

Reliability of test methods for metallic products - Final Report to the Drinking Water Inspectorate

*Final Report to the Department for Environment, Food
and Rural Affairs*

**RELIABILITY OF TEST METHODS FOR METALLIC PRODUCTS - FINAL
REPORT TO THE DRINKING WATER INSPECTORATE**

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RELIABILITY OF TEST METHODS FOR METALLIC PRODUCTS - FINAL REPORT TO THE DRINKING WATER INSPECTORATE

EXECUTIVE SUMMARY

I Benefits

The development of a short term laboratory procedure to test a metal's acceptability for use with drinking water would minimise the costs involved as well as facilitate the development of new alloys or the determination of limitations on use based on water compositions of established alloys.

II Objectives

1. To Pilot and Round Robin test a variant of the test procedure used in the first Round Robin i.e. using disposal plastic centrifuge tubes as the reaction vessels and a more stringent control of temperature.
2. To develop a statistical based method to determine the outcome of a test.

III Reasons

The results of the first Round Robin test (see WRc-NSF report DWI 4079 July 2002) showed the good intra-laboratory and poor inter-laboratory reproducibility observed in previous studies. Significant correlations between the concentrations of metals leached were observed a possible interpretation of which was competition for the dissolved oxygen in the test water. To test this idea, a procedure was devised using closed test tubes as the reaction vessels. By using disposable plastic centrifuge tubes, the new procedure also significantly reduced the cost of testing.

Although the Pilot established that the original ideas as to the cause of the correlations between the concentrations of metal leached was not correct, it was decided that a limited second Round Robin test of the new procedure would be of value.

IV Conclusions

1. This work has developed a test procedure, based on plastic centrifuge tubes as the reaction vessels, that significantly increases the practical convenience and significantly reduces the cost of carrying out the testing of metals.
2. Strong correlations have been found between the concentrations of the major elements, i.e. copper, lead and zinc, that leach from the copper alloys. All show an exponential increase in concentration with time in the leachate water.
3. The amount of metal leached showed little sensitivity to the depth of immersion of the test coupon, suggesting little sensitivity to the level of dissolved oxygen in the test water. This in turn suggests that the contamination level achieved cannot be under the simple control of the alloy corrosion rate.
4. The exponential increases with time of a particular metal in the leachate water, found by the different test laboratories, in most cases do not appear to be going to

the same equilibrium value. This suggests that the contamination level achieved cannot be under the simple control of the solubility of the corrosion product formed.

5. The levels of copper and zinc leached in the tests were so far below their respective PCV's that the acceptability for these elements of the alloys tested could be made unambiguously. This was not the case for lead.
6. Although the differences between measured lead concentrations at the three laboratories were considerable, a statistical procedure to decide the outcome of the test, that takes these 'between laboratory' differences into account, can be suggested.

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1. INTRODUCTION

The results of the first Round Robin test showed a strong correlation between the combined level of copper and zinc leached into the test water with that of lead for both the CZ132 and LG4 alloys tested. For details see WRc-NSF report DWI 4079 July 2002. A possible explanation of this outcome, that the phases of each alloy were competing for the dissolved oxygen in the test water, was examined by one of the testing laboratories. This was done by exposing coupons at different depths in a test water thereby creating different diffusion path lengths to the atmospheric oxygen. This “second pilot” study was carried out using plastic centrifuge tubes with screw top lids to assist the achievement of consistent exposure conditions. Other consequences of this change included significantly reducing the cost of the testing and an increase in the coupon surface area to test water volume (s/v) ratio of 2.5 times *i.e.* from 13,500 mm²/l to 33,750 mm²/l. See Appendix A for the report of this work.

Although the results showed similar correlations between the elements leached as seen previously, they also established that the contamination was not being controlled by the level of dissolved oxygen. Probably as a result of the higher s/v ratio, the stagnation graphs showed a more well defined exponential increase towards an equilibrium value than had been seen in the previous studies. This shape of curve implies a process controlled by the solubility of the corrosion product layers formed rather than the corrosion process.

Because of the practical and cost advantages of using plastic centrifuge tubes as the reaction vessels, it was decided to carry out a second more limited Round Robin test using this variant of the test procedure. An extra stagnation sample of 24 hours was added to the final assessment to encourage the fuller development of the stagnation curve.

Test programme

In three laboratories, five replicate samples of the standard CZ132 coupons were exposed to 40 ml of Test Solution 2 (pH 7.5, alkalinity 150 mg CaCO₃/l, 10 mg/l of both chloride and sulphate) in capped plastic centrifuge tubes. As *per* the original method, the coupons were conditioned over 16 days using 24-hour stagnation periods. None of these leachate solutions were retained for metal analysis.

At the end of the 16 day conditioning period, the standard *metal leaching vs. stagnation time* procedure was carried out using stagnation periods of 1, 2, 4, 8, 16 and 24 hours. The leachate solutions obtained were analysed for Cu, Pb and Zn.

Appendix B contains the standard test procedure used in each laboratory.

2. RESULTS

Average stagnation curves of five replicates

The results of this work are summarised in the Tables 1 and 2 below. The Pilot study results are averages of the data given in Appendix A (i.e. it has been assumed that depth of submersion of the coupons is indeed without effect). The increase in leachate concentration against stagnation time are presented in Figures 1, 2 and 3 for the individual elements analysed (Cu, Pb, Zn). Figure 4 shows the stagnation curve for all three metals combined as their micro-gram equivalents per litre.

Table 1 Test water analyses

Lab. Ref.	Run Day	Ambient Temp °C	pH	Alkalinity mgCaCO ₃ /l	Chloride mg/l	Sulphate mg/l
ITS	0	23	7.5	152	11	<10
TW	0	23.3	7.5	143	10	8.3
WRc	0	23.5	7.51	145	12.1	9.81
ITS	Stag.1	23	7.5	154	11	<10
TW	Stag.1	23.3	7.5	149	11	8.9
WRc	Stag.1	23.5	7.54	157	16.5	9.23
Tolerances:		23 +/- 1	7.5 +/- 0.2	150 +/- 7.5	10 +/- 2	10 +/- 2

Note: Stag.1 = 1st of the stagnation days in which metal leachate samples were prepared.

Table 2a Summary of Stagnation Results - Average metal concentration mg/l
Copper

Lab Ref	Stagnation Time (hrs)					
	1	2	4	8	16	24
Pilot II *	21.18	39.92	61.52	143.4	103.36	-
ITS	68.8	117.6	142.6	230.4	338.8	389.2
TW	35.4	62.2	94.2	138.6	192.4	185.6
WRc	51.7	78.4	127	168	227	216

Lead

Lab Ref	Stagnation Time (hrs)					
	1	2	4	8	16	24
Pilot II	15.84	21.96	32.08	52.8	68.82	-
ITS	16.76	26.32	42.14	42.7	83.94	89.84
TW	11.28	16.96	18.52	26.8	37.8	33.74
WRc	18.1	25.0	40.4	53.9	75.1	88.3

Zinc

Lab Ref	Stagnation Time (hrs)					
	1	2	4	8	16	24
Pilot II	65.32	121.8	226.4	472.2	498.4	-
ITS	47	89.8	146.6	220	281.6	394.2
TW	57.4	94.4	126.6	287.4	361.8	464.2
WRc	54.8	79.6	130	159	199	188

* Derived from results in Appendix A

**Table 2b Summary of Stagnation Results - Average metal concentration
mg-equivalents/l***

Copper

Lab Ref	Stagnation Time (hrs)					
	1	2	4	8	16	24
Pilot II	0.67	1.26	1.94	4.52	3.26	-
ITS	2.17	3.71	4.49	7.26	10.68	12.27
TW	1.12	1.96	2.97	4.37	6.06	5.85
WRc	1.63	2.47	4.00	5.29	7.15	6.81

Lead

Lab Ref	Stagnation Time (hrs)					
	1	2	4	8	16	24
Pilot II	0.15	0.21	0.31	0.51	0.66	-
ITS	0.16	0.25	0.41	0.41	0.81	0.87
TW	0.11	0.16	0.18	0.26	0.36	0.33
WRc	0.17	0.24	0.39	0.52	0.72	0.85

Zinc

Lab Ref	Stagnation Time (hrs)					
	1	2	4	8	16	24
Pilot II	2.00	3.73	6.93	14.44	15.25	-
ITS	1.44	2.75	4.48	6.73	8.61	12.06
TW	1.76	2.89	3.87	8.79	11.07	14.20
WRc	1.68	2.43	3.98	4.86	6.09	5.75

*
 $\mu\text{g-equivalents for Cu} = \mu\text{g}/31.73$
 $\text{Pb} = \mu\text{g}/103.61$
 $\text{Zn} = \mu\text{g}/32.69$

The correlation between the copper and zinc contamination, and that between copper plus zinc and lead, are illustrated in Figures 5 and 6 respectively.

Differences between laboratories and test procedures

In order to test whether the differences between laboratories and between test procedures (Pilot for WRC-NSF only, Round Robin 1 Solution 2, and Round Robin 2) are statistically significant, analysis of variance (ANOVA) was carried out. This compares the differences between replicates to the differences between laboratories / test procedures.

The ANOVA confirmed that the differences between laboratories for Round Robin 2 are all significant, for all three metals. Figures 7 to 9 illustrate the differences. Similarly there are differences between Round Robin 1 and Round Robin 2 at the same laboratory. Figures 10 to 12 illustrate the differences for lead, which are summarised in Table 3.

Table 3 Sixteen hour stagnation concentrations for Lead

Lab	Run	Second Pilot	RR1 ¹	RR2
ITS		-	66	84
WRC-NSF		45	42	75
TW		-	65	38

Note 1. Results from 1st Round Robin for Solution 2 only

Note 2. Low values are shown in ***bold italics***

The ANOVA analysis of these results (Appendix D) showed that there are two main groups:

- Low values between 38 and 45: NSF Pilot, NSF RR1 & TW RR2
- High values between 65 and 84: ITS RR1 & RR2, NSF RR2 & TW RR1

3. DISCUSSION

It is immediately obvious from the Figures that the new test procedure has not improved the inter-laboratory reproducibility. It is apparent that, apart from the lead results from ITS and WRc-NSF laboratories and the combined metal curve from the Pilot and the ITS laboratory, the exponential stagnation curves for each metal are not tending to the same maximum, i.e. saturated solubility, value. This implies that the level of contamination cannot be under simple solubility control. As the study of the effects of depths of immersion of the test samples indicated that the contamination was not under simple corrosion control either, see Appendix A, this leaves us with some hybrid of the two mechanisms.

The 16-day ageing period of the test coupons used in the current test procedure is unlikely to ensure the full development of a corrosion product layer. This implies that the corrosion rate ought still to be a major factor in determining the contamination level in the water. Slight differences in the exposure conditions of the coupons could affect the physical form of the deposit produced during the ageing stage. These effects might continue to influence the service performance of the material in the long term because of the often critical nature of the initially formed film.

Interpretation of test results

In none of the tests of copper alloys, carried out in this or in any other similar programmes, has the leached levels for copper or zinc approached their PVC values, (2,000 and 5,000 $\mu\text{g/l}$ respectively). Thus the decision as to the acceptability of these alloys from the point of view of these elements can be made unambiguously. This is not the case for lead. This is in a large measure due to the much lower PCV for lead (currently 50 $\mu\text{g/l}$) which would test the sensitivity of any procedure.

The current British Standard, DD 256:2002, recognises that amongst the possible outcomes of a test, as well as the usual pass or fail options, there can be a “null” result where the data does not allow a definitive decision to be made. The results of the present study can be used to define the limits of the null outcome for lead.

The lead results from all the tests carried out in this project are summarised in Table 4.

Table 4 Weighted average stagnation time⁽¹⁾ concentrations for Lead (mg/l) after a 16 day ageing period

	Solution 1	Solution 2	Solution 3
DZR			
NSF Pilot I	13	17	24
ITS RR1	33	32	25
WRC-NSF RR1	15	25	17
TW RR1	6	26	25
ITS RR2		36	
NSF RR2		37	
TW RR2		20	
Gun Metal			
ITS RR1	24	37	24
NSF RR1	11 ⁽²⁾	25	25
TW RR1	8	16	16

Notes: (1) Calculated by using the 1 and 2 hour stagnation results twice in combination with the 4, 8 & 16 hour results *i.e.* equivalent to a residents time of 4.86 hours.

(2) Excluding one outlier

These results can be used to define the outcome of the test as follows:

1. Between-laboratory variability is greatest for Solution 1 (6 – 33 µg/l) and least for Solution 3 (16 – 25 µg/l).
2. For each laboratory and programme stage, the highest lead concentrations are measured in Solution 2, with one exception – the Pilot study. We can therefore concentrate attention on Solution 2.
3. We assume that the between laboratory variability of the DZR tests in Solution 2 can be applied to future tests (or a slightly larger variability to be on the safe side). We then ask: ‘What information about the ‘true’ result (i.e. the mean of the results of tests at many laboratories) do the results of tests at one, two or three laboratories provide? In general terms the answer is that the test result(s) need to be lower than the PCV by a factor that allows for uncertainty about the ‘true’ result.
4. The possible outcomes of the test can then be defined as follows:
 - a) If the average stagnation concentration (after adjustment of the data using whatever calibration factor is considered appropriate, ASC) is ≤ 0.44 times the PCV of an element, the material passes the test for that element.
 - b) If the average stagnation concentration (after adjustment of the data using whatever calibration factor is considered appropriate) is > 1.56 times the PCV of an element, the material fails the test for that element.

- c) If the average stagnation concentration (after adjustment of the data using whatever calibration factor is considered appropriate) is between 0.44 and 1.56 times the PCV of an element, the outcome is a null result for that element.
- d) If the same set of tests were done at 2 (or 3) laboratories, the ‘null result’ band is narrower – see Table 5. Before applying Table 5, a check on the validity of assumption 3 above should be made using an F-test to compare variances.

Table 5 Decisions based on test results

Number of laboratories	Pass	Fail	Null result
1	ASC ≤0.44	ASC >1.56	0.44 < ASC ≤1.56
2	ASC ≤0.60	ASC >1.40	0.60 < ASC ≤1.40
3	ASC ≤0.68	ASC >1.32	0.68 < ASC ≤1.32

4. CONCLUSIONS

1. This work has developed a test procedure, based on plastic centrifuge tubes as the reaction vessels, that significantly increases the practical convenience and significantly reduces the cost of carrying out the testing of metals.
2. Strong correlations have been found between the concentrations of the major elements, i.e. copper, lead and zinc, that leach from the copper alloys. All show an exponential increase in concentration with time in the leachate water.
3. The amount of metal leached showed little sensitivity to the depth of immersion of the test coupon, suggesting little sensitivity to the level of dissolved oxygen in the test water. This in turn suggests that the contamination level achieved cannot be under the simple control of the alloy corrosion rate.
4. The exponential increases with time of a particular metal in the leachate water, found by the different test laboratories in most cases do not appear to be going to the same equilibrium value. This suggests that the contamination level achieved cannot be under the simple control of the solubility of the corrosion product formed.
5. The levels of copper and zinc leached in the tests were so far below their respective PCV's that the acceptability for these elements of the alloys tested could be made unambiguously. This was not the case for lead.
6. Although the differences between measured lead concentrations at the three laboratories were considerable, a statistical procedure to decide the outcome of the test, that takes these 'between laboratory' differences into account, can be suggested.

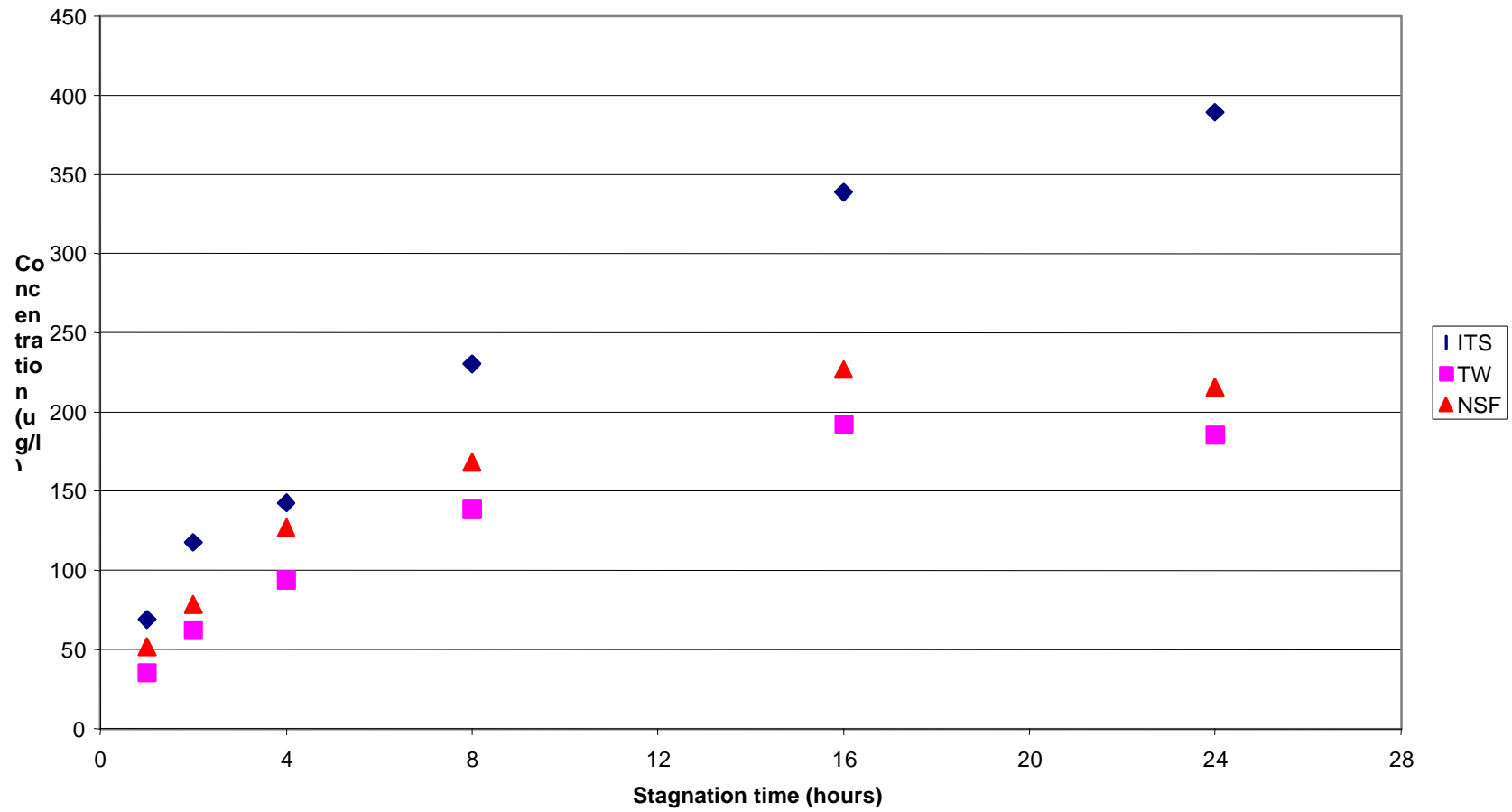


Figure 1 Copper stagnation concentrations – average of 5 replicates

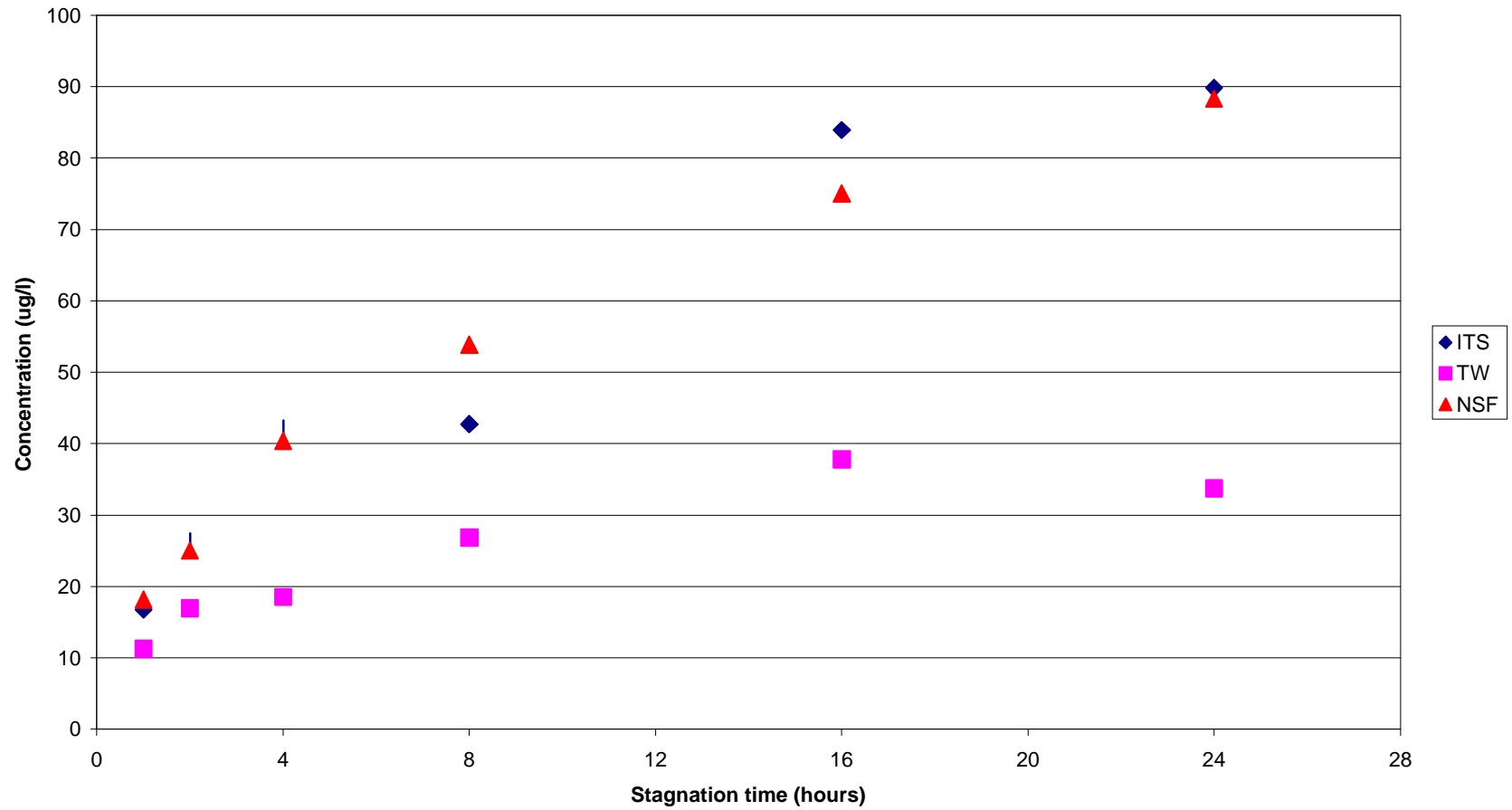


Figure 2 Lead stagnation concentrations – average of 5 replicates

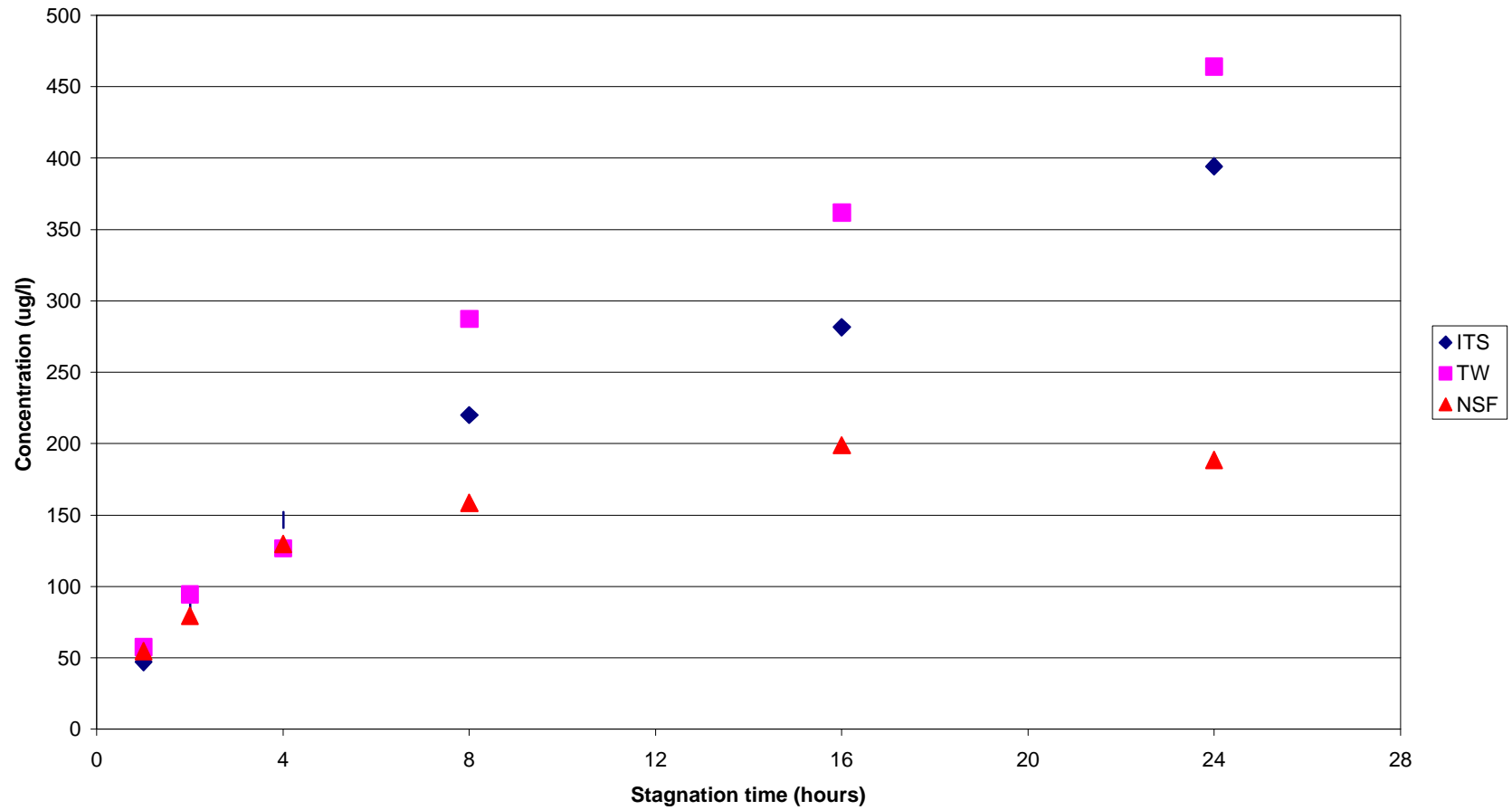


Figure 3 Zinc stagnation concentrations – average of 5 replicates

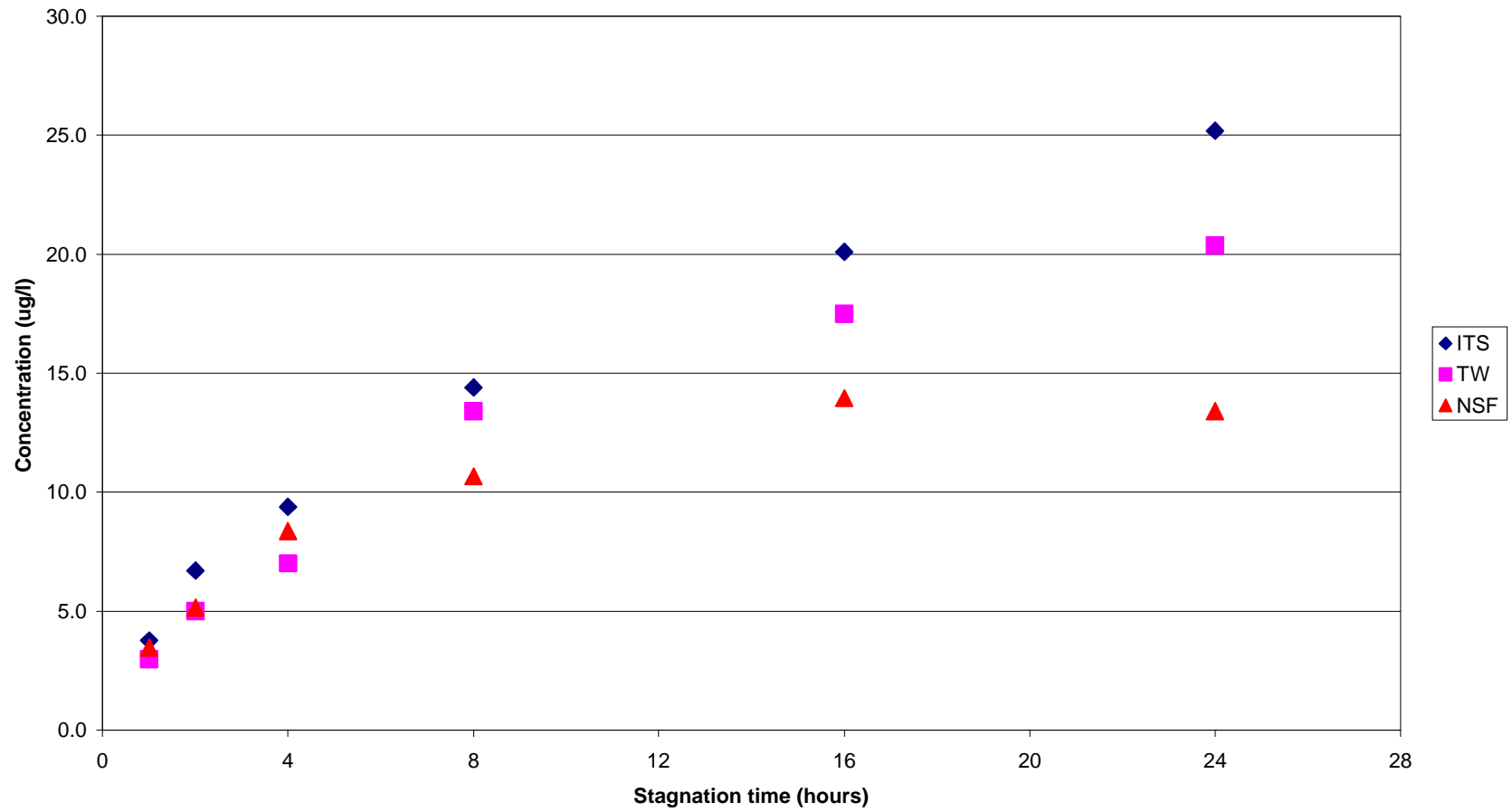


Figure 4 Sum of 3 metals gm equivalents – average of 5 replicates

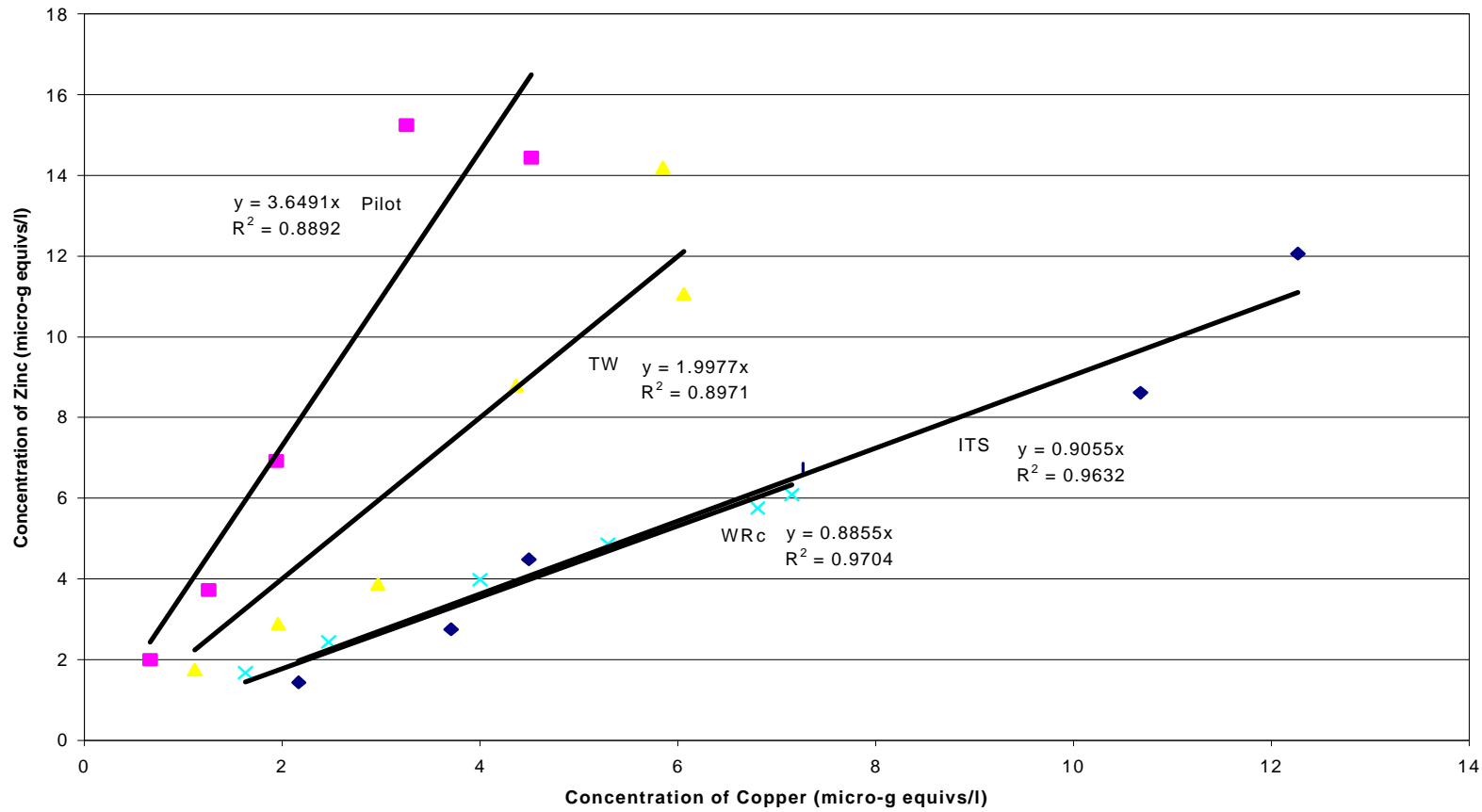


Figure 5 Correlations between Levels of Copper and Zinc Leaching

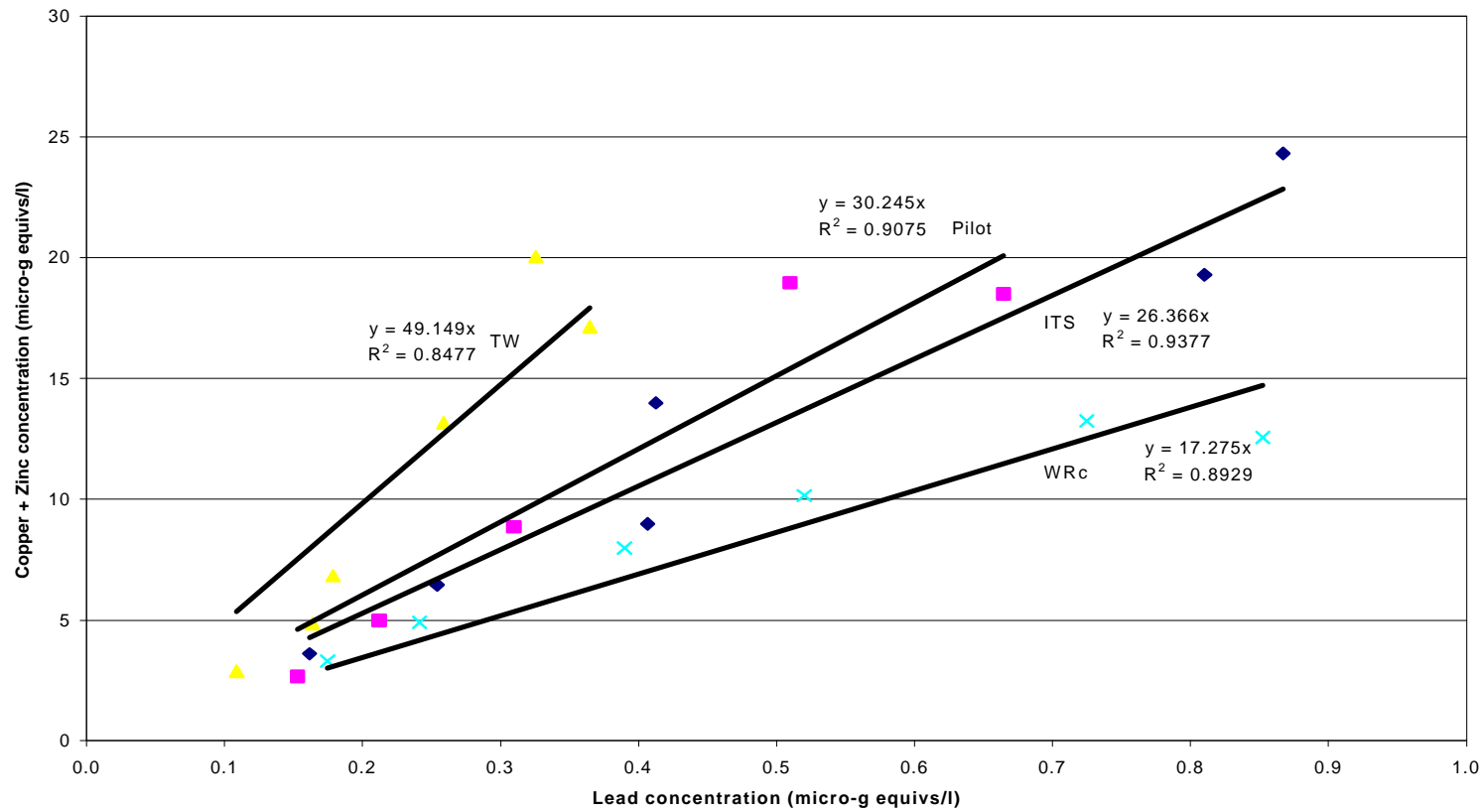


Figure 6 Copper + Zinc versus Lead Leaching

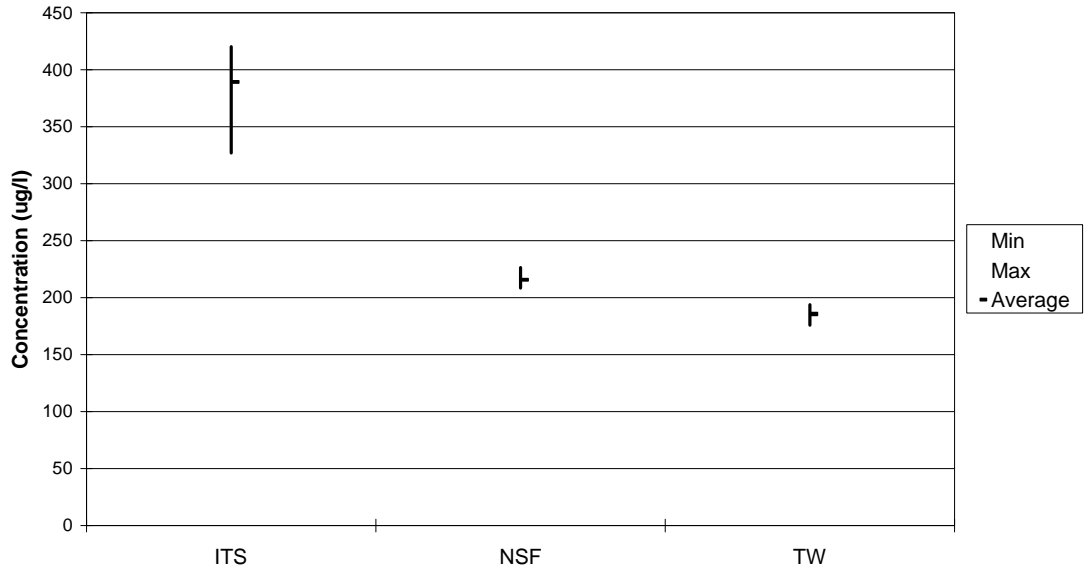


Figure 7 Copper, 2nd Round robin, 24 hour stagnation concentrations

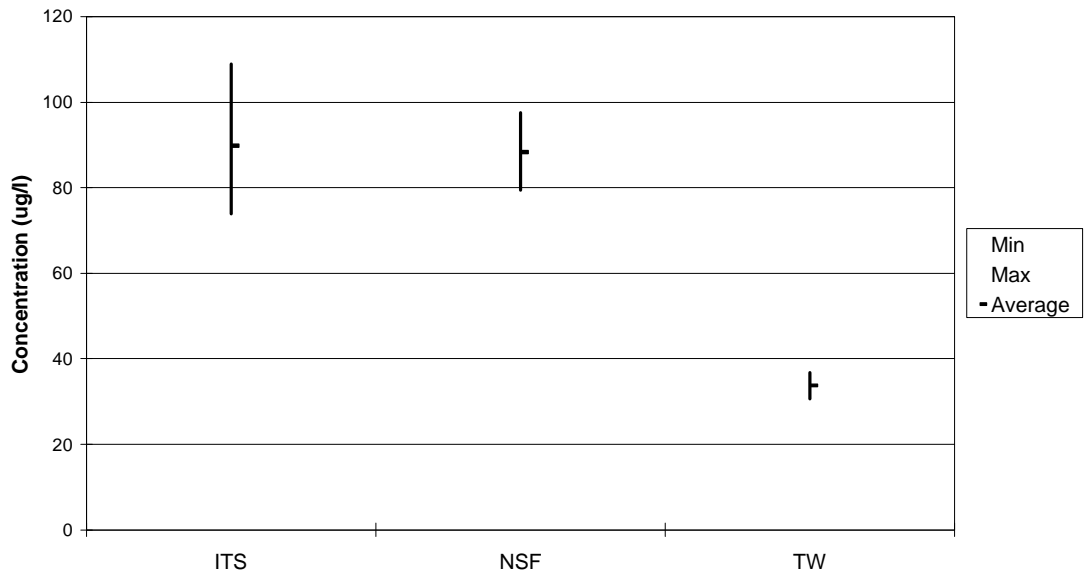


Figure 8 Lead, 2nd Round Robin, 24 hour stagnation concentrations

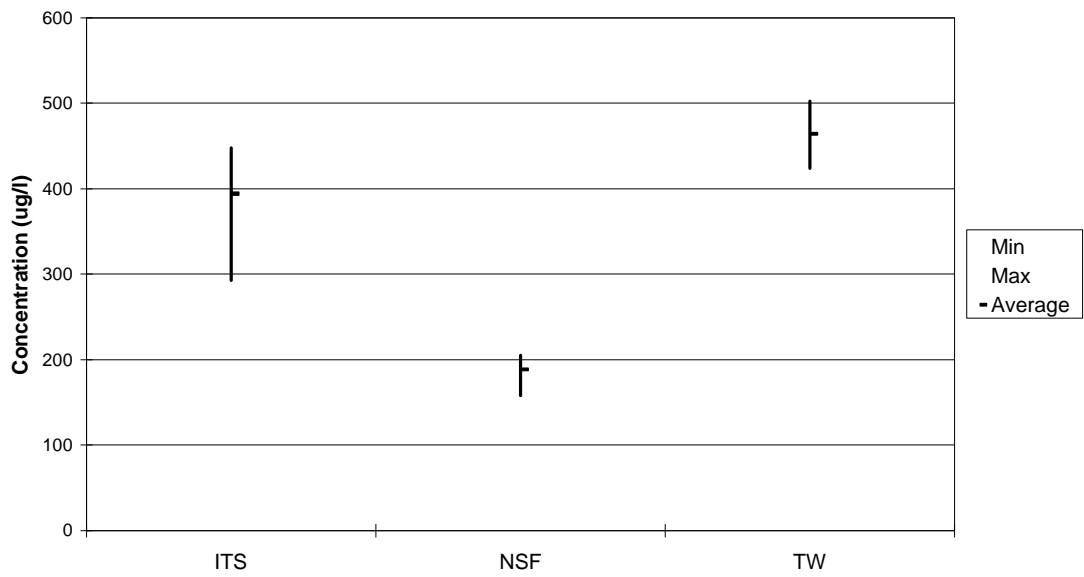


Figure 9 Zinc, 2nd Round Robin, 24 hour stagnation concentrations

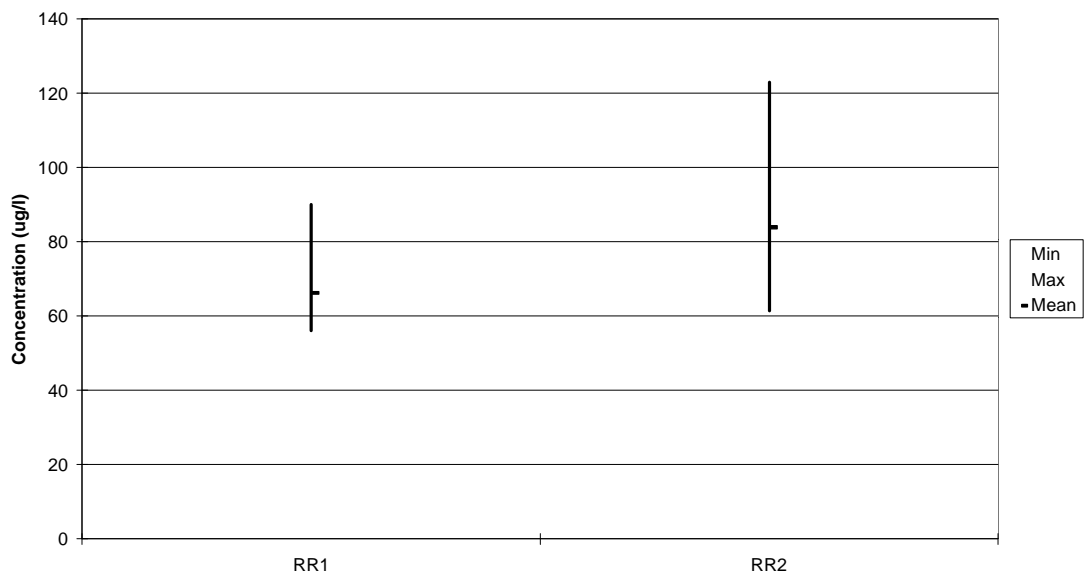


Figure 10 ITS Lead 16 hour stagnation concentrations

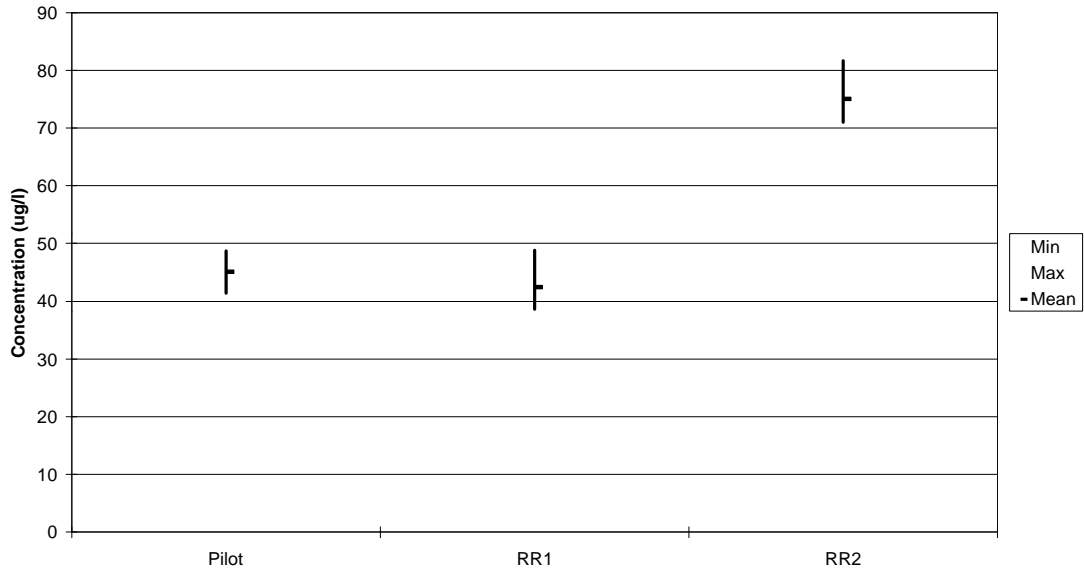


Figure 11 WRC-NSF Lead 16 hour stagnation concentrations

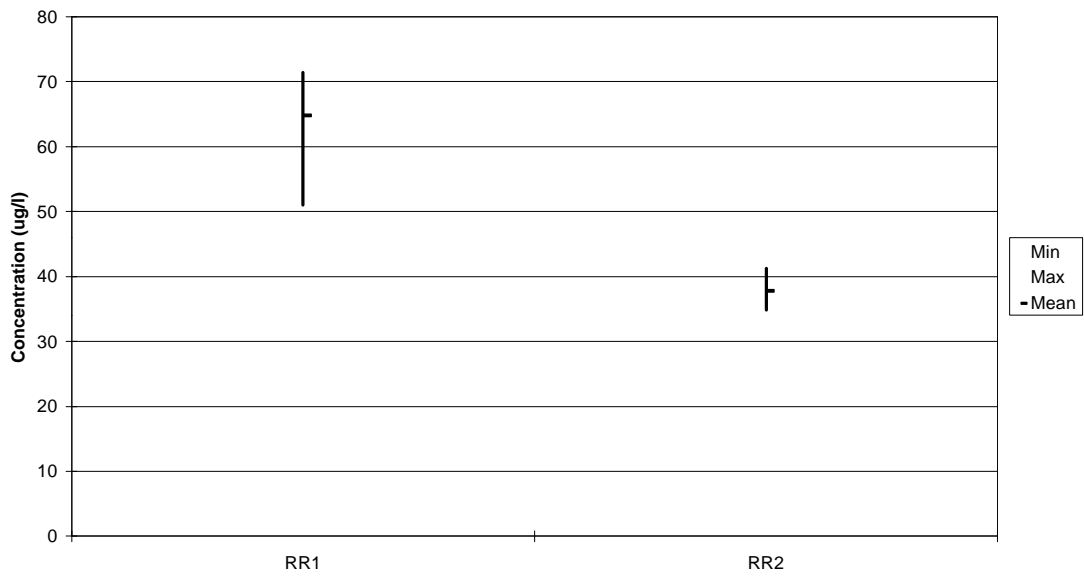


Figure 12 TW Lead 16 hour stagnation concentrations

APPENDIX A REPORT ON THE EFFECT OF DEPTH OF IMMERSION STUDY – SECOND PILOT USING MODIFIED DD 256:2002 PROCEDURE

Introduction

The results of the first Round Robin test showed a strong correlation between the combined level of copper and zinc leached into the test water with that of lead for both the CZ132 and LG4 alloys tested. For details see WRc-NSF report DWI 4079 July 2002. A possible explanation of this outcome could be that the phases of each alloy were competing for the same limited resource *i.e.* the dissolved oxygen in the test water. Slight differences in the depths of immersion of the test coupons might then explain the differences in the test results between laboratories. It was decided to test this hypothesis by exposing coupons at different depths in a test water thereby giving them different lengths to their respective diffusion paths to atmospheric oxygen.

Test method

Five replicate samples of the standard CZ132 coupons were exposed to 40 ml of Test Solution 2 (alkalinity 150 mg CaCO₃/l, 10 mg/l of both chloride and sulphate) in capped plastic centrifuge tubes. As *per* the original method, the coupons were conditioned over 16 days using 24 hour stagnation periods. None of the leachate solutions were retained for metal analysis.

At the end of the 16 day conditioning period, the standard *metal leaching vs. stagnation time* procedure was carried out using stagnation periods of 1, 2, 4, 8 & 16 hours. The solutions obtained were analysed for Cu, Pb & Zn.

Results and Discussion

The results of this work, in units of µg/l and µg-equivalents/l, are given in the Tables 1a & 1b below. The increase in leachate concentration, for the individual elements analysed (Cu, Pb, Zn), against stagnation time is presented in Figure 1. These results show a better defined exponential pattern than that observed in the original Round Robin test. This may reflect the significantly higher surface area of coupon to test water volume in the modified procedure used in this work. If thought desirable, the ratio could be restored to the value specified in DD 256:2002 by reducing the coupon length when using test-tubes as the reaction containers.

The relationship between the concentration of copper plus zinc leached with that for lead found in the Round Robin was observed even more strongly in this work; see Figure 2. However, it is quite clear from the results that the depth of immersion of the coupon is having little influence of the level of metal leached, see Table 1a. This means the relationship observed cannot arise, as originally thought, by the different phases of the alloy competing for the diffusion limited supply of dissolved oxygen.

This leaves a correlation in the rates of dissolution of the respective corrosion products formed by the elements concerned the exact value of which is determined by the ratio of the surface areas of the different phases in the alloy. This idea is supported by the fact that the correlation becomes less convincing at high concentrations of the elements (see Figure 2) when the rates of dissolution will significantly reduce as equilibrium solubility levels are approached.

Conclusions

It is clear from the results of this work that the depth of immersion of the test coupons does not affect the leaching of metals in the test procedure followed.

This means that the level contamination is not being controlled by the local concentration of dissolved oxygen, and hence the rates of corrosion achieved, which leaves the rate of dissolution of the corrosion products formed as the controlling mechanism.

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Table 1. Results of effect of depth of submersion experiment

a) Metal concentrations as mg/l

Depth of submersion	Metal	Stagnation Time (hrs)				
		1	2	4	8	16
	Cu					
Surface		22	44.3	75.1	118	106
Surface		19.2	32.6	64.3	153	127
5 mm		22	59.7	64.6	180	105
Deep		22.1	32.8	59.1	151	100
Deep		20.6	30.2	44.5	115	78.8
	Pb					
Surface		11.7	22	29.7	46.8	64
Surface		13	19.5	30.3	51.8	72.2
5 mm		14.9	21.9	27.9	48.4	59.5
Deep		19.5	22.7	33.3	54.5	74.7
Deep		20.1	23.7	39.2	62.5	73.7
	Zn					
Surface		64.3	128	232	537	538
Surface		52.9	105	189	296	455
5 mm		68.5	136	229	427	500
Deep		79.7	140	263	617	580
Deep		61.2	100	219	484	419

b) Metal concentrations as mg-equivalents*/l

	Stagnation Time (hrs)	1	2	4	8	16
Depth of submersion	Metal					
	Cu					
Surface		0.69	1.40	2.37	3.72	3.34
Surface		0.61	1.03	2.03	4.82	4.00
5 mm		0.69	1.88	2.04	5.67	3.31
Deep		0.70	1.03	1.86	4.76	3.15
Deep		0.65	0.95	1.40	3.62	2.48
	Pb					
Surface		0.11	0.21	0.29	0.45	0.62
Surface		0.13	0.19	0.29	0.50	0.70
5 mm		0.14	0.21	0.27	0.47	0.57
Deep		0.19	0.22	0.32	0.53	0.72
Deep		0.19	0.23	0.38	0.60	0.71
	Zn					
Surface		1.97	3.92	7.10	16.43	16.46
Surface		1.62	3.21	5.78	9.05	13.92
5 mm		2.10	4.16	7.01	13.06	15.30
Deep		2.44	4.28	8.05	18.87	17.74
Deep		1.87	3.06	6.70	14.81	12.82

* μg -equivalents for Cu = $\mu\text{g}/31.73$
Pb = $\mu\text{g}/103.61$
Zn = $\mu\text{g}/32.69$

Figure 1. Concentration of metals vs. Stagnation Time

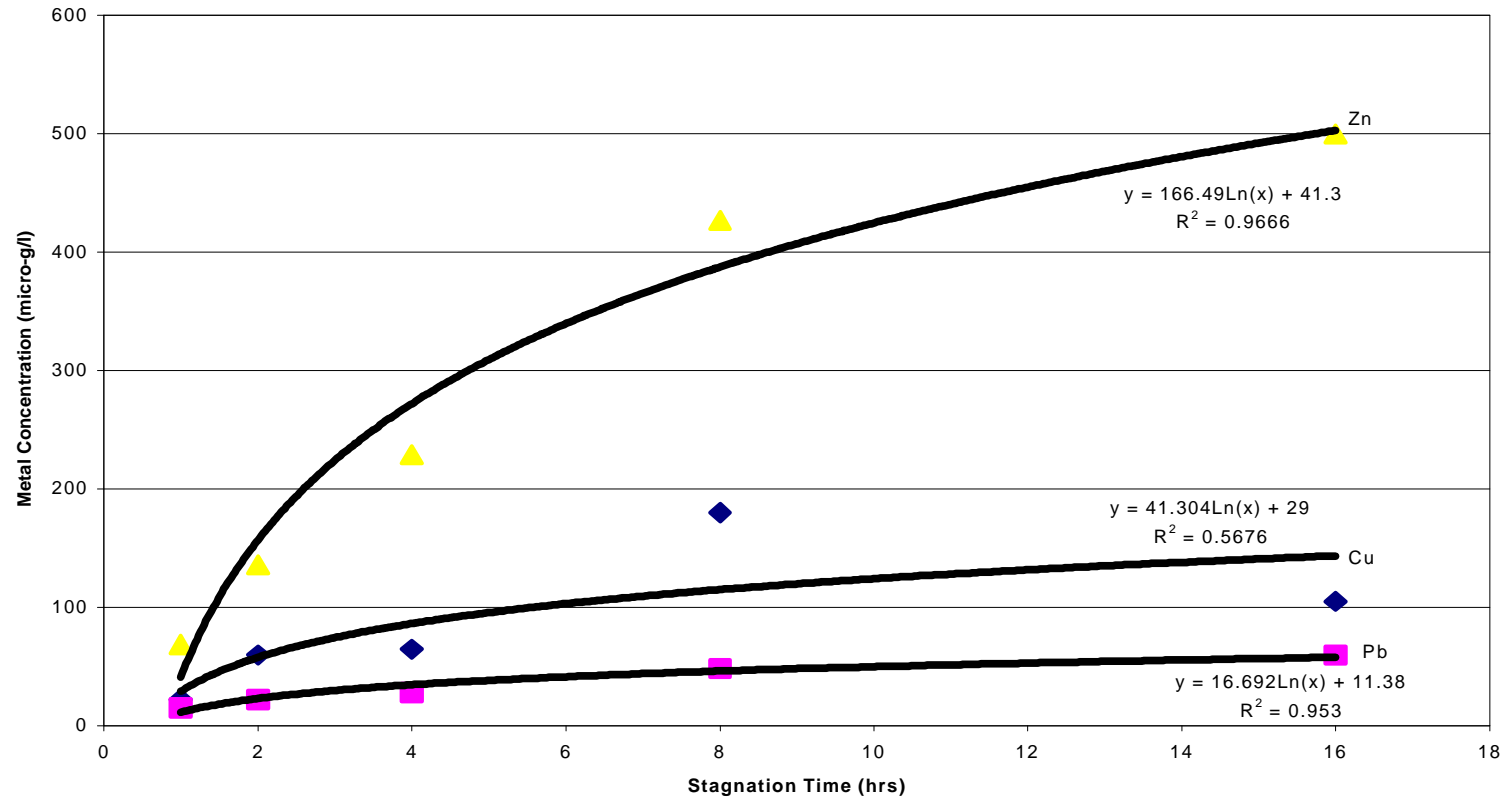
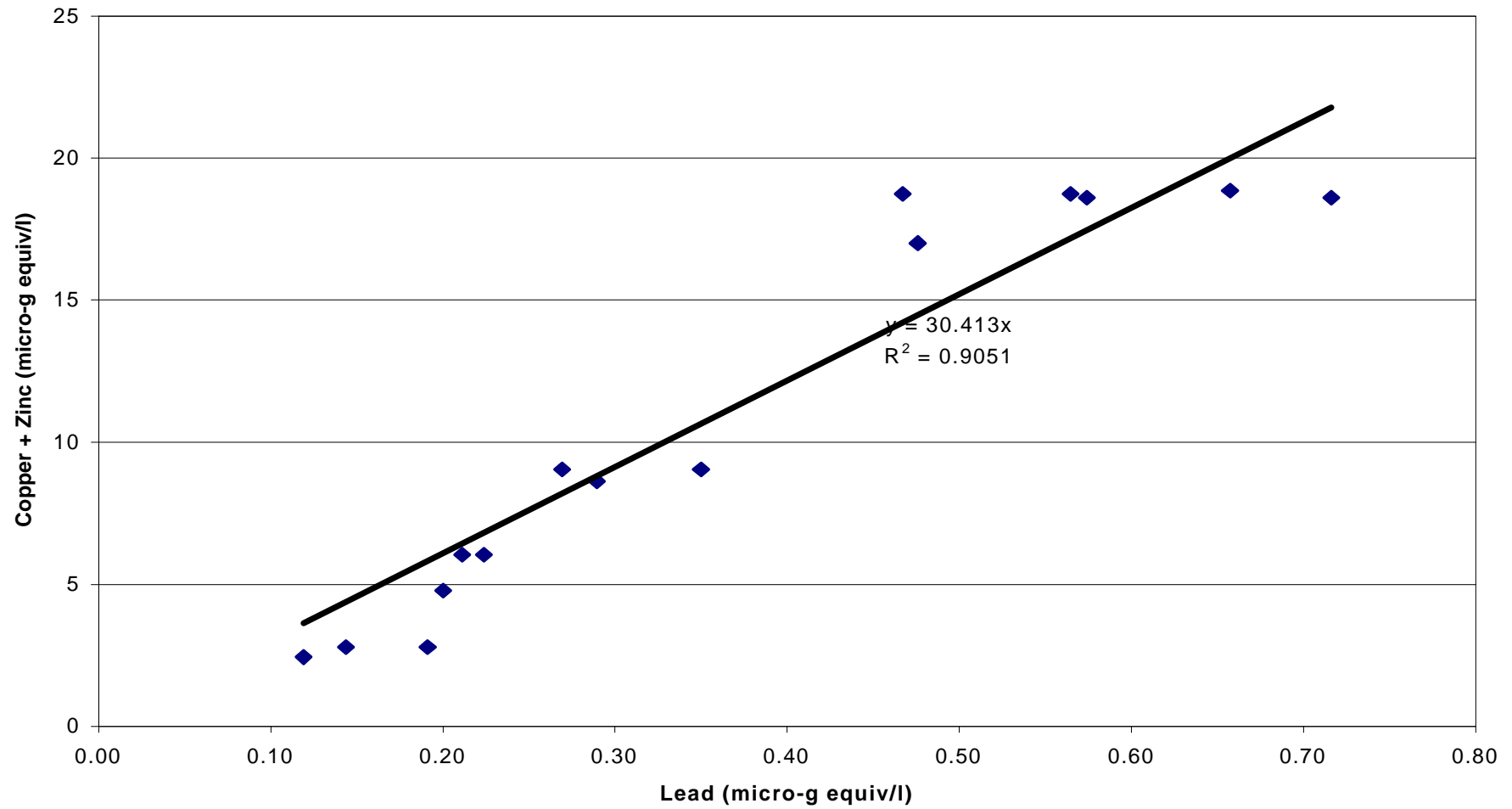


Figure 2. Concentrations of Copper + Zinc vs Lead



APPENDIX B METHOD FOR BS7766 ROUND-ROBIN 2 EXERCISE

Reagents

- a) *Water*, conforming to grade 3 of BS EN ISO 3696 should be used throughout.
- b) *Nitric acid*, concentrated, $(70 \pm 5)\%$ by mass, analytical reagent grade, suitable for use in atomic absorption spectrometry.
- c) *Test Solution*. Prepare a bulk 20 litres of the test solution by dissolving 2.220 ± 0.005 gm of calcium hydroxide, 0.328 ± 0.002 gm of sodium chloride and 0.284 ± 0.002 gm of sodium sulphate (all dried at 105°C for 1 hour) in water and making up to 20 litres ± 100 ml with water in an aspirator. Record the weights of each component taken.

The nominal concentrations of each component are given in the table below:

pH (at test extraction)	Alkalinity (mg/l CaCO_3)	Chloride (mg/l)	Sulphate (mg/l)
7.50 ± 0.20	150	10	10

The pH of the solution should be lowered by bubbling carbon dioxide gas through the bulk solution. Initially the solution will turn cloudy, as carbonate is produced, but as more carbon dioxide is passed through the test solution this carbonate will dissolve to give a clear solution. At this stage the bulk solution should be stored, capped, in the aspirator at room temperature under an atmosphere of carbon dioxide.

Note: It is prudent to prepare and lower the pH of the bulk test solution a few days before the anticipated start of the extraction procedure.

At the start of each extraction period, a portion of the bulk solution (conveniently 1 litre) should be drawn off and brought to, and maintained at, the test temperature ($23 \pm 1^\circ\text{C}$) in an incubator or water bath. The pH of this aliquot of test solution should then be adjusted to $\text{pH } 7.50 \pm 0.20$ by bubbling filtered air through the solution. The test solution aliquot is then ready for use in the extraction test.

Note: Unused test solution can be returned to the bulk container, and the carbon dioxide atmosphere replenished.

The test water shall be analysed for the specific inorganic ions, after pH adjustment to 7.50 ± 0.20 for the alkalinity determination, immediately after its initial preparation. Subsequently, if the same batch of solution is being used, only the alkalinity need be

checked, once each day during the stagnation tests, carried out after the conditioning stage, to obtain the data for the *metal release versus time* graph (see below).

Apparatus

- a) pH meter, with temperature compensation, calibrated against appropriate buffer solutions.
- b) Test containers, suitably sized so as to hold the test coupon submerged within a volume of 40 ml of test solution. Suitable containers are 50 ml plastic centrifuge tubes with plastic screw caps.

The test coupon should be threaded with nylon line which can then be threaded through a small hole in the screw cap and then tied around a piece of tubing or other material so that when the screw cap is in place, the test coupon is fully submerged, with the top edge at least 10mm, and no more than 25mm, below the liquid surface.

- c) Incubator or water bath capable of maintaining $23 \pm 1^\circ\text{C}$.

Number of Specimens

Prepare a total of 5 replicate test specimens.

Blanks

A blank test sample is required each day during the stagnation test, carried out after the conditioning stage, to obtain data for the metal release versus time graph (see below). Each blank shall contain a length of the nylon thread used to support the test coupons and which comes into contact with the test solution. As far as possible each blank should be taken through exactly the same procedure as the test coupons.

Pre-treatment of coupon specimens

At the commencement of the test, give each test specimen three immersions of approximately 2 s in industrial methylated spirit or methanol, followed by three similar immersions in water and then in a portion of the test solution to which the specimen will be exposed.

Extraction Procedure

a) Test Coupon Conditioning Stage

Immediately after the 2 s immersion in the test solution, suspend the specimen in a test container containing 40 ± 1 ml of the test solution, screw the cap onto the container. Ensure that the test coupon is fully submerged in the test solution (as described above)

and that it is not touching the wall of the test container. Store in an incubator or water bath for 24 hr as the first 24 hr extraction period.

Following each extraction period lift the cap and test specimen gently clear of the surface of the test solution and allow it to drain for approximately 2 s before touching its lower edge momentarily on the liquid surface. Then re-immense it and repeat the procedure twice. Transfer the test specimen immediately to another test container containing a fresh 40 ± 1 ml portion of test solution (brought to the correct temperature and pH as described above).

Discard the old test extract.

Repeat the extraction procedure for a minimum of a further 15 days.

b) Metal Release vs Time

At the end of the 16 day coupon-conditioning series of 24 hr extractions, a second stage of extractions is carried out.

The data required shall be obtained by consecutively exposing each test specimen to different samples of the test water for different periods and determining the concentration of metals in these extracts.

For the sake of reproducibility, and to avoid the necessity of overnight working, the stagnation times to be used, and their order of application, shall be 4, 2, 1, 0.5 hours (during day 1), 16 hours (overnight following), 8 hours (during the next day) and 24 hours.

Note that, due to reasons of practicability, there can be a delay between the completion of the 16 day conditioning period and the time when the stagnation procedure can be started. During this delay, the 24h extract test should be continued, so that the test materials are maintained under the original test conditions.

Suspend the specimen in a test container containing 40 ± 1 ml of the test solution, screw the cap onto the container. Ensure that the test coupon is fully submerged in the test solution (as described above) and that it is not touching the wall of the test container. Store at $(23 \pm 1) ^\circ\text{C}$ in an incubator or water bath for the first stagnation period.

Following each stagnation period, lift the cap and test specimen gently clear of the surface of the test solution and allow it to drain for approximately 2 s before touching its lower edge momentarily on the liquid surface. Then re-immense it and repeat the procedure twice. Transfer the test specimen immediately to another test container containing a fresh 40 ± 1 ml portion of test solution (brought to the correct temperature and pH as described above).

The container with the stagnation period test extract should then be acidified by adding 0.40 ± 0.05 ml of concentrated nitric acid. Cap the container with a new cap, mix the contents and leave to stand for a minimum of 12 hours before analysis for Copper, Zinc and Lead.

Repeat the extraction procedure for the remainder of the stagnation periods.

APPENDIX C RESULTS

ITS Results

Analysis of Test Water

Date	Run Day	Ambi-ent		Alkalinity	Chloride	Sulphate
		Temp	pH	mgCaCO3/l	mg/l	mg/l
	0	23	7.5	152	11	<10
	1	23	7.5	-	-	-
	2	23	7.5	-	-	-
	3	23	7.5	-	-	-
	4	23	7.5	-	-	-
	5	23	7.5	-	-	-
	6	23	7.5	-	-	-
	7	23	7.5	-	-	-
	8	23	7.5	-	-	-
	9	23	7.5	-	-	-
	10	23	7.5	-	-	-
	11	23	7.5	-	-	-
	12	23	7.5	-	-	-
	13	23	7.5	-	-	-
	14	23	7.5	-	-	-
	15	23	7.5	-	-	-
	16	23	7.5	-	-	-
Stagnation						
	Day					
	1	23	7.5	154	11	<10
	2	23	7.5	155	-	-
	3	23	7.5	154	-	-

Notes: Only single batch of test solution used to carry out the test.

ITS Results continued

Leachate Concentration vs Stagnation Time - DZR Brass Coupons

	Time (Hrs)			Time (Hrs)		
	1.0			2.0		
	Cu	Pb	Zn	Cu	Pb	Zn
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
Replicate 1	65	18.5	57	114	31.3	96
Replicate 2	73	16.2	45	113	25.80	89
Replicate 3	74	21.2	39	118	30.1	76
Replicate 4	72	16.2	42	130	27.5	84
Replicate 5	60	11.7	52	113	16.9	104
Average	68.8	16.76	47	117.6	26.32	89.8
	Time (Hrs)			Time (Hrs)		
	4			8		
Replicate 1	138	45.7	131	220.0	43.9	217
Replicate 2	133	40	147	236	40.3	242
Replicate 3	141	52.8	129	230	50.9	193
Replicate 4	147	42.3	141	233	40.8	207
Replicate 5	154	29.9	185	233	37.8	241
Average	142.6	42.14	146.6	230.4	42.74	220
	Time (Hrs)			Time (Hrs)		
	16			24		
Replicate 1	341	84.7	289	389	94.5	426
Replicate 2	409	79.3	350	420	87.3	448
Replicate 3	335	122.9	263	412	109.0	415
Replicate 4	314	71.3	258	398	84.5	389
Replicate 5	295	61.5	248	327	73.9	293
Average	338.8	83.94	281.6	389.2	89.84	394.2
Day 1 Blank	<4	<0.5	10			
Day 2 Blank	9	<0.5	<4			
Day 3 Blank	<4	<0.5	9			

Thames Results

Analyses of the Test Water

Date	Run Day	Ambient	pH	Alkalinity	Chloride	Sulphate
		Temp		mgCaCO3/l	mg/l	mg/l
20/10/02	0	23.3	7.5	143	10	8.3
21/10/02	1	23.3	7.5	-	-	-
22/10/02	2	23.3	7.5	-	-	-
23/10/02	3	23.3	7.5	-	-	-
24/10/02	4	23.4	7.5	-	-	-
25/10/02	5	23.3	7.5	-	-	-
26/10/02	6	23.3	7.5	-	-	-
27/10/02	7	23.3	7.5	-	-	-
28/10/02	8	23.3	7.5	-	-	-
29/10/02	9	23.3	7.5	-	-	-
30/10/02	10	23.3	7.5	-	-	-
31/10/02	11	23.3	7.5	-	-	-
01/11/02	12	23.3	7.5	-	-	-
02/11/02	13	23.3	7.5	-	-	-
03/11/02	14	23.3	7.5	-	-	-
04/11/02	15	23.3	7.5	-	-	-
05/11/02	16	23.3	7.5	-	-	-
Stagnation						
	Day					
06/11/02	1	23.3	7.5	149	11	8.9
07/11/02	2	23.3	7.5	149	-	-
08/11/02	3	23.3	-	-	-	-

Note: Only a single batch of test solution used to carry out the test.

Thames Water Results continued

Leachate Concentration vs Stagnation Time - DZR Brass Coupons

	Time (Hrs) 1.0			Time (Hrs) 2.0		
	Cu	Pb	Zn	Cu	Pb	Zn
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
Replicate1	36	11.1	56	69	18.7	101
Replicate2	36	11.5	57	58	14.20	83
Replicate3	35	11.8	58	62	17.1	92
Replicate4	35	10.7	55	58	14.9	92
Replicate5	35	11.3	61	64	19.9	104
Average	35.4	11.28	57.4	62.2	16.96	94.4

	Time (Hrs) 4			Time (Hrs) 8		
	Cu	Pb	Zn	Cu	Pb	Zn
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
Replicate1	101	21.6	142	122.0	27.3	315
Replicate2	93	16.6	117	151	27	270
Replicate3	95	18.8	132	139	27.2	283
Replicate4	90	16	119	142	24.3	291
Replicate5	92	19.6	123	139	28.2	278
Average	94.2	18.52	126.6	138.6	26.8	287.4

	Time (Hrs) 16			Time (Hrs) 24		
	Cu	Pb	Zn	Cu	Pb	Zn
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
Replicate1	171	39.6	406	179	36.7	502
Replicate2	199	35.2	325	194	33.6	461
Replicate3	200	41.2	359	191	35.6	465
Replicate4	191	34.8	346	188	32.1	469
Replicate5	201	38.2	373	176	30.7	424
Average	192.4	37.8	361.8	185.6	33.74	464.2

Day 1 Blank	LT 20	LT 0.5	LT 18	LT 20	LT 0.5	LT 18
Day 2 Blank	LT 20	LT 0.5	LT 18	LT 20	LT 0.5	LT 18

Note: LT = less than the limit of detection for that metal.

WRc-NSF Results

Analyses of the Test Water

Date	Run Day	Ambient		Alkalinity	Chloride	Sulphate
		Temp	pH	mgCaCO3 /l	mg/l	mg/l
25/10/02	0	23.5	7.51	145	12.1	9.81
26/10/02	1	24.0	7.55	-	-	-
27/10/02	2	23.0	7.52	-	-	-
28/10/02	3	23.5	7.46	-	-	-
29/10/02	4	23.5	7.53	-	-	-
30/10/02	5	23.0	7.5	-	-	-
31/10/02	6	23.5	7.52	-	-	-
01/11/02	7	23.5	7.55	-	-	-
02/11/02	8	23.0	7.48	-	-	-
03/11/02	9	23.0	7.51	-	-	-
04/11/02	10	24.0	7.54	-	-	-
05/11/02	11	24.0	7.48	-	-	-
06/11/02	12	23.5	7.47	-	-	-
07/11/02	13	24.0	7.56	-	-	-
08/11/02	14	23.5	7.51	-	-	-
09/11/02	15	24.0	7.54	-	-	-
10/11/02	16	23.5	7.53	-	-	-

Stagnation

	Day					
11/11/01	1	23.5	7.54	157	Yes	Yes
12/11/01	2	24.0	7.48	150	-	-
13/11/01	3	23.5	7.51	150	-	-

WRc-NSF results continued

Leachate Concentration vs Stagnation Time - DZR Brass Coupons

	Time (Hrs)			Time (Hrs)		
	1.0			2.0		
	Cu ug/l	Pb ug/l	Zn ug/l	Cu ug/l	Pb ug/l	Zn ug/l
Replicate 1	48.7	18.1	51.8	71.2	24.6	75.2
Replicate 2	53.8	17.7	55.2	82.4	25.7	82.9
Replicate 3	55.1	18.3	53.7	91.7	26.5	83.8
Replicate 4	47.3	18.1	57.8	71.3	24.9	80.9
Replicate 5	53.4	18.5	55.4	75.4	23.4	75.0
Average	51.7	18.1	54.8	78.4	25.0	79.6
	Time (Hrs)			Time (Hrs)		
	4			8		
Replicate 1	122	39.6	127	160	54.3	152
Replicate 2	135	45.2	133	155	55.7	169
Replicate 3	133	39.9	132	182	51.1	152
Replicate 4	115	38.0	130	161	55.1	159
Replicate 5	129	39.1	127	183	53.1	161
Average	127	40.4	130	168	53.9	159
	Time (Hrs)			Time (Hrs)		
	16			24		
Replicate 1	214	71.0	182	214	97.5	158
Replicate 2	233	76.3	196	226	95.7	201
Replicate 3	260	81.7	217	217	79.4	192
Replicate 4	207	74.2	212	208	83.5	205
Replicate 5	221	72.1	187	213	85.5	186
Average	227	75.1	199	216	88.3	188
Day 1 Blank	0.8	3.5	17.3			
Day 2 Blank	0.7	2.4	9.7			
Day 3 Blank	0.7	2.4	9.7			

APPENDIX D ANALYSIS OF VARIANCE: GENSTAT OUTPUT

GenStat Release 6.1 (PC/Windows 98) 10 December 2002
10:35:27
Copyright 2002, Lawes Agricultural Trust (Rothamsted Experimental
Station)

GenStat Sixth Edition
GenStat Procedure Library Release PL14

Data imported from Excel file: D:\My Documents\statistics\RJO's\Pb 16hr
stag
ANOVA data.xls
on: 10-Dec-2002 10:39:18
taken from sheet "data", cells B1:H6

Summary statistics

Summary statistics for ITS_RR1

Number of values = 5
Mean = 66.20
Minimum = 56.00
Maximum = 90.00
Variance = 185.20

Summary statistics for ITS_RR2

Number of values = 5
Mean = 83.9
Minimum = 61.5
Maximum = 122.9
Variance = 550.8

Summary statistics for NSF_Pilot

Number of values = 5
Mean = 45.10
Minimum = 41.40
Maximum = 48.70
Variance = 7.17

Summary statistics for NSF_RR1

Number of values = 5
Mean = 42.44
Minimum = 38.60
Maximum = 48.80
Variance = 19.01

Summary statistics for NSF_RR2

Number of values = 5
Mean = 75.06
Minimum = 71.00
Maximum = 81.70
Variance = 17.90

Summary statistics for TW_RR1

Number of values = 5
Mean = 64.78
Minimum = 51.01
Maximum = 71.41
Variance = 82.07

Summary statistics for TW_RR2

Number of values = 5
Mean = 37.80
Minimum = 34.80
Maximum = 41.20
Variance = 7.68

```

59  "General Analysis of Variance."
60  BLOCK "No Blocking"
61  TREATMENTS treatment
62  COVARIATE "No Covariate"
63  ANOVA [PRINT=aovtable,information,means; FACT=32; FPROB=yes;
PSE=diff] concentration

```

***** Analysis of variance *****

Variate: concentration

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
treatment	6	9406.5	1567.8	12.62	<.001
Residual	28	3479.5	124.3		
Total	34	12886.0			

***** Tables of means *****

Variate: concentration

Grand mean 59.3

treatment	ITS RR1	ITS RR2	NSF Pilot	NSF RR1	NSF RR2	TW RR1	TW RR2
mean	66.2	83.9	45.1	42.4	75.1	64.8	37.8

*** Standard errors of differences of means ***

Table	treatment
replicates	5
degrees of freedom	28
standard error differences	7.05

***** Kruskal-Wallis One-Way Analysis of Variance *****

Full data set again

Value of H = 28.69

	ITS_RR1	ITS_RR2	NSF_Pilot	NSF_RR1	NSF_RR2	TW_RR1	TW_RR2
Sample size	5	5	5	5	5	5	5
Mean rank	22.40	29.20	11.60	8.60	28.60	21.80	3.80

Degrees of freedom = 6
Chi-square p-value < 0.001

Two outliers deleted

ITS RR1 90.00 & ITS RR2 122.90

Identifier	Minimum	Mean	Maximum	Values	Missing
concentration	34.80	56.48	84.70	33	0

84 **"General Analysis of Variance."**

85 BLOCK "No Blocking"
 86 TREATMENTS treatment
 87 COVARIATE "No Covariate"
 88 ANOVA [PRINT=aovtable,information,means; FACT=32; FPROB=yes;
 PSE=diff] concentration

88.....

***** Analysis of variance *****

Variate: concentration

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
treatment	6	6761.33	1126.89	33.52	<.001
Residual	26	874.05	33.62		
Total	32	7635.39			

***** Tables of means *****

Variate: concentration

Grand mean 56.5

treatment	ITS RR1	ITS RR2	NSF Pilot	NSF RR1	NSF RR2	TW RR1	TW RR2
37.8	60.2	74.2	45.1	42.4	75.1	64.8	
5 rep.	4	4	5	5	5	5	5

*** Standard errors of differences of means ***

Table	treatment
replicates	unequal
degrees of freedom	26
standard error of differences	4.10 min.rep
	3.89 max-min
	3.67 max.rep

APPENDIX E DERIVATION OF TEST OUTCOME RULES

Key assumption

The differences between the results of the 7 DZR solution 2 tests, expressed as proportions of the mean, represent the variability between laboratories that can be expected in future.

Derivation of rules

Table E.1 shows the estimation of between laboratory variability, as a standard deviation.

Table E.1 Estimation of between laboratory variability

	DZR solution 2 results	Ratio to mean
WRC-NSF Pilot	17	0.617
ITS RR1	32	1.161
WRC-NSF RR1	25	0.907
TW RR1	26	0.943
ITS RR2	36	1.306
WRC-NSF RR2	37	1.342
TW RR2	20	0.725
Mean	27.6	
Standard Deviation		0.28

If a test (of 5 replicates) is carried out at laboratory A (say), then the best estimate of the mean result that would be obtained over many laboratories (the ‘true mean’) is the result at the first. Further, we can be confident that true mean is less than:

$$\text{Result at laboratory A} * (1 + \text{multiplier} * 0.28)$$

The multiplier is 2.0, obtained from the t distribution with 5 degrees of freedom and a single tail of 10%.

Similarly we can be confident that the true mean is greater than:

Result at laboratory A * (1 - multiplier * 0.28)

Similarly, if tests at N (= 2 or more) laboratories are carried out, the 80%ile range for the true mean is:

Mean of results at N laboratories * (1 +/- multiplier * 0.28 / N)

The values for N = 1, 2 and 3 are shown in the main text, table 5.