the two, however, the Shimadzu UV-mini 1240 was found to be well suited to the analysis as it had inbuilt facility to do the Absorbance subtraction, specified in section 4.4.3 of the test protocol.

Sipper units were made available for both instruments and the test protocol was evaluated using them. It was found that the use of sipper units is not recommended as they were found to consume too much analyte and often caused foaming of the sample resulting in poor reading reproducibility. Several manufacturers offer DIP probes for their units. Although demonstration units were not able to be obtained for testing, the use of such units would greatly ease the measurement procedure. Unfortunately, they are any expensive option costing approx. \$7000 (on top of the cost of the spectrophotometer).

Reporting capabilities of the machines in this stipulated price range is limited. Varian indicated that they would be prepared to produce a custom package for their spectrophotometer to automate the implementation of this test in an easy to follow procedure with full reporting. However their instrumental offering was by far the most expensive option and exceeded the \$10,000 threshold.

Section 3.2 of the test protocol also specifies the cuvettes required for the test. Biolab Australia (see Appendix B for contact details) can supply both Hellma brand and Starna Brand cuvettes meeting

the specification defined in section 3.2 of the test protocol. Implementing laboratories should obtain both 10.00 mm and 1.00 mm cells. Costs for these cells are approximately \$ 200 ea.

Table 2 - Summary of the pros and cons of the available spectrophotometric equipment available.

Spectrophotometer	Pros	Cons
Shimadzu UV-mini 1240	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Meets or exceeds the specifications of the Test protocol. • Can perform the measurements and calculations specified in the Test Protocol automatically. • Small footprint • Less than \$10,000 • Can be fitted with sipper unit and DIP transmission probe. • Methods and Data can be stored in non-volatile memory. • Has been tested using the Test Protocol. 	<ul style="list-style-type: none"> • Limited reporting capabilities. • Only supports ESC/P printers for output.
Metertech SP-8001	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Meets or exceeds the specifications of the Test protocol. • Small footprint • Less than \$10,000 • Can be fitted with sipper unit. • Can print to a laser printer. • Has been tested using the Test Protocol 	<ul style="list-style-type: none"> • Can not perform the measurements and calculations specified in the Test Protocol automatically. • A DIP transmission probe is not available. • Only methods can be stored in non-volatile memory. • Limited reporting capabilities
Helios Beta	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Meets or exceeds the specifications of the Test protocol. • Can perform the measurements and calculations specified in the Test Protocol automatically. • Methods and Data can be stored in non-volatile memory • Small footprint • Can be fitted with sipper unit. 	<ul style="list-style-type: none"> • More than \$10,000. • A DIP transmission probe is not available. • Limited reporting capabilities
Helios Gamma	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Meets or exceeds the specifications of the Test protocol. • Small footprint • Can be fitted with sipper unit. • Less than \$10,000 	<ul style="list-style-type: none"> • Can not perform the measurements and calculations specified in the Test Protocol automatically. • A DIP transmission probe is not available. • Only methods can be stored in non-volatile memory. • Limited reporting capabilities
Labomed Spectro UV-VIS RS	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Can be fitted with sipper unit. • Cheap 	<ul style="list-style-type: none"> • Does not meet the specifications of the Test protocol. • Cannot perform the measurements and calculations specified in the Test Protocol automatically. • A DIP transmission probe is not available. • No method or data storage capability. • Very limited reporting capabilities • Large footprint

... table continued on next page

Spectrophotometer	Pros	Cons
Perkin Elmer EZ301	<ul style="list-style-type: none"> • Meets or exceeds the specifications of the Test protocol. • Can perform the measurements and calculations specified in the Test Protocol automatically. • Has advanced/unlimited report capability. • Methods and Data can be stored. • Can be fitted with sipper unit and DIP transmission probe. 	<ul style="list-style-type: none"> • More than \$10,000. • Limited reporting capabilities • Requires an external computer for operation. • More than \$10,000 • Large footprint
Cecil 1000 series	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Can be fitted with sipper unit. • Small footprint 	<ul style="list-style-type: none"> • Does not meet the specifications of the Test protocol. • Cannot perform the measurements and calculations specified in the Test Protocol automatically. • A DIP transmission probe is not available. • No method or data storage capability. • Very limited reporting capabilities • Cannot output to a printer.
Cecil 2000 series	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Meets or exceeds the specifications of the Test protocol. • Can perform the measurements and calculations specified in the Test Protocol automatically. • Data and Methods can be stored in non-volatile memory • Small footprint • Can be fitted with sipper unit • Integral Printer 	<ul style="list-style-type: none"> • Price unknown • A DIP transmission probe is not available. • Limited reporting capabilities
Varian Cary 50	<ul style="list-style-type: none"> • Meets or exceeds the specifications of the Test protocol. • Can perform the measurements and calculations specified in the Test Protocol automatically. • Has advanced/unlimited report capability. • Methods and Data can be stored. • Can be fitted with sipper unit and DIP transmission probe. 	<ul style="list-style-type: none"> • Requires an external computer for operation. • More than \$10,000 • Large footprint
Lightwave S2000	<ul style="list-style-type: none"> • Stand alone instrument, does not require a computer. • Meets the specifications of the Test protocol. • Methods and Data can be stored in non-volatile memory. • Very small footprint • Less than \$10,000. 	<ul style="list-style-type: none"> • Cannot perform the measurements and calculations specified in the Test Protocol automatically. • A sipper unit and DIP transmission probe are not available. • Cannot output to a printer. • Limited reporting capabilities

2 – SAMPLING AND SAMPLE TREATMENT

Samples for rinse performance may need to be stored before testing, possibly for periods of up to 2 weeks. Therefore testing was required to determine possible losses of sodium dodecylbenzene sulfonate (SDBS) due to adsorption or bacterial/oxidative degradation. Sample stability testing was evaluated as follows:

MATERIALS AND METHODS

Reference Standard Preparation

A reference standard solution was prepared to match the specifications for “Standard Detergent” as defined by AS/NZS 2040.1. The standard was prepared to contain nominally 1000 mg/L sodium dodecylbenzene sulfonate. This was achieved by quantitatively transferring 1.0012 g sodium dodecylbenzene sulfonate, 2.3043 g sodium tripolyphosphate, 2.9192 g sodium sulfate and 0.7658 g sodium disilicate into a 1 L volumetric flask and making to the mark using purified (18 MΩ/cm resistivity) water. All test solutions used in the reproducibility and repeatability studies were prepared by dilution of this Reference Standard.

Test Solution Preparation

The test solution used for stability testing was prepared by dilution of the Reference Standard as prepared above. 500 mL of 10 mg/L SDBS test solution was prepared by pipetting 10 mL of the 1000 mg/L SDBS “Standard Detergent” Reference Standard into a 1 L volumetric flask, and making to the mark using conditioned water. The conditioned water was supplied by Test Research, Australian Consumers’ Association, Marrickville.

Stability Study

The test solution prepared above was distributed into four clean 100 mL borosilicate glass bottles and four clean 100 mL high density polyethylene (HDPE) bottles. Two of the glass bottles and two of the HDPE bottles were purged of air by bubbling nitrogen through the test solutions for 10 minutes before tightly capping the bottles. The remaining bottles were capped with air remaining inside the bottles. The bottles were then stored as per the following matrix:

Stored at 20 °C	Stored in Refrigerator
Glass bottle, nitrogen purged	Glass bottle, nitrogen purged
Glass bottle, not nitrogen purge	Glass bottle, not nitrogen purge
HDPE bottle, nitrogen purged	HDPE bottle, nitrogen purged
HDPE bottle, not nitrogen purged	HDPE bottle, not nitrogen purged

The remaining test solution was then immediately tested as per test protocol AM No.03A for SDBS concentration. The solutions in the above matrix were tested as per the test protocol at the following time intervals: 24 hours, 7 days, 14 days, 21 days. After testing, the nitrogen purged samples were re-purged with nitrogen before being placed back into the appropriate storage as indicated in the above matrix.

RESULTS AND DISCUSSION

Testing over the period of 21 days revealed that there was no loss of SDBS in any of the storage methods studied or bottle types used. The study does not, however, preclude the possibility of bacterial contamination of the samples, which may result in SDBS degradation/loss. Consequently, regardless of this study's findings, it is recommended that samples for testing be stored in alcohol washed or autoclaved HDPE or borosilicate glass bottles and that the bottles be filled completely and stoppered such that no air remains inside the bottle. Ideally, samples should be analysed immediately after collection, however if this is not possible the samples should be stored in the refrigerator until analysed.

3 – INTERFERENCE TESTING

For the test protocol to be effective, materials other than SDBS that possess strong ultraviolet absorbances must be absent. The effect of possible interferences on the test protocol were evaluated as follows:

MATERIALS AND METHODS

Interference from other components of the Standard Detergent

Possible interference from chloride, tripolyphosphate, sulfate and disilicate ions was evaluated by measuring the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] (as detailed in section 4.4.1 of the test protocol) of concentrations of 0 mg/L, 1 mg/L, 10 mg/L, 50 mg/L, 100 mg/L, 250 mg/L and 1000 mg/L of each of the aforementioned ions. Interference would be considered significant if an increase in the Difference Absorbance of more than 0.004 (i.e. an increase of twice the S/N) above that value obtained for the 0 mg/L blank was found.

Interference from material washed from the AS-9 Test swatches

Possible interference from material washed from the AS-9 test swatches was evaluated by placing a swatch of AS-9 cloth in a bottle with 500 mL of a 250 mg/L solution of sodium dodecyl sulfate. (**Note:** sodium dodecyl sulfate is non UV absorbing at 224 nm). The bottle was then placed in an ultrasonic bath and ultrasonicated for 10 minutes. The Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] of the solution from the bottle was then compared with Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] of original 250 mg/L sodium dodecyl sulfate solution.

RESULTS AND DISCUSSION

Interference from other components of the Standard Detergent

The results from the analysis of possible interfering ions present in standard detergent are summarised in Table 3.

Table 3 - Difference Absorbance versus concentration of possible interfering ions present in standard detergent

Concentration (mg/l)	Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$]			
	Chloride	Tripolyphosphate	Sulfate	Disilicate
0	0.008	0.008	0.004	0.007
1	0.007	0.009	0.004	0.006
10	0.007	0.008	0.004	0.006
50	0.007	0.009	0.005	0.007
100	0.007	0.009	0.006	0.008
250	0.008	0.009	0.006	0.009
1000	0.010	0.013	0.010	0.027

No significant increase (i.e. more than 0.004) in the Difference Absorbance was noted for any of the tested ions solution relative to the blank at concentrations below 250 mg/L. As the possible concentrations for these ions in samples being tested for rinse performance are never likely to be higher than 250 mg/L, interference from the other ions present in standard detergent can be ignored.

Interference from material washed from the AS-9 Test swatches

The results from the analysis of possible interference from material washed from the AS-9 test swatches are summarised in the table below:

Table 4 - Difference Absorbance measurements from the testing a Interferences from AS-9 swatches

Sample	Difference Absorbance [$A_{Diff} = A_{224} - A_{280}$]
Purified water (18M Ω /cm resistivity)	0.011
250 mg/mL sodium dodecyl sulfate (SDS)	0.011
Liquor from 250 mg/mL SDS + AS-9 swatch	0.029

A significant increase of nine times the S/N was noted as a result of material extracted from the AS-9 swatch. While this is a significant increase, it must be born in mind that typical concentrations of the material from the AS-9 swatches with be on the order of 100 times less than in the test liquor used above. Thus, the effect of the material washed from the AS-9 swatches on the analysis using the test protocol is not considered to have a significant impact on the implementation of the test protocol.

4 – ACCURACY AND PRECISION TESTING, LIMITS OF DETECTION/QUANTIFICATION

Accuracy and Precision of the test protocol were evaluated as follows:

MATERIALS AND METHODS

Reference Standard Preparation

A reference standard solution was prepared to match the specifications for “Standard Detergent” as defined by AS/NZS 2040.1. The standard was prepared to contain nominally 1000 mg/L sodium dodecylbenzene sulfonate. This was achieved by quantitatively transferring 1.0012 g sodium dodecylbenzene sulfonate, 2.3043 g sodium tripolyphosphate, 2.9192 g sodium sulfate and 0.7658 g sodium disilicate into a 1 L volumetric flask and making to the mark using purified (18 MΩ/cm resistivity) water. All test solutions used in the reproducibility and repeatability studies were prepared by dilution of this Reference Standard.

Test Solution Preparation

All test solutions used in the accuracy and precision testing regimes were prepared by dilution of the Reference Standard as prepared above. The 10 mg/L, 15 mg/L, 50 mg/L and 200 mg/L SDBS samples used for the repeatability and reproducibility study were prepared by pipetting 1.0 mL, 1.5 mL, 5 mL and 20 mL respectively of the 1000 mg/L SDBS “Standard Detergent” Reference Standard into 100 mL volumetric flasks, and making to the mark using conditioned water. The conditioned water was supplied by Test Research, Australian Consumers’ Association, Marrickville.

Repeatability (Single Analyst) Studies

Repeatability studies were conducted over a period of 5 days. Calibration standards were prepared as detailed in section 4.2 of test protocol AM No.03A (see Appendix A). The calibration standards were prepared at the start of the repeatability study and the same standards were used throughout the period of the study. The 15 mg/mL and 50 mg/mL SDBS test solutions were also prepared at the start of the study by pipetting 1.5 mL and 5 mL respectively of the 1000 mg/L SDBS “Standard Detergent” Reference Standard into 100 mL volumetric flasks, and making to the mark using conditioned water. The conditioned water was supplied by Test Research, Australian Consumers’ Association, Marrickville. The same 15 mg/mL and 50 mg/mL SDBS test solutions were used throughout the period of the study. Both the calibration standards and the 15 mg/mL and 50 mg/mL test solutions were stored in the fridge when not in use.

Repeatability was assessed by taking 2 or 3 measurements a day following Test Protocol AM No.03A (see Appendix A). The same spectrophotometer (Shimadzu UV-mini 1240), analyst and cells were used throughout the repeatability study. Repeatability using the 10.00 mm optical path length cell was performed using the 15 mg/L standard, repeatability using the 1.00 mm optical path length cell was performed using the 50 mg/L standard. Calibration, as detailed in section 4.3 of test protocol AM No.03A, was performed before each measurement cycle.

Reproducibility (Multilaboratory) Studies

Inter laboratory reproducibility was simulated using two different analysts and three different spectrophotometers (Shimadzu UV-mini 1240, Metertek SP-8001, Varian Cary-3) to analyse 15 mg/mL and 50 mg/mL SDBS test solutions using 10.00 mm and 1.00 mm optical path length cells

respectively. The 15 mg/mL and 50 mg/mL SDBS test solutions were prepared at the start of the study by pipetting 1.5 mL and 5 mL respectively of the 1000 mg/L SDBS “Standard Detergent” Reference Standard into 100 mL volumetric flasks, and making to the mark using conditioned water. The same 1.00 mm and 10.00 mm optical path length cells and the same 15 mg/mL and 50 mg/mL SDBS test solutions were used by both analysts.

Reproducibility was assessed by each analyst taking measurements following Test Protocol AM No.03A (see Appendix) using the 10.00 mm optical path length cell for the 15 mg/L standard and the 1.00 mm optical path length cell for the 50 mg/L standard. The measurement was repeated by each analyst for each of the three spectrophotometers. Before each measurement on each of the three spectrophotometers, each analyst prepared fresh calibration standards (as detailed in section 4.2 of test protocol AM No.03A - see Appendix A) and performed the calibration procedure detailed in section 4.3 of test protocol AM No.03A.

RESULTS AND DISCUSSION

Repeatability (Single Analyst)

The results from the repeatability (single analyst) are presented in Table 5.

Table 5 - Data from Repeatability (Single Analyst) study. The concentrations of SDBS presented in the table were calculated using the procedure outlined in section 4.4.3 of Test Protocol AM No.03A

Sample	Measured SDBS in 15 mg/L standard – 10.00 mm cell (mg/L)	Measured SDBS in 50 mg/L standard – 1.00 mm cell (mg/L)
Day 1 – Measurement 1	15.099	50.476
Day 1 – Measurement 2	15.082	51.033
Day 1 – Measurement 3	15.074	51.014
Day 2 – Measurement 1	15.167	50.743
Day 2 – Measurement 2	15.160	50.871
Day 3 – Measurement 1	15.032	50.743
Day 3 – Measurement 2	15.112	50.532
Day 3 – Measurement 3	15.143	51.033
Day 4 – Measurement 1	15.046	50.731
Day 4 – Measurement 2	15.009	51.615
Day 4 – Measurement 3	15.213	50.710
Day 5 – Measurement 1	15.220	50.871
Day 5 – Measurement 2	15.154	50.989
Average	15.116	50.874
Standard Deviation	0.067	0.287

The concentrations of SDBS presented in the above table were calculated using the procedure outlined in section 4.4.3 of test protocol AM No.03A. Based on the experimental results presented in Table 5 the estimated single analyst precision (at 95 % confidence level, $t_{0,025,12} = 2.179$) is ± 0.97 % using a 10.00 mm optical path length cell, and ± 1.2 % using a 1.00 mm optical path length cell.

Reproducibility (Multilaboratory) Studies

The results from the reproducibility (interlaboratory) study are presented in Table 6.

Table 6 - Data from Reproducibility (Interlaboratory) study. The concentrations of SDBS presented in the table were calculated using the procedure outlined in section 4.4.3 of Test Protocol AM No.03A. Spectrophotometer 1 was a Shimadzu UV-mini 1240, Spectrophotometer 2 was a Metertek SP8001, Spectrophotometer 3 was a Varian Cary 3.

Sample	Measured SDBS in 15 mg/L standard – 10.00 mm cell (mg/L)	Measured SDBS in 50 mg/L standard – 1.00 mm cell (mg/L)
Analyst 1 – Spectrophotometer 1	14.915	49.437
Analyst 2 – Spectrophotometer 1	15.079	49.815
Analyst 1 – Spectrophotometer 2	14.871	50.413
Analyst 2 – Spectrophotometer 2	15.460	49.698
Analyst 1 – Spectrophotometer 3	15.117	51.785
Analyst 2 – Spectrophotometer 3	15.441	51.648
Average	15.147	50.466
Standard Deviation	0.253	1.020

Based on the experimental results presented in Table 6 the estimated interlaboratory precision (at 95 % confidence level, $t_{0.025,5} = 2.571$) is ± 4.3 % using a 10.00 mm optical path length cell, and ± 5.2 % using a 1.00 mm optical path length cell.

Limits of Detection and Quantification

The Limit of Detection (LOD) and Limit of Quantification (LOQ) as defined by this study were determined using the following definitions:

$$\text{LOD: } y_{lod} = y_{blank} + 3s_y$$

$$\text{LOQ: } y_{loq} = y_{blank} + 10s_y$$

where,

y_{lod} and y_{loq} are the Difference Absorbance [$A_{Diff} = A_{224} - A_{280}$] signals (as detailed in section 4.4.1 of the test protocol) at the LOD and LOQ respectively.

s_y is the residual standard deviation measured from the linear regression data used to general calibration plots (as detailed in section 4.4.3 of the test protocol).

The LOD and LOQ when using the 10.00 mm optical path length cell was derived from seven sets of calibration data. Each set of calibration data comprised at least 14 discrete measurements in the calibration range defined by section 4.3.1 of the test protocol.

The LOD and LOQ when using the 10.00 mm optical path length cell were found to be (0.45 ± 0.12) mg/L SDBS and (1.46 ± 0.18) mg/L SDBS respectively.

The LOD and LOQ when using the 1.00 mm optical path length cell was derived from nine sets of calibration data. Each set of calibration data comprised at least 14 discrete measurements in the calibration range defined by section 4.3.2 of the test protocol.

The LOD and LOQ when using the 1.00 mm optical path length cell were found to be (1.34 ± 0.13) mg/L SDBS and (4.46 ± 0.23) mg/L SDBS respectively.

5 – INITIAL VERIFICATION SAMPLE MEASUREMENTS

To gauge the accuracy, repeatability and usefulness of the developed protocol, a set of 30 samples were supplied by the Principal to be measured for sodium dodecylbenzene sulfonate (SDBS) concentration. The results of those analyses are present in the following table:

Sample	Description	SDBS (mg/L)
1 *	Average Rinse (25-75?)	33.43 ± 0.51
2 #	0-5	9.284 ± 0.090
3 #	Excellent Rinse (10-50?)	18.36 ± 0.18
4 #	between 1 and 20	19.70 ± 0.19
5 #	0-5	0.062 ± 0.099
6 #	Conditioned Water	1.967 ± 0.033
7 #	Conditioned Water	2.566 ± 0.061
8 #	0-5	9.113 ± 0.088
9 *	Wash (150-300)	191.3 ± 1.8
10 *	between 20 and 50	30.16 ± 0.54
11 *	Poor Rinse (50-200?)	101.95 ± 0.94
12 #	Conditioned Water	1.850 ± 0.027
13 *	Poor Rinse (50-200?)	111.8 ± 1.8
14 #	Excellent Rinse (10-50?)	13.14 ± 0.13
15 *	between 250 and 350	299.0 ± 1.4
16 *	between 250 and 350	299.8 ± 1.3
17 *	Average Rinse (25-75?)	42.42 ± 0.51
18 #	Conditioned Water	1.72 ± 0.14
19A *	Wash (150-300)	173.4 ± 2.1
19B *	Wash (150-300)	173.7 ± 2.1
19C *	Wash (150-300)	160.4 ± 1.9
20 #	between 1 and 20	9.858 ± 0.096
21 *	between 250 and 350	289.8 ± 3.5
22 #	between 1 and 20	19.58 ± 0.19
24 *	between 250 and 350	290.2 ± 3.5

.....table continued on next page

Sample	Description	SDBS (mg/L)
25 *	Poor Rinse (50-200?)	112.6 ± 2.2
26 #	between 1 and 20	9.999 ± 0.097
27 #	between 1 and 20	19.47 ± 0.19
28 *	between 20 and 50	30.46 ± 0.37
29 #	between 1 and 20	19.70 ± 0.19
30 #	0-5	14.75 ± 0.14
A #	Distilled Water	0.90 ± 0.22
B #	Distilled Water	0.700 ± 0.025
C #	Distilled Water	0.254 ± 0.019
D #	Distilled Water	0.135 ± 0.050
F #	Distilled Water	0.212 ± 0.037
G #	Conditioned Water	2.550 ± 0.027

Comments:

Sodium dodecylbenzene sulfonate concentration was determined using Test Protocol AM No.03A (see Appendix) using both 1.00 mm (as signified by a superscripted * next to the sample code) and 10.00 mm (as signified by a superscripted # next to the sample code) optical path length cells. The results presented are the mean value from 5 replicate measurements. The quoted error is the 95% confidence limit, based on 4 degrees of freedom and $t_{0.025,4} = 2.776$. Based on the calibration data for the measurements (using $y_{loq} = y_{blank} + 10s_y$), the limit of quantification (LOQ) for measurements using the 1.00 mm optical path length cell is 4.5 mg/L and 1.5 mg/L for measurements using the 10.00 mm optical path length cell. Values in the above table that fall below the appropriate LOQ may be considerably less accurate than the 95% confidence interval may imply.

6 – CONDUCTIVITY AND ALKALINITY MEASUREMENTS

For comparative testing purposes, analysis of select samples was also performed by Conductivity and Total Alkalinity (as defined by ISO 9963-1:1994). Test samples examined were of the Reference Standard made to 10 mg/L, 50 mg/L and 200 mg/L SDBS (for details of sample preparation refer to “Test Solution Preparation” in Section 4 – Accuracy and Precision Testing, Limits of Detection/Quantification on page 3) and a choice (as specified by Robert Foster, Energy Efficient Strategies) of samples supplied to this study by Energy Efficient Strategies. The results of these tests are summarised in Table 7 and Table 8 below:

Table 7 - Conductivity and Total Alkalinity measurements of test solutions of synthetic "Standard Detergent"

Description	Conductivity @ 25 °C (mS/m)	Total Alkalinity (mmol/L)
10 mg/mL SDBS "Standard Detergent" test solution	19.5 ± 0.2	0.658 ± 0.012
50 mg/mL SDBS "Standard Detergent" test solution	49.0 ± 0.2	1.339 ± 0.018
200 mg/mL SDBS "Standard Detergent" test solution	158.4 ± 0.6	3.995 ± 0.043
Conditioned Water (Test Research, ACA/Choice Labs)	14.4 ± 0.1	0.273 ± 0.009

Table 8 - Conductivity and Total Alkalinity measurements of samples supplied by Energy Efficient Strategies.

Sample	Description	Conductivity @ 25 °C (mS/m)	Total Alkalinity (mmol/L)
1	Average Rinse	44.1 ± 0.2	2.406 ± 0.028
3	Excellent Rinse	87.7 ± 0.2	2.338 ± 0.028
6	Conditioned Water	14.5 ± 0.1	0.278 ± 0.008
9	Wash	230.5 ± 1.0	9.443 ± 0.094
11	Poor Rinse	154.4 ± 0.4	7.287 ± 0.074
12	Conditioned Water	73.9 ± 0.2	1.521 ± 0.02
14	Excellent Rinse	28.5 ± 0.2	1.402 ± 0.019
17	Average Rinse	99.9 ± 0.4	3.065 ± 0.034
19A	Wash	234.5 ± 1.0	6.697 ± 0.068
25	Poor Rinse	198.4 ± 0.4	6.787 ± 0.07

Comments:

Total Alkalinity was determined by potentiometric titration as per ISO Standard 9961-1:1994 using 0.02 M HCl titrant and 20 mL sample volume. The results are expressed as Total Alkalinity titratable to pH 4.5 and are the mean result of triplicate analyses. The quoted error is the 95% confidence limit, based on 2 degrees of freedom and $t_{0.025,2} = 4.303$

Conductivity was determined using a TPS Model LC-84 conductivity meter. The meter was calibrated to 140.9 mS/m @ 25.00 °C using a 0.0100 M KCl conductivity standard. All conductivities were measured at 25.00 °C. The results are presented as the mean result of triplicate analyses. The quoted error is the 95% confidence limit, based on 2 degrees of freedom and $t_{0.025,2} = 4.303$.

APPENDIX A

Test Protocol AM No. 03A

Department of Chemistry, Macquarie University	AM No. 03A
Test Method for the Determination of Sodium Dodecylbenzene Sulfonate in Aqueous Detergent Solutions by Ultraviolet Absorption.	Page 1 of 4

1.0. Scope and Purpose

To outline a procedure to determine the concentration of sodium dodecylbenzene sulfonate (SDBS) in aqueous detergent solutions. Principally, the method will be used to determine the concentration of SDBS in both the wash water and the water retained in the load at the end of a wash program as defined by AS/NZS test method AS 2040.1:1998.

2.0. Summary of Test Method

This test procedure employs the measurement of the absorbance of ultraviolet light by a sample water at the absorbance maxima for sodium dodecylbenzene sulfonate (224 nm) and at a background point of 280 nm. The measurement of a background point at 280 nm enables correction for background absorbance due to turbid samples. The concentration of sodium dodecylbenzene sulfonate (SDBS) present in the sample water is calculated from the above absorbances and data obtained from solutions of known SDBS concentration.

3.0. Apparatus and Reagents

3.1 Spectrophotometer

The spectrophotometer must be suitably equipped for measurements of liquid samples in the ultraviolet region (specifically 224 nm). Minimum configuration for liquid handling must include a cell holder for 10 mm quartz cells. Either single beam or dual beam instruments may be used for this test, however the instrument must have a photometric repeatability of at least ± 0.002 Abs at 0.5 Abs for readings at 224 nm and 280 nm. The instrument must also have a wavelength accuracy and repeatability of at least ± 1.0 nm and ± 0.5 nm respectively with a spectral bandwidth of not more than 5 nm.

3.2 Spectrophotometer Cells

All cells used in this procedure must be made of quartz with better than 80% transmission at 200 nm. The optical path length for the cell used will depend on the concentrations to be measured. Use the appropriate path length for the concentrations indicated. For 1 mg/L to 25 mg/L SDBS solutions use a 10.00 mm path length cell, for 10 mg/L to 250 mg/L SDBS solutions use a 1.00 mm path length cell. Typically, the 1.00 mm optical path length cell can be used for most analyses.

3.3 Reagents and Glassware

Purified water (18M Ω /cm resistivity)
 One (1) 1 L volumetric flask
 Five (5) 100 mL volumetric flasks

4.0 Procedure

4.2. Preparation of Standard Solutions

4.2.1 SDBS stock standard solution (1000 mg/L)

Quantitatively transfer 1.000 g sodium dodecylbenzene sulfonate (SDBS) into a 1 L volumetric flask. Add 500 mL purified water and mix gently to dissolve. Avoid vigorous shaking as this

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results in frothing. When all solid has dissolved, make to the mark using purified water and mix thoroughly. This solution may be stored in the fridge in an airtight container for up to 4 weeks.

4.2.2 Working Standard solutions for Sample working range 10-250 mg/L SDBS

Prepare the following working standards by pipetting the indicated amount of the 1000 mg/L SDBS solutions into a 100 mL volumetric flask. Make up to the mark using the purified water and mix thoroughly.

	Volume of 1000 mg/L SDBS to add to 100 mL volumetric flask
Standard 1 (10 mg/L)	1 mL
Standard 2 (20 mg/L)	2 mL
Standard 3 (50 mg/L)	5 mL
Standard 4 (100 mg/L)	10 mL
Standard 5 (250 mg/L)	25 mL

4.2.3 Working Standard solutions for Sample working range 1-25 mg/L SDBS

Prepare a 100 mg/L SDBS solution by pipetting 10 mL of 1000 mg/L SDBS solution into a 100 mL volumetric flask. Make up the mark using the purified water. Use this 100 mg/L SDBS solution for the following standards by pipetting the indicated amount of the 100 mg/L SDBS standard into a 100 mL volumetric flask. Make up to the mark using the purified water and mix thoroughly.

	Volume of 100 mg/L SDBS to add to 100 mL volumetric flask
Standard 1 (1 mg/L)	1 mL
Standard 2 (2 mg/L)	2 mL
Standard 3 (5 mg/L)	5 mL
Standard 4 (10 mg/L)	10 mL
Standard 5 (25 mg/L)	25 mL

4.3. Calibration Procedure

4.3.1 For Sample working range 1-25 mg/L SDBS

Using a 10 mm optical path length cell filled with purified water, measure the absorbance at 224 nm (A_{224}) and 280 nm (A_{280}). Calculate the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] and record this value as 0 mg/L SDBS. For each of the Standards 1-5 (from section 3.2.3) measure the absorbance at 224 nm and 280 nm, calculating and recording the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] for each.

4.3.2 For Sample working range 10-250 mg/L SDBS

Using a 1 mm optical path length cell filled with purified water, measure the absorbance at 224 nm (A_{224}) and 280 nm (A_{280}). Calculate the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] and record this value as 0 mg/L SDBS. For each of the Standards 1-5 (from section 4.2.2) measure

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the absorbance at 224 nm and 280 nm, calculating and recording the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] for each.

4.3.3 Calculation of Calibration Parameters

Using the data from either 3.3.1 or 3.3.2, calculate a linear regression with offset from the recorded data. Use the calculation formulae given in the Appendix X.1 for $y=mx + b$ determine values for the slope (m) and intercept (b). Alternately use the regression functions of a spreadsheet to determine slope and intercept. The x,y pairs to be used for the regression are the concentration of SDBS (x) and the Difference Absorbance (y). **Visually** confirm there is a linear correlation with concentration by plotting Concentration vs. Difference Absorbance. A coefficient of determination (r^2) of better than 0.99 should be obtained.

4.4. Determination of SDBS in sample water

4.4.1 For Sample working range 1-25 mg/L SDBS

4.4.1.1 – Using a 10.00 mm optical path length cell filled with conditioned water (or whatever water was used to make up the sample), measure the absorbances at 224 nm (A_{224}) and 280 nm (A_{280}). Calculate the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] and record this value as A_{Cond} . Repeat the measurement in triplicate (by discarding cell contents and refilling) or until variations in A_{Cond} between replicates are not more than ± 0.002 AU from the average.

4.4.1.2 – Using the same 10.00 mm optical path length cell used in 4.4.1.1, measure the absorbances at 224 nm (A_{224}) and 280 nm (A_{280}) for the sample. Calculate the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] and record this value as A_{Samp} . Repeat the measurement in triplicate (by discarding cell contents and refilling) or until variations in A_{Samp} between replicates are not more than ± 0.002 AU from the average. The observed absorbance readings should not be greater than 1.0. If sample absorbance is greater than 1.0, then you need to use a 1.00 mm cell. You will need to recalibrate (as directed in 4.3.2) using the 1.00 mm cell, and proceed as directed in 4.4.2.

4.4.2 For Sample working range 10-250 mg/L SDBS

4.4.2.1 – Using a 1.00 mm optical path length cell filled with conditioned water (or whatever water was used to make up the sample), measure the absorbances at 224 nm (A_{224}) and 280 nm (A_{280}). Calculate the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] and record this value as A_{Cond} . Repeat the measurement in triplicate (by discarding cell contents and refilling) or until variations in A_{Cond} between replicates are not more than ± 0.002 AU from the average.

4.4.2.2 – Using the same 10.00 mm optical path length cell used in 4.4.2.1, measure the absorbances at 224 nm (A_{224}) and 280 nm (A_{280}) for the sample. Calculate the Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] and record this value as A_{Samp} . Repeat the measurement in triplicate (by discarding cell contents and refilling) or until variations in A_{Samp} between replicates are not more than ± 0.002 AU from the average. The observed absorbance readings should not be greater than 1.0. If sample absorbance is greater than 1.0, then you need to dilute the sample to a known volume using conditioned water (or whatever water was used to make up the sample).

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4.4.3 Calculation of SDBS concentration

Calculate the concentration of sodium dodecylbenzene sulfonate in the sample water as follows:

$$\text{SDBS Concentration, mg / L} = \frac{A_{\text{Samp}} - A_{\text{Cond}} - b}{m}$$

where, A_{Samp} = Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] of sample water
 A_{Cond} = Difference Absorbance [$A_{\text{Diff}} = A_{224} - A_{280}$] of conditioned water
 m = value for slope, calculated as directed in 4.3.3
 b = value for intercept, calculated as directed in 4.3.3

5.5. Precision

5.5.1 Repeatability (Single Analyst)

Based on experimental results from duplicate determinations by the same analyst on different days, the estimated precision (at 95 % confidence level, 12 df.) is ± 0.97 % using a 10.00 mm optical path length cell, and ± 1.2 % using a 1.00 mm optical path length cell.

5.5.2 Repeatability (Interlaboratory)

Based on experimental results, the interlaboratory precision of this method is statistically estimated (at 95 % confidence level, 4 df.) to be ± 4.3 % using a 10.00 mm optical path length cell, and ± 5.2 % using a 1.00 mm optical path length cell.

5.5.2 Limit of Quantification

Based on experimental results, the limit of quantification (LOQ) for the method using a 10.00 mm optical path length cell is 1.5 mg/L SDBS. The LOQ for the method using a 1.00 mm optical path length cell is 4.5 mg/L SDBS.

X.0 Appendices (Non-mandatory Information)

X.1. Linear Regression

A linear calibration line is described by the equation $y = mx + b$, where:

$$\text{Slope } m = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sum (x - \bar{x})^2} \text{ or } \frac{S_{xy}}{S_{xx}}$$

$$\text{Intercept } b = \bar{y} - b\bar{x}$$

The coefficient of determination (r^2) can be determined thus:

$$\text{Coefficient of Determination, } r^2 = \left(\frac{S_{xy}}{\sqrt{S_{xx}S_{yy}}} \right)^2$$

where

$$S_{xx} = \sum (x - \bar{x})^2$$

$$S_{yy} = \sum (y - \bar{y})^2$$

$$S_{xy} = \sum (x - \bar{x})(y - \bar{y})$$

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APPENDIX B

UV Spectrophotometer Suppliers

Contact Details

BIOLAB (Aust) LTD
2 Clayton Road, Clayton, VIC, 3168
Tel: 1300 735 292 Fax: 1800 067 639

EDWARDS INSTRUMENT CO
15 Bellingham Street, Narellan, NSW, 2567
Tel: (02) 9820 2122 Fax: (02) 4647 1444

RADIOMETER PACIFIC PTY LTD
Unit 2, 277 Lane Cove Road, North Ryde, NSW, 2113
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APPENDIX C

Scope of Works

Document prepared by Energy Efficient Strategies

Development of a measure for Rinse Performance in Washing Machines covered by AS 2040.1:1998

OVERVIEW

Standards Australia (working group EL 15/4) is seeking to develop a reliable test method for measuring the rinse performance of washing machines. Such an indicator of machine rinse effectiveness is required for incorporation into AS/NZS 2040. It is needed so existing voluntary and any future mandatory water efficiency rating schemes can be based on pertinent, accurate and reproducible test results.

Existing measures used for measuring rinse performance (eg ANSI/AHAM and IEC) have all depended on measuring concentrations of alkali. All have fallen into disuse because of doubts of their accuracy. At a meeting of the EL 15/4 standards committee in October 2002 it was agreed that an alternative method should be trailed

The recommended method relates to detergent dissolved in the retained water in a wet load (That is at the end of the spin cycle). It depends upon UV spectrophotometry measurement of the concentration of sodium dodecylbenzene sulfonate (SDS) in the aqueous liquor held in the wet load on completion of the program. SDS is the surfactant in AS/NZS wash performance test.

It is believed that tests based on SDS measurement will be significantly more accurate and reproducible than tests based upon measurement of alkalinity. UV spectrophotometry measurement of SDS concentration is more accurate than pH measurement of alkalinity.

To facilitate a measure of rinse performance three factors will need to be determined. These are:

1. The conditioned dry mass of the load.
2. The mass of water retained in the load at the end of a program,
3. The concentration of SDS dissolved in the water retained in a load at the end of a program,

Test Labs currently engaged in wash performance testing to AS 2040.1:1998 already have procedures for determining the first two factors. It is the focus of this contract to develop an acceptable method for determining the third factor

In developing an acceptable method for determining the concentration of SDS the contractor must have regard to the following considerations:

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- The test should be relatively simple to perform. It should be capable of being performed by laboratory technicians currently engaged in conducting tests to AS 2040.1:1998.
 - The test should not involve hazardous materials such as chloroform. Test labs currently engaged in conducting tests to AS 2040.1:1998 do not have facilities for handling such materials.
 - Test equipment such as the UV spectrophotometer must be reasonably affordable (at least less than \$10,000 but ideally less than \$5,000 AU)
 - It is expected that a resolution of 0.1 ppm in the rinse liquor would be required.
 - Limitations on rinse liquor extraction techniques mean that the quantity of available liquor may be quite small (possibly as low as 20ml in some cases). The developed technique must be capable of providing accurate readings from samples of this size

TESTING REQUIREMENTS

There are two main steps involved in the testing requirements, both these steps are included in the scope of these works.

Step 1 – Development Phase

The contractor shall undertake testing and development as necessary to establish a reliable method for determining the concentration of SDS dissolved in the water retained in a load at the end of a program

The required accuracy of the measurement technique will need to be 0.1 ppm or better within the range 0 to 1 ppm. (Note: Samples of Wash water (see step 2) are likely to have a concentration in the range 1 – 10 ppm, for these samples dilution with 10 parts of distilled water may be required)

Such development would be expected to include (but not necessarily limited to the following:

- Review of available UV spectrophotometry equipment and any modifications that may be required.
- Prepare samples for testing using analytical grade SDS diluted to various levels within the range 0 to 1 ppm¹. As part of the contract, the contractor is to supply the principal with a sealed container with 50g of analytical grade SDS.

¹ Samples should be prepared using conditioned water typically used by test laboratories for conducting rinse performance tests. This water should be tested first to determine if the UV spectrophotometer picks up any background levels of SDS. This water will be supplied upon request from the laboratories of Test Research in Sydney

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- Conduct tests on prepared samples as a means of refining and verifying the measurement technique. It is expected that the characteristic SDS UV absorption at 223.1nm shall be used to quantify the amount of SDS present using Beer's Law
 - Conduct comparative tests using the following techniques:
 - Alkalinity test in accordance with ISO standard 9963-1 : 1994 Water Quality Determination – Alkalinity – Part 1
 - conductivity
 - ICP Analysis (subject to cost – this is to be separately costed in the tender)

The contractor shall provide advice on suitable extraction techniques for the removal of rinse liquor from washed and spun clothes loads. Advice shall also be provided on suitable methods for sampling, handling, storing and transporting samples to MacQuarie University (for the purposes of completing step 2).

As part of Step 1 the contractor shall conduct tests as necessary to determine if aging of the sample presents any problems in terms of possible degradation of SDS content over time. A sample of water to be supplied from the conditioned water supply of Test Research laboratories in Sydney should be mixed with a sample of the top load detergent (also to be supplied by Test Research in Sydney). The concentration of the SDS should then be measured at the following intervals:

- Within 1 hour
- The following day
- At one week
- At two weeks

Step 2 – Initial Verification Phase

To gauge the accuracy, repeatability and usefulness of the developed measurement technique the contractor shall be supplied with a set of 22 samples (min. 20ml each) to be measured for SDS concentration. The samples to be supplied shall include the following:

1. 5 Samples of supply water (Sydney, Melbourne x 2, Auckland, Adelaide)
2. 2 Samples of water extracted from a reconditioned load soaked in distilled water
3. 2 samples of wash water recovered from actual tests to AS 2040.1 – one from a top loader and one from a front loader (if possible)
4. 2 samples of rinse liquor extracted from an actual test to AS 2040.1 using a cycle designed to give a poor rinse, one from a top loader and one from a front loader

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5. 2 samples of rinse liquor extracted from an actual test to AS 2040.1 using a cycle designed to give an average rinse, one from a top loader and one from a front loader
 6. 2 samples of rinse liquor extracted from an actual test to AS 2040.1 using a cycle designed to give a good rinse, one from a top loader and one from a front loader
 7. 5 laboratory mixed samples of known concentrations - mixed using distilled water
 8. 5 laboratory mixed samples of known concentration – mixed using conditioned test laboratory water
 9. 5 samples that are duplicate of one or more of the above samples (to test repeatability)

The 30 samples will be identified only by alpha numeric characters (ie a blind test) and results are to be supplied to the project manager using these identifiers.

REPORTING REQUIREMENTS

Two reports are required to be prepared:

A brief report at the end of Step 1 detailing

- the options for equipment to be used and their cost.
- the test procedure developed.
- the accuracy of the measurement.

A complete report at the end of step 2 detailing

- all items covered in the report from step 1.
- the test results from the 30 blind tests conducted.