EXTRACTION WATER JUSTIFICATION REPORT

Background

Several European nations have developed metal extraction tests for some materials used in drinking waters[1], with the oldest program (Denmark) having been in operation for approximately 14 years[2]. Scandinavian countries have generally adopted the "Nordtest" method for assessing the potential for lead release by plumbing components in contact with drinking water. The "Nordtest" method is similar to the "BSI" testing protocol, but they differ slightly in the acceptance criteria to be applied[1]. Table I gives the composition of the extractant water used for the Nordtest method. Unfortunately, little information is available on the rationale for the composition of the challenge water, and the discussions leading up to its adoption by the European community. The water would only be considered to be moderately aggressive (at the most) by many standards.

Much of the published literature on the effects of water on brass, bronze, and other lead-containing alloys reflects field experiences and laboratory studies revolving around the phenomenon of "dezincification." Many of these studies have been recently reviewed[3,4]. Jester has pointed out that because the standard materials used for small valves and fittings in the United States have tended to be red brasses with low percentages of zinc, the terrible problems with dezincification prevalent in Great Britain and some other places in northern Europe have generally been avoided[5]. Thus, relatively little research has been done in the United States that was directed towards understanding the corrosion or leaching of metals from plumbing fittings. Only in the past several years have studies attempted to isolate the contribution of fittings to metal concentrations in the water, aside from the contribution of soldered joints. Therefore, there are extensive gaps in being able to predict metal uptake into the water given differences in water chemistry, differences in manufacturing process, or differences of a few percent in metal concentrations in various alloys.

Table I. Nordtest solution components[1]. The amounts given are weights dissolved in 1 litre of test water.

Method 1

Reagent	Weight Added
NaCl	50 mg
Na_2SO_4	50 mg
$CaCO_3$	50 mg
CO_2 gas	until $CaCO_3$ is dissolved; then
Air	until pH = 7.0 (± 0.1)

Method 2

Reagent	Weight Added
NaCl	50 mg
Na_2SO_4	50 mg
$Ca(OH)_2$	37 mg
CO_2 gas	until pH < 5; then
Air	until pH = 7.0 (± 0.1)

Preliminary Studies by NSF

Several types of pipe and coupon material (such as brass) from plumbing products were tested by NSF using test waters buffered at pH 5, 8, and 10[6]. This testing procedure included three "conditioning" extractions, followed by three 24-hour extractions with the test waters. For brass, the leaching of copper and zinc was greatest at pH 5, and least at pH 10. The same trend was followed for zinc from galvanized pipe, and copper from copper pipe. Curiously, the leaching of lead from brass was higher at pH 10 than at pH 5 or pH 8. This behavior was at conflict with what had been indicated in various field and laboratory studies of lead solubility in potable water systems[7-9], so it warranted further investigation.

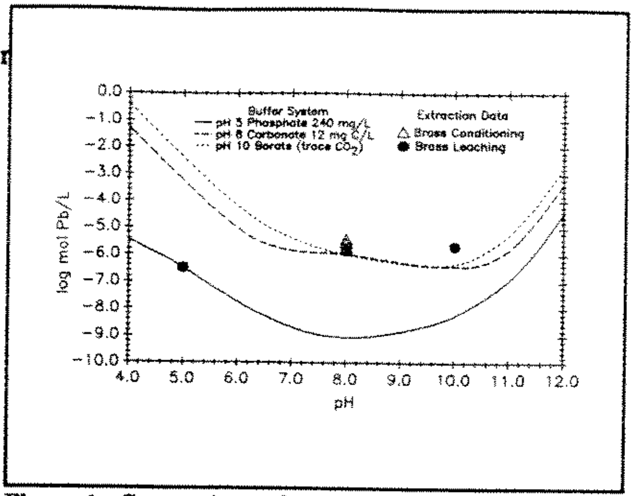


Figure 1 Comparison of computed lead solubility with theoretical model.

Computations were made of the theoretical equilibrium solubility of the three metals, along the lines previously outlined for lead[7,9,10], copper[10], and zinc[10]. The equilibrium constant data for lead is much more reliable than that for zinc and copper, because critical selections could be made that were consistent with extensive experimental evidence. The results of these calculations are shown, along with the observed leaching test data, in figures 1-3. The pH 10 water was assumed to contain a small amount of carbon dioxide, which would be probable for the solutions prepared in the laboratory. An equilibrium amount was assumed, approximately 1.6 mg C/L. The pH 5 system contained 240 mg PO_4/L, a known potable water corrosion inhibitor.

The quantitative predictions of the lead model match the experimental data quite well. The other two metals show the predicted trends in solubility. This execersise showed convincingly that the strategy of pH buffering using salts that have a profound effect on metal corrosion can not give test results that have any meaning when applied to realistic field situations for the plumbing materials.

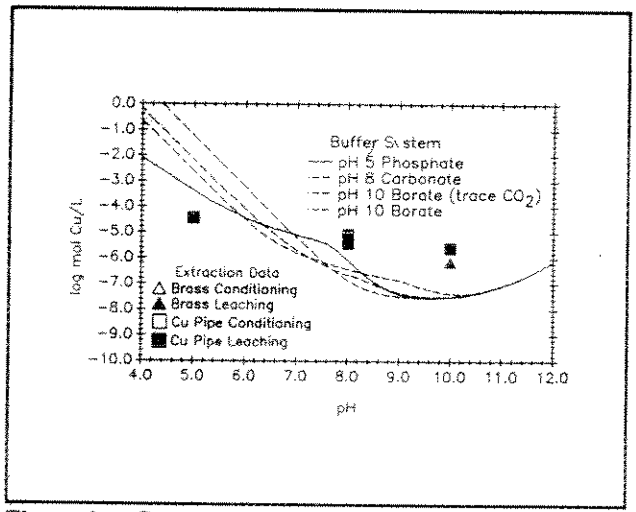


Figure 2 Comparison of theoretical copper solubility and data from brass and copper pipe leaching tests.

Leaching by pH Buffered Solutions

To explore the behavior of various brass materials, leaching tests were started using a variety of different solutions, that were chosen to be consistent with those proposed for different parts of NSF Standard 61[11]. Laboratories from four different manufacturers conducted different combinations of tests. Recipes for the solutions used in this four-part round of testing are given in Table II. In general, the analyses were performed in triplicate on devices replicated in triplicate. The testing protocol was one of "dump and fill"; in other words, the leachate contained within the device was collected, and after rinsing with test water, the device was refilled for another 24-hour dwell period. Some tests were also performed on brass bar stock, but the results were not only variable within pieces replicated by each company, but also between companies at the same water quality. Review of the data suggested that the material itself was inhomogeneous with respect to the lead distribution in the brass, and the act of cutting added to the variability by "smearing" the lead at the surface where the cuts were made.

The most notable characteristic of this round of testing was that there was substantial variability of the readings from the three individuals of each device tested. There were also notable problems with matrix effects in the analyses of some of the organics at pH 5 and pH 10. Several solutions were exchanged between testing laboratories to look at reproducibility of the analytical methods. Generally poor correlation was obtained. The trend in the leaching behavior was that the mean metal concentrations in the leachate solutions decreased sharply over a very short period of time, and then tended to decrease much more slowly throughout the remainder of the test periods. Results of the many tests described by Table II are available, but will not be included in this report.

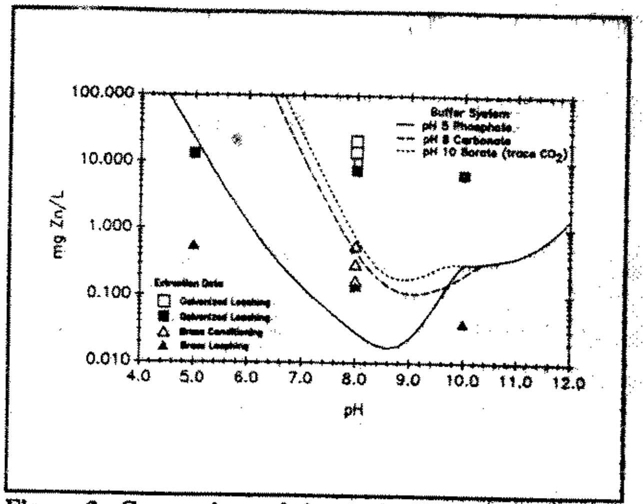


Figure 3 Comparison of theoretical zinc solubility and data from brass and galvanized pipe leaching tests.

Unbuffered Water Tests

At this point, the decision was made that pursuing the buffered solutions would not lead to a scientifically defensible challenge water. Because the effect of different major water chemistry parameters on the behavior of brass was not known very well, five simple solutions were devised to test the effects of two fundamental background constituents: pH, and alkalinity (through the combination of pH and dissolved inorganic carbon concentration, DIC). A review of the corrosion literature with respect to brass behavior had been done[3], which revealed a very large number of potentially important parameters which would vary greatly over the vast number of U. S. water supplies. Some of these significant variables, aside from pH and DIC, were the concentrations of sulfate, chloride, chlorine residual, hardness (in terms of calcium carbonate precipitation potential), the flow velocity, and temperature. Representing U. S. water conditions overall would be impossible. Therefore, the five test solutions, described in Table III, were used to explore the most basic chemical relationships. The five waters represented two acidic waters with a ten-fold difference in DIC, two slightly basic waters representing many treated or untreated waters, with relatively extreme alkalinities, and a pH 10 water that might be representative of some lime-soda softened waters, or soft waters having the pH adjusted for lead and copper corrosion control.

Initial experimentation with these five waters revolved around three companies (A, B, and C), using the "dwell and dump" protocol for approximately three months. The schedule for a 14-day period is summarized in Table IV. Triplicate readings were taken of triplicate devices, as before. Mean concentration data for copper, zinc, and lead are shown in Figures 4 through 18 for each test water, with lines representing the data from each of the three companies. Figures 19 through 27 show the same data, arranged with each line representing one of the 5 different challenge waters for each metal and company. The concentrations reported for companies A and C are those directly observed in the solution contained within the tested devices. The concentrations reported by company B had been adjusted to a 1-liter hypothetical volume basis by dividing by the volume of the device, so they are systematically lower than those for companies A and C by a factor of approximately 8 to 11 (the volume of the device was not reported).

The data are plotted on a semi-logarithmic scale, to enable reading the wide range in concentrations with reasonable precision. An important property of semi-logarithmic plots is that data following an exponentially decreasing trend will plot as a straight line with a negative slope. The rapidly decreasing mean metal levels observed at the start of many of the tests is thus clearly shown by the linear trend and negative slope in many of these graphs. Data on individual means of the triplicate readings are available, but could not be readily plotted without making the graphs very confusing.

Table IV. Protocol for unbuffered waters stagnant water faucet tests.

Day	Event
0	Rinse for 15 min with tap water. Fill with test water (TW).
1	Dump water, rinse (TW) and refill.
2	Same.
3	Same.
4	Analyze leachate. Rinse (TW) and refill.
5	Dwell
6	Dwell
7	Dwell
8	Dwell
9	Same as day 1.
10	Same.
11	Analyze leachate. Rinse (TW) and refill.

For copper leaching from the brass faucets, the trends in these leaching tests tended in many cases towards consistent or higher concentrations over time, rather than the decrease that was expected. The pH 5 waters showed more of an initial decrease than the other three test waters. Thus, the trend of leaching behavior is a function of water quality, as well as the concentrations themselves. For companies A and B, the most aggressive test waters were those with high DIC, namely waters 4 and 2. For company C, waters 4 and 1 were the most aggressive. For companies A and C, the least aggressive water was water #5, which would be consistent with solubility considerations[10]. For company B, the least aggressive water was water #1, which was the pH 5 water with low DIC. There was a considerable systematic difference in mean concentration between the companies that probably can not be accounted for by volume differences alone.

For zinc, the most aggressive waters were consistently the pH 5 waters. The third most aggressive water was usually water #4, except for the end of the company C experiments. Only a few of the zinc leaching tests showed the initial rapid decrease that was expected. Considerable variability was seen within the same run over time.

For lead, there was considerable random variation in concentration over time, even on the logarithmic scale. Also, there were considerable differences in mean concentrations obtained within a test water type that was beyond differences in volume of device. For instance, data from company B, with the normalization to 1 L volume, was frequently between that for companies A and C, particularly for test waters 3, 4, and 5. Company to company variability frequently exceeded differences from one test water type to another for a given company. For company A, the order of aggressiveness changed throughout the run, though water 1 (pH 5, low DIC) consistently yielded the highest lead levels. Water 5 (pH 10) was usually the least aggressive. For company B, the most aggressive water switched between water 1 and water 3, with water 4 very close during a large part of the run. Water 2 or water 5 was the least aggressive during various parts of the experiment. The data from company C showed water 1 to be the most aggressive, with all four other waters giving very similar results. In these experiments, the exponential decrease in lead leaching over time was most evident.

Additional Test Protocols

Several different alternate extraction protocols were investigated, that go beyond the scope of this report. Experiments were also being conducted during the spring and summer of 1989 using deionized water as the leaching solution. Data are not yet available on the results of the deionized water experiments. One alternative testing protocol was that including "ageing" by city tap water between 24-hour extractions. Following an initial 15 minute flush with city water, the faucets were rinsed with deionized water. The faucets were filled with extraction water (water #2 or water #4) after rinsing with the extractant water, and were left to dwell for 24 hours. Following the emptying of the faucets and collection of the leachate, city water was then run for 48 hours at 0.25 gpm. Next, the faucets were rinsed with extractant water and left to dwell for 24 hours, as before. After sample collection, another period of 48 hours of 0.25 gpm city water flushing was done. This weekly schedule was followed for 4 weeks. Results of one of these experiments for lead leaching is given in Figure 28.

Conclusions

1. The trend in lead leaching behavior was that the mean concentration in the leachate solutions decreases sharply over a short period of time at the beginning of exposure, and then tends to decrease much more slowly thereafter. This trend was observed in data from tests with all test waters tried. This supports the idea that contributions of lead from brass devices in field situations reach levels near or below detection levels after (at most) a few years.

2. There are many complex water chemistry interrelationships governing the metal leaching from metal plumbing materials. The range of important variables found in over 88,000 U. S. water supplies can not be adequately simulated by a practical number of challenge waters.

3. The order of aggressiveness of the five waters tested differs from one metal tested to another. Materials other than brass were not tested. However, variation in aggressiveness

from one material to another would also be expected, based on evidence in the potable water corrosion literature (eg. references 10, 12-14, and the whole publication cited in reference 9).

4. The order of aggressiveness of the five waters was not entirely consistent from testing laboratory to testing laboratory. Hence, there is probably a significant sensitivity to some aspect of solution preparation that should be considered to enable reproducible results.

5. There was wide variability in leachate metal concentrations from faucet to faucet for the same test conditions. This variability was often greater than differences between one test water and another, or from one company's product to that of another. The latter may or may not be attributable to real differences in product leaching behavior. This variability obscures differences in product behavior under different water qualities, and suggests that presently an increase in the number of test waters will not necessarily improve the prediction of product or material behavior under actual service conditions.

6. Because no single test water could be found that would be a reasonable challenge and would also give the same relative behavior for all metals investigated, water #4 was selected as a viable compromise of reproducible preparation and aggressivity to a variety of metals. The single challenge water proposed provides as reasonable an approximation of product bahavior as two or three challenge waters. The latter would increase the costs of testing out of proportion to the probable information gain.

7. The proposed test water should provide no particular interferences for routine methods of analysis of targeted organics and inorganic metals.

8. Current secondary MCL's for zinc and corrosivity, and future regulations for corrosivity (through lead and copper) will reduce the range in water qualities to which devices and materials should be reasonably exposed. Many materials, such as galvanized and lead pipe, have been known to give poor performance in a variety of water conditions (such as low pH for both, low hardness and alkalinity for galvanized pipe), so they should not be tested outside of normal applicability.

9. These kinds of leaching tests do not take into account any galvanic corrosion that might result in an actual field installation. Therefore, being overly concerned with the test water composition without substantial further fundamental research is not warranted.

References

1. Mattson, E. & Eistrat, K. Lead Release from Leaded Copper Alloys in Tap Water. *Swedish Corr. Inst. Report 1986-02-28*, (1986).

2. Nielsen, K. Measurementsand Test Procedure for Cadmium and Lead Pick Up in the Water from Drinking Water Installations. *Scand. Corrosion Consr.* 7th, pp. 36-46 (1975).

3. Schock, M. R., & Neff, C. H. Trace Metal Contamination from Brass Fittings, *Jour. AWWA*, 80:11:47 (1988).

4. Oliphant, R. Dezincification by Potable Water of Domestic Plumbing Fittings: Measurement and Control. *Water Research Centre Technical Report TR88*, 1978.

5. Jester, T. C. Dezincification Update. *Jour. AWWA*, 77:10:67 (1985).

6. National Sanitation Foundation Drinking Water Additives Program, "Pipes and Related Products Task Group Exposure Methods Study," Unpublished, November, 1987.

7. Schock, M. R. Response of Lead solubility fo Dissolved Carbonate in Drinking Water. *Jour. AWWA*, 72:12:695 (1980). Errata 73:3:36 News (1981).

8. Schock, M. R. & Gardels, M. C. Plumbosolvency Reduction by High pH and Low Carbonate: Solubility Relationships. *Jour. AWWA*, 75:2:87 (1983).

9. Schock, M. R. & Wagner, I. The Corrosion and Solubility of Lead in Drinking Water. Chapter 4 in *Internal Corrosion of Water Distribution Systems*, AWWA Research Foundation/DVGW-Forschungstelle cooperative Research Report (1985).

10. Schock, M. R. Treatment or Water Quality Adjustment to Attain MCL's in Metallic Potable Water Plumbing Systems. *Proc. of the Seminar on Plumbing Materials and Drinking Water Quality*, USEPA, Cincinnati, OH, May 16-17 (1984), EPA/600/9-85/009.

11. National Sanitation Foundation , Drinking Water System Components- Health Effects, *NSF Standard Number 61*, June 1988.

12. James M. Montgomery Consulting Engineers, Inc. *Water Treatment Principles & Design*, John Wiley & Sons, New York, 1985.

13. USEPA, *Corrosion Manual for Internal Corrosion of Water Distribution Systems*, Office of Drinking Water, EPA 570/9-84-001 (April 1984). Identical to AWWA's *Corrosion Control for Operators*.

14. Snoeyink, V. L., & Jenkins, D. *Water Chemistry*, John Wiley & Sons (1980).

Table II. Water formulations for leaching tests with buffered pH (mL added per L of test water).

	Test #1		Test #2		Test #3			Test #4							
pH	5	10	6.4	9.4	5	8	10	5	5	5	5	10	10	10	10
Hardness	50	0	550	250	0	0	0	20	20	300	300	20	20	300	300
DIC	0	0	0	0	0	12	0	0	0	0	0	0	0	0	0
o-PO4	119	0	950	0	237	0	0	237	237	237	237	0	0	0	0
Borate	0	167	0	668	0	0	668	0	0	0	0	668	668	668	668
Sodium	29	86	53	258	57	23	345	57	57	57	57	345	345	345	345
Chloride	18	0	195	177	0	0	0	7	7	106	106	7	7	106	106
Chlorine	0	0	1	1	0	0	0	0	1,2	0	1,2	0	1,2	0	1,2
Solution															
NaHCO3															
0.04 M						25									
KH2PO4															
0.2 M			50												
Na2B4O7															
0.1 M		12.5		50			50					50	50	50	50
NaOH															
0.2 M			11.6	6.2											
0.1 M		12.5					50					50	50	50	50
CaCl2															
0.1 M				25											
0.05 M								4	4	60	60	4	4	60	60
MgCl2															
0.22 M			25												
0.04 M	12.5														
NaH2PO4															
0.1 M	12.5				25			25	25	25	25				

Notes:

1. Chloride and sodium concentrations are approximate. Chlorine residual was created by sodium hypochlorite addition, and pH was adjusted with HCl or NaOH.

2. Units of concentration are mg/L of species as indicated. Hardness is: mg CaCO3/L.

3. DIC = Dissolved inorganic carbon, mg C/L.

Table III. Water formulations for leaching tests with unbuffered pH (mL added per L of test water).

pH	5	5	8	8	10
Total Alkalinity	2	21	12	500	73
Hardness	0	0	0	0	0
DIC	12	120	2	120	12
o–PO4	0	0	0	0	0
Borate	0	0	0	0	0
Sodium	23	230	5	230	46
Chloride	34	339	0	5	37
Chlorine	2	2	2	2	2
Solution					
NaHCO3					
0.1 M	10	100		100	
0.01 M			20		
Na2CO3					
0.1 M					10
HCl					
1 M	0.95	9.55		0.13	0.55
0.01 M			0.23		50

Notes: *1. Chloride and sodium concentrations are approximate. Chlorine residual was created by sodium hypochlorite addition, and pH was adjusted with HCl or NaOH.*

2. Units of concentration are mg/L of species as indicated. Hardness and Total Alkalinity are mg CaCO3/L.

3. DIC = Dissolved inorganic carbon, mg C/L.

DWELL / DUMP TEST PROTOCOL

WATER TYPE 1 - COPPER

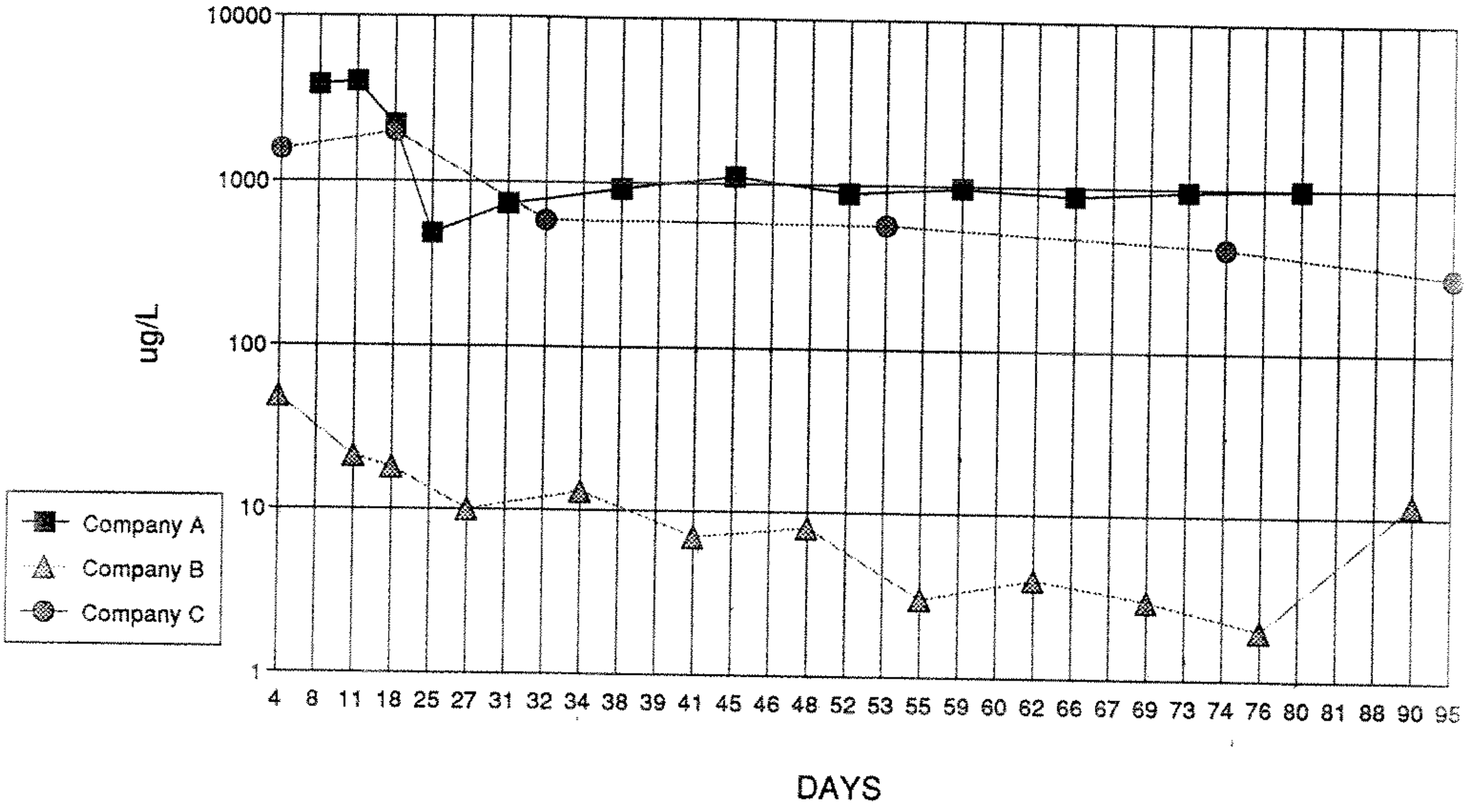
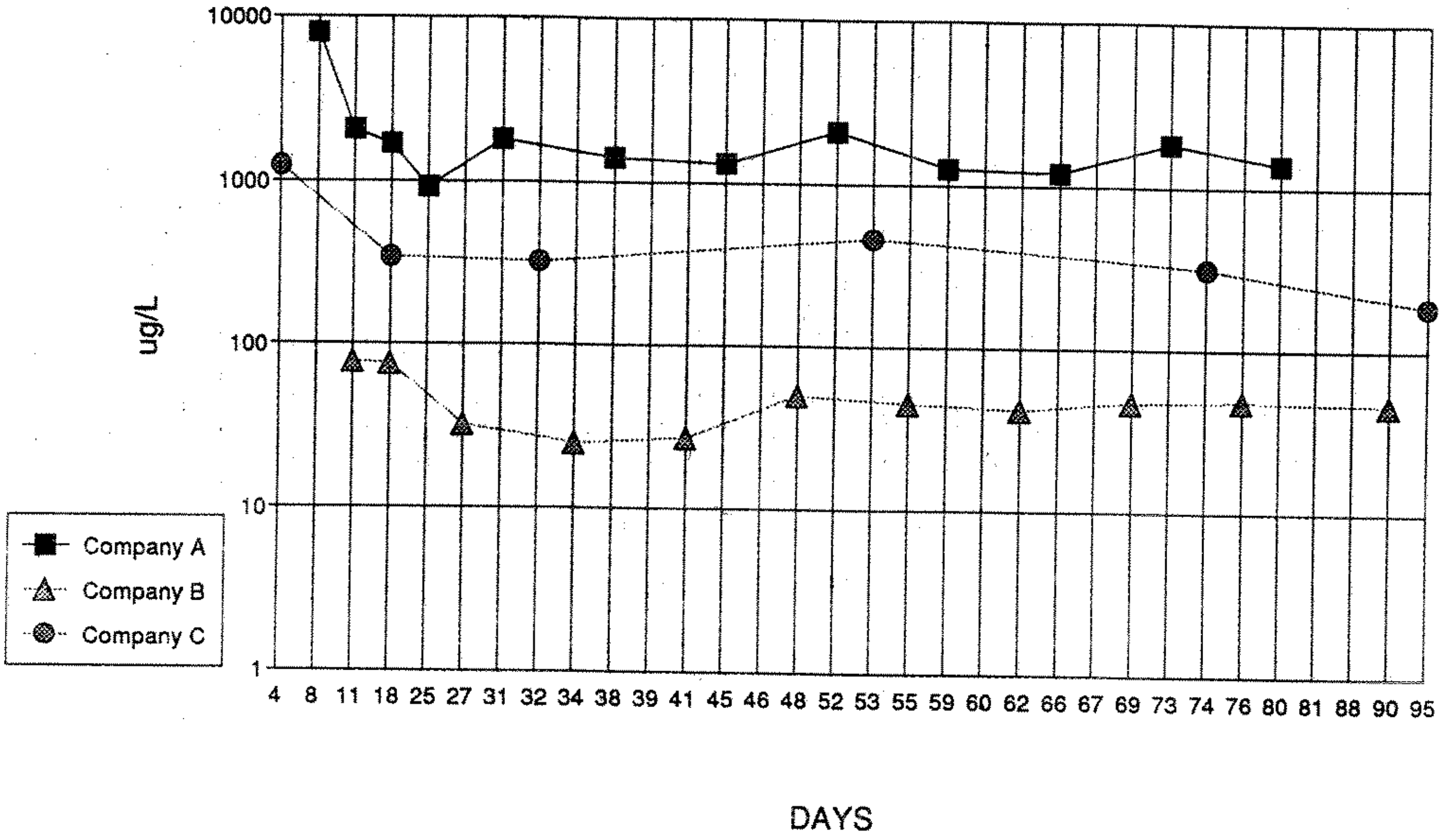


Figure 4



DWELL / DUMP TEST PROTOCOL

WATER TYPE 2 - COPPER

Figure 5

DWELL / DUMP TEST PROTOCOL

WATER TYPE 3 - COPPER

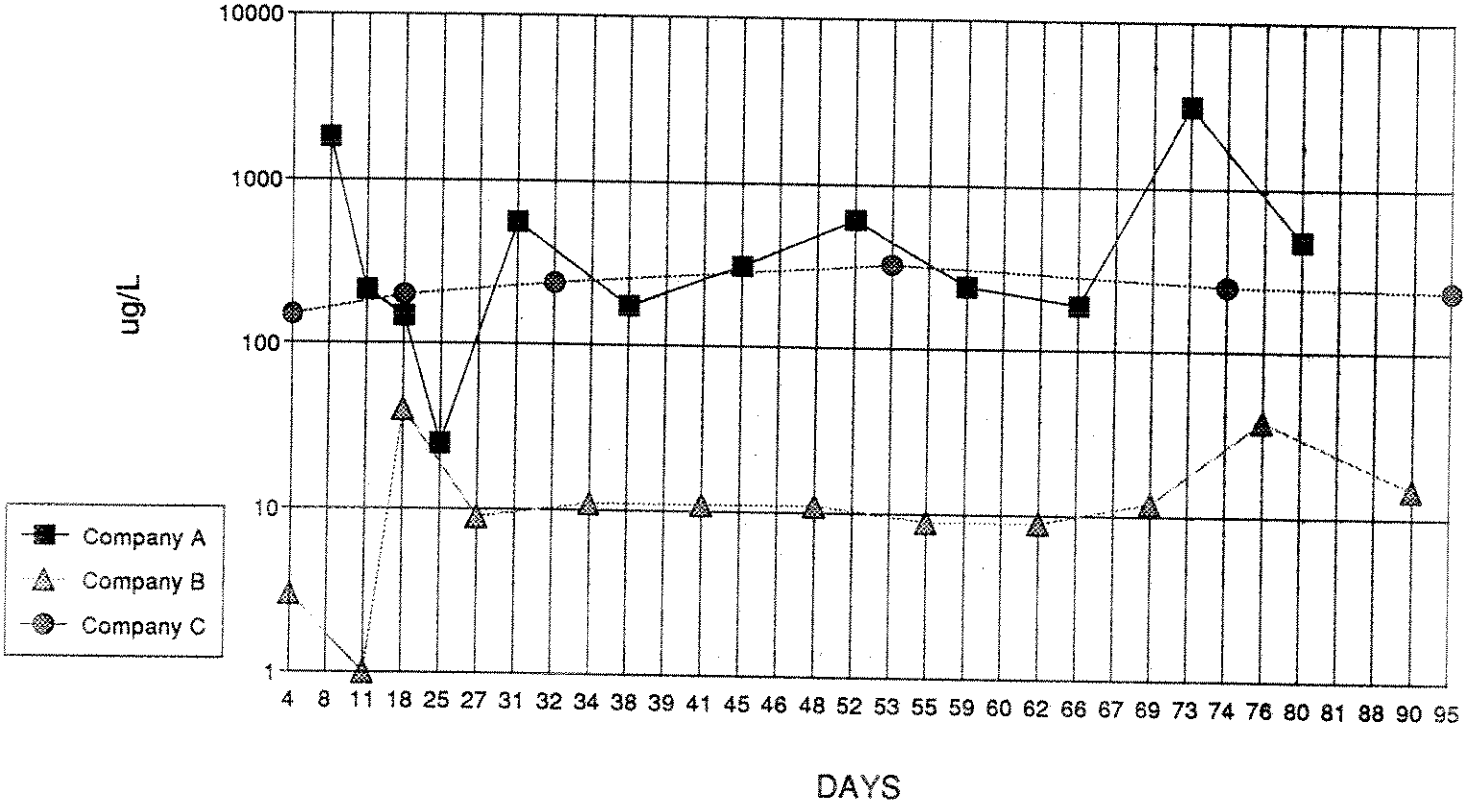


Figure 6

DWELL / DUMP TEST PROTOCOL

WATER TYPE 4 - COPPER

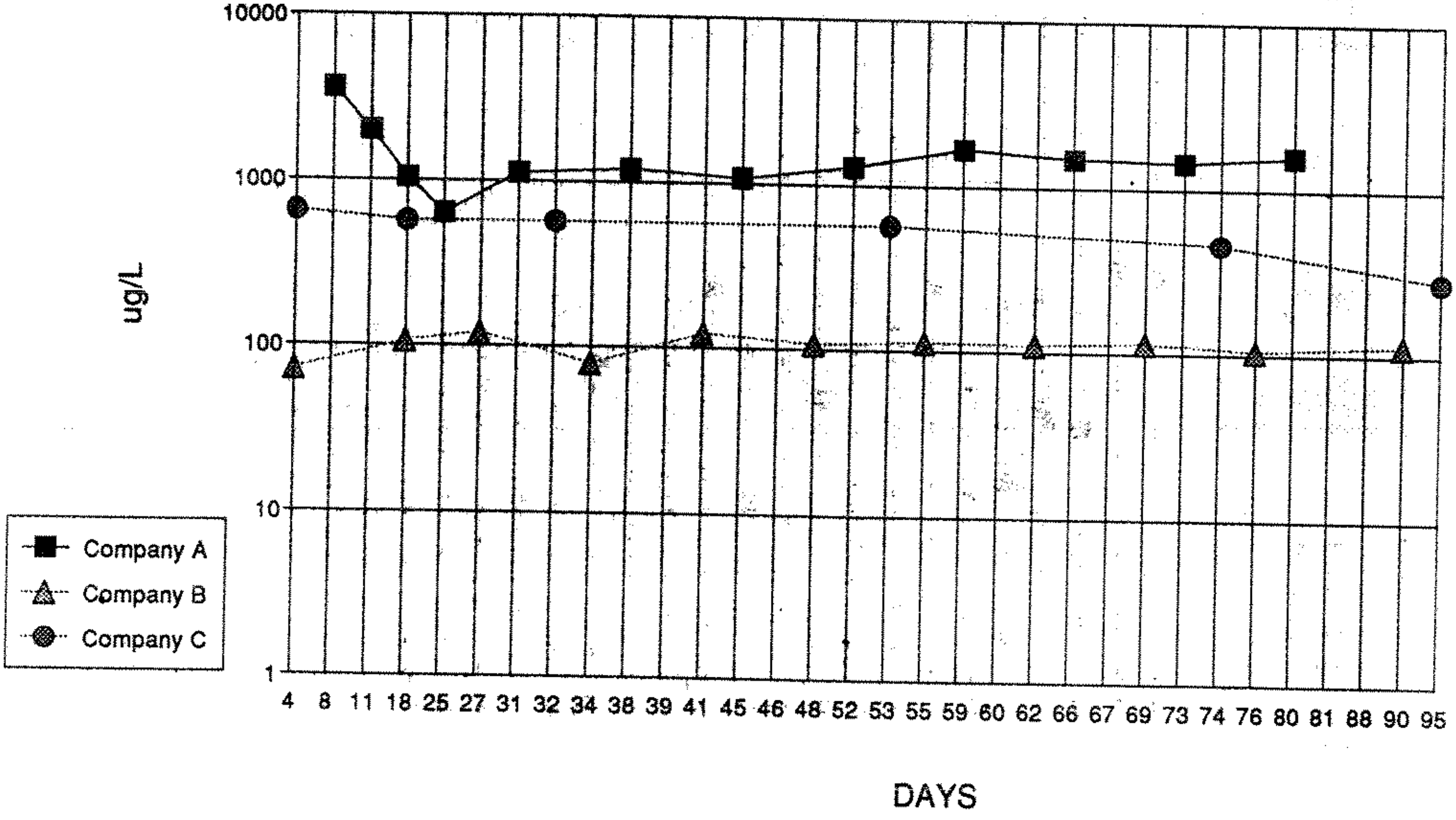


Figure 7

DWELL / DUMP TEST PROTOCOL

WATER TYPE 5 - COPPER

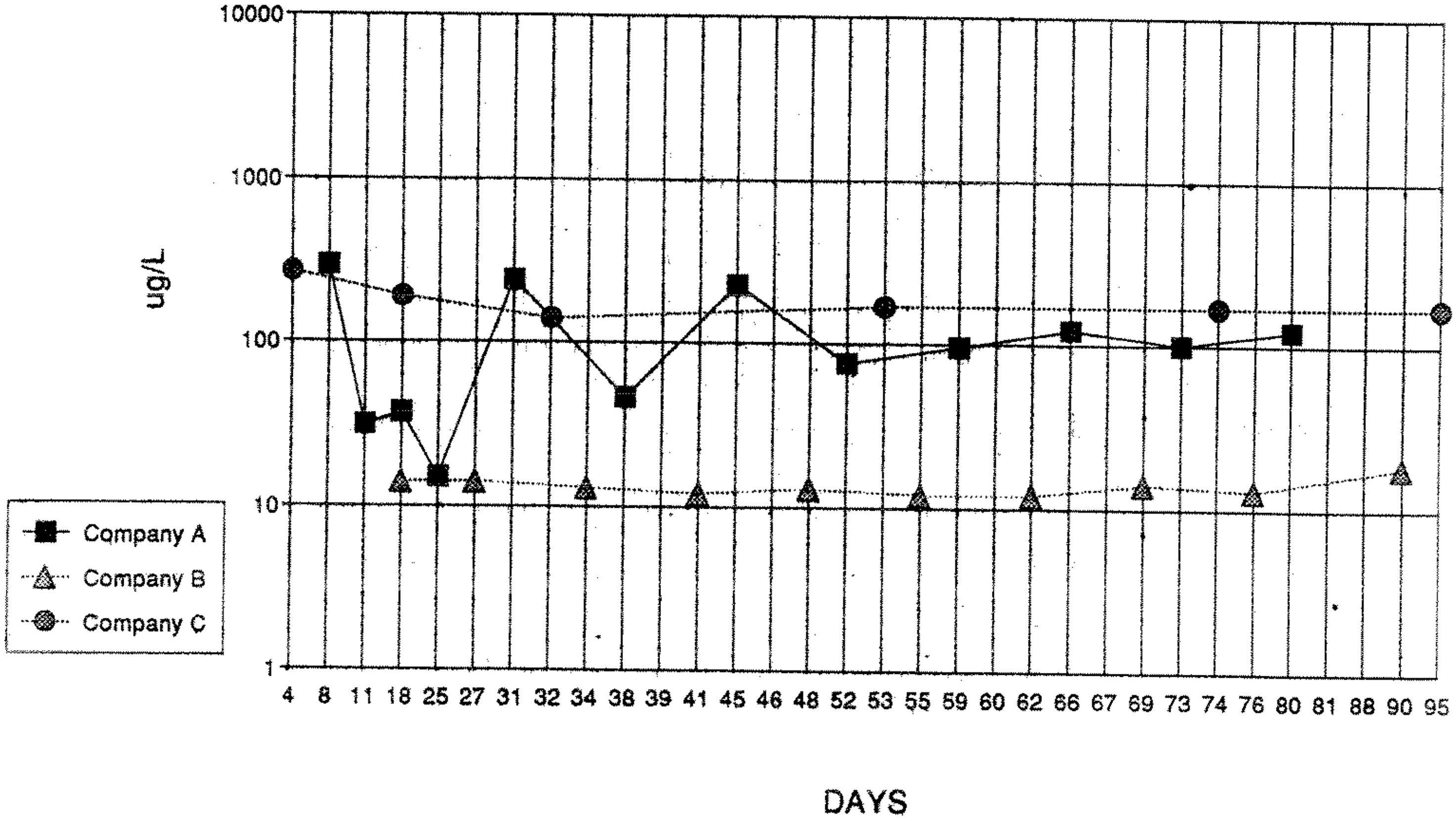
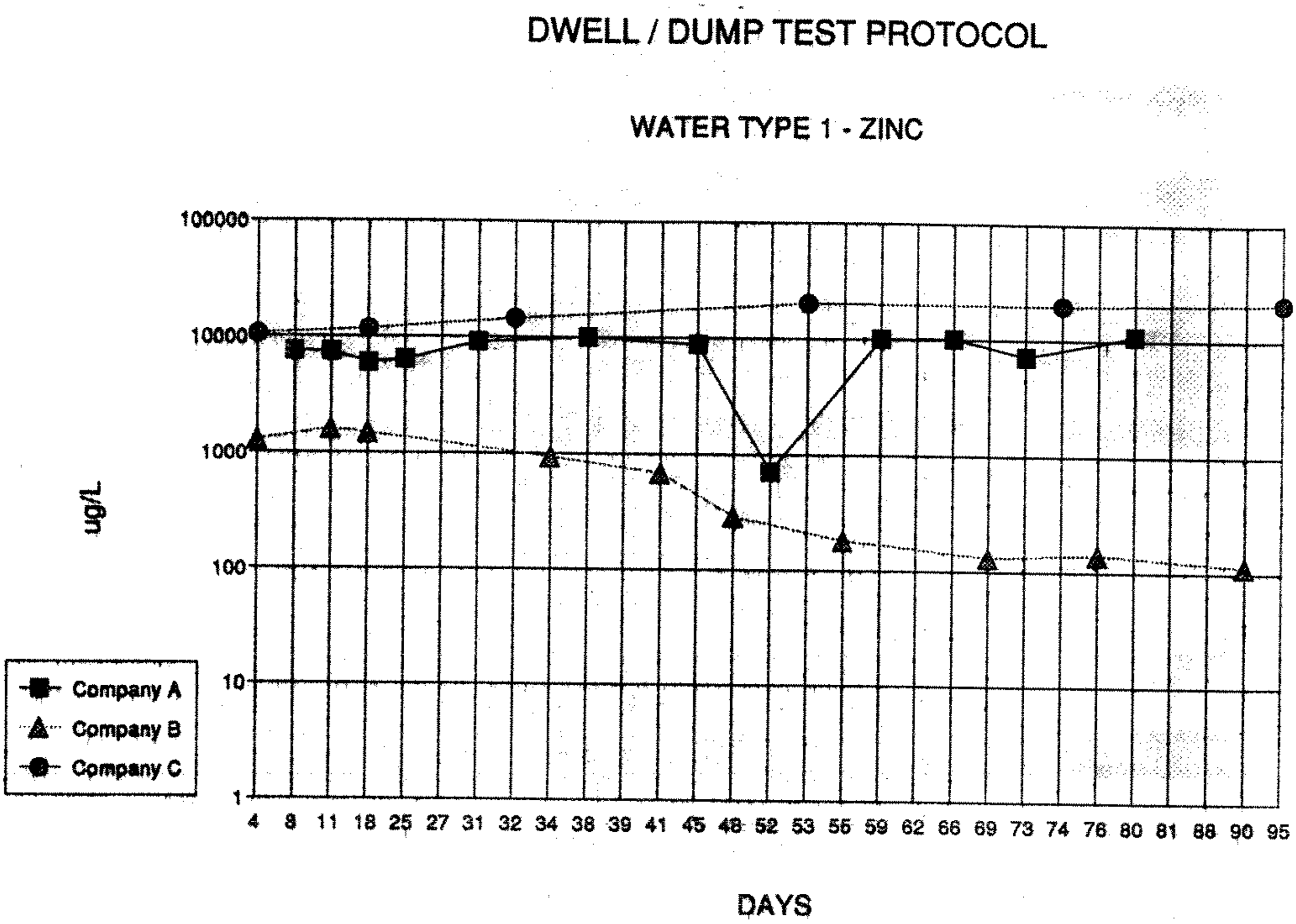


Figure 8



DWELL / DUMP TEST PROTOCOL

WATER TYPE 1 - ZINC

Figure 9

DWELL / DUMP TEST PROTOCOL

WATER TYPE 2 - ZINC

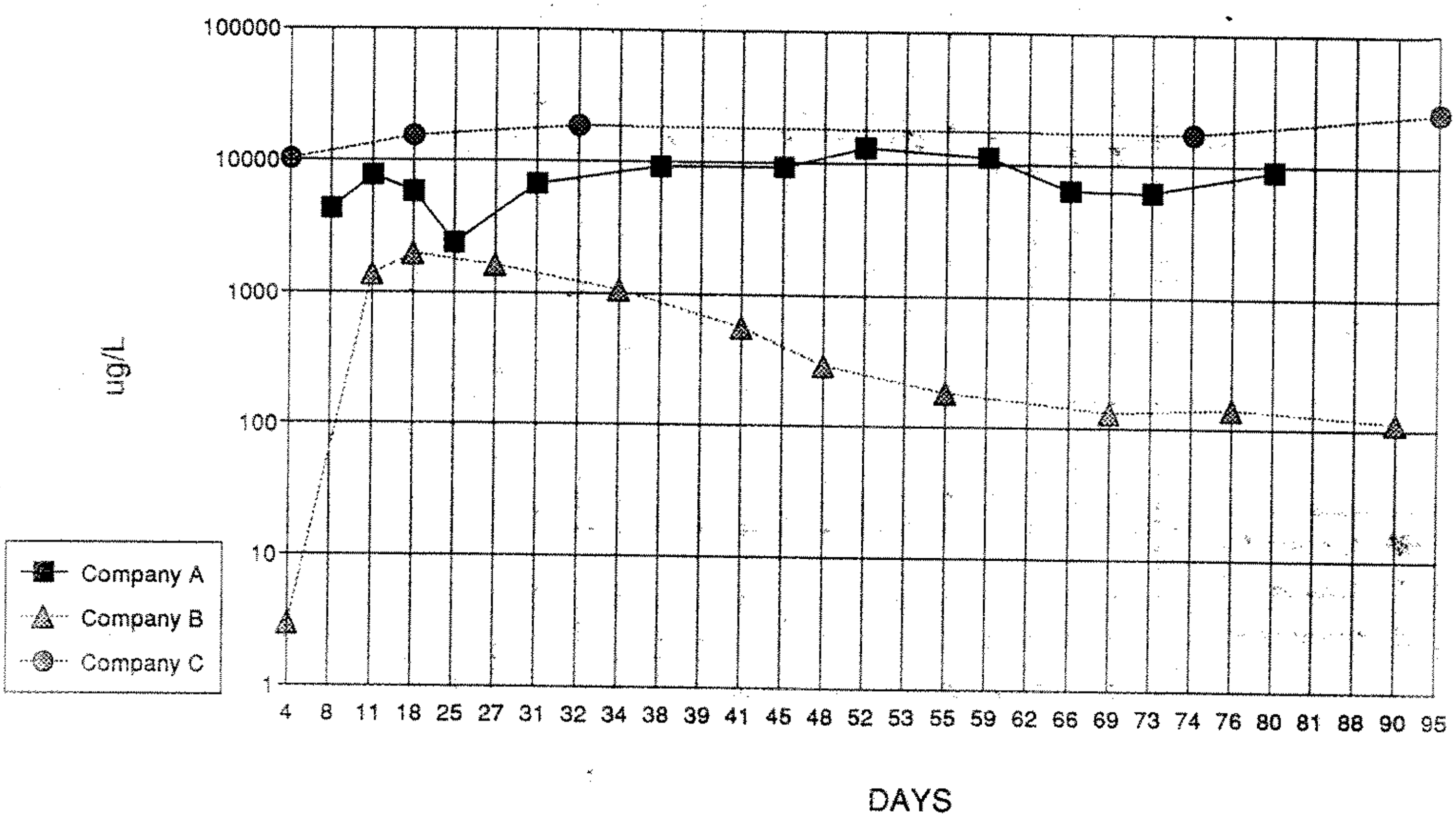


Figure 10

DWELL / DUMP TEST PROTOCOL

WATER TYPE 3 - ZINC

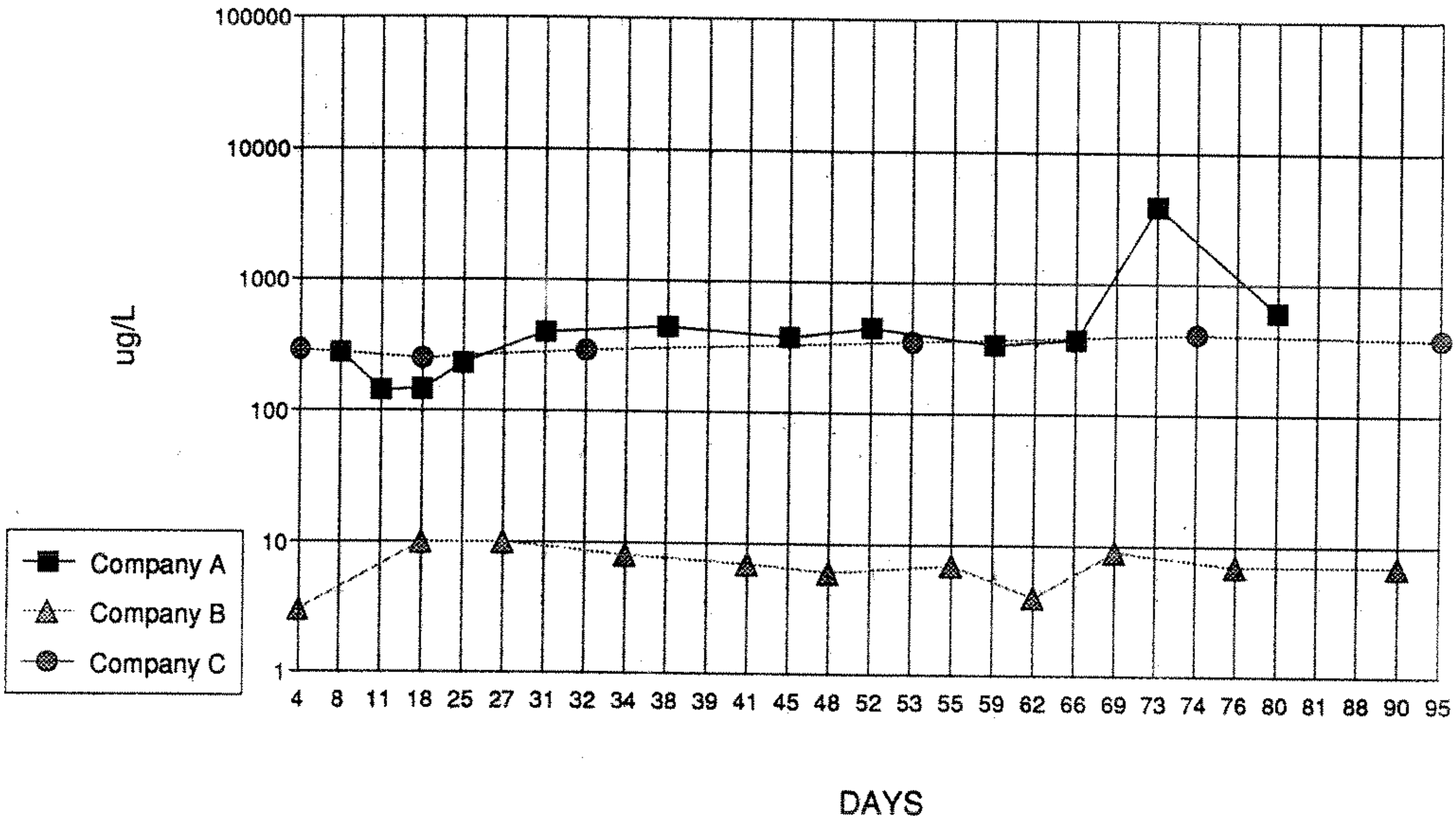


Figure 11

DWELL / DUMP TEST PROTOCOL

WATER TYPE 4 - ZINC

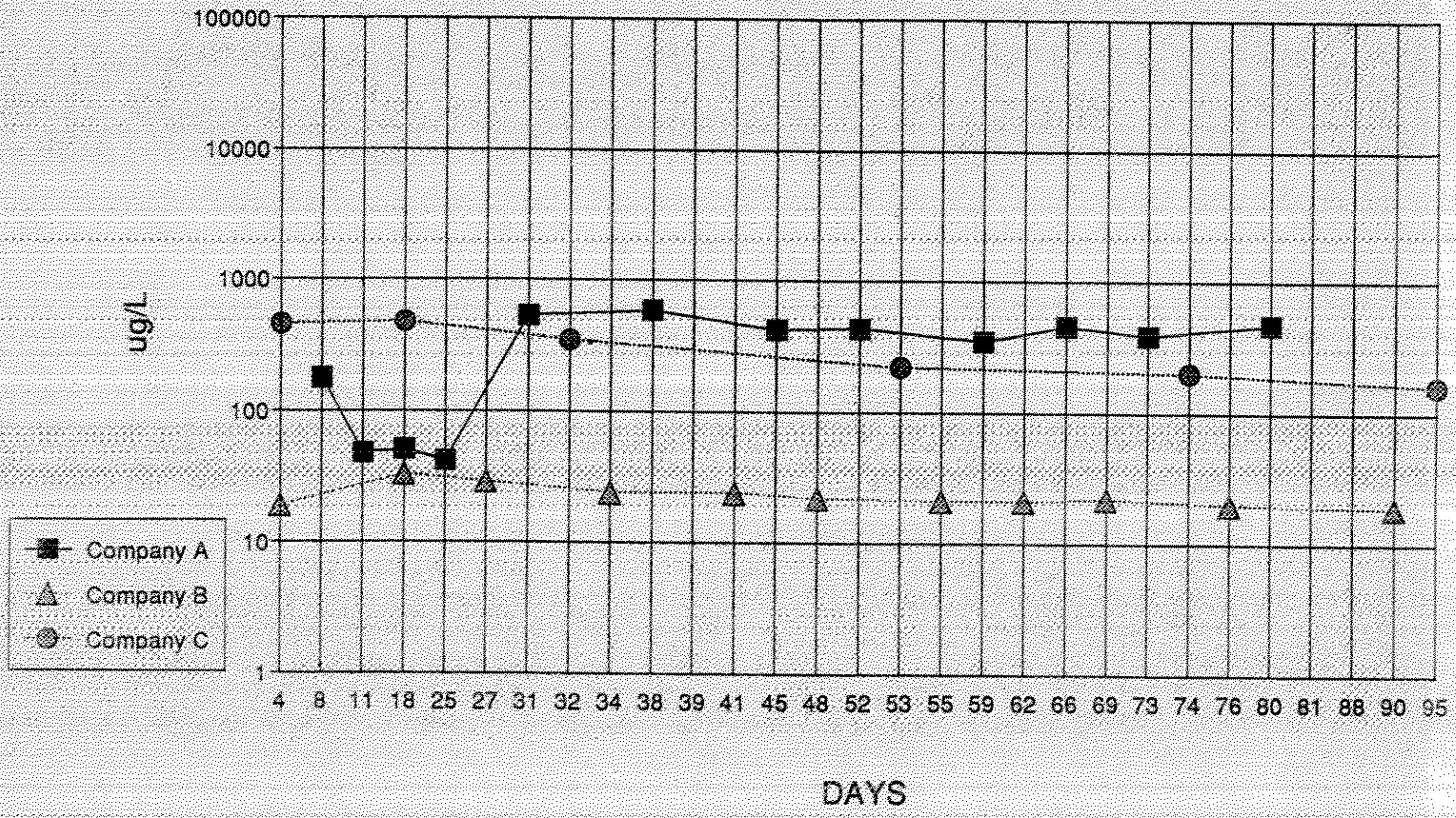


Figure 12

DWELL / DUMP TEST PROTOCOL

WATER TYPE 5 - ZINC

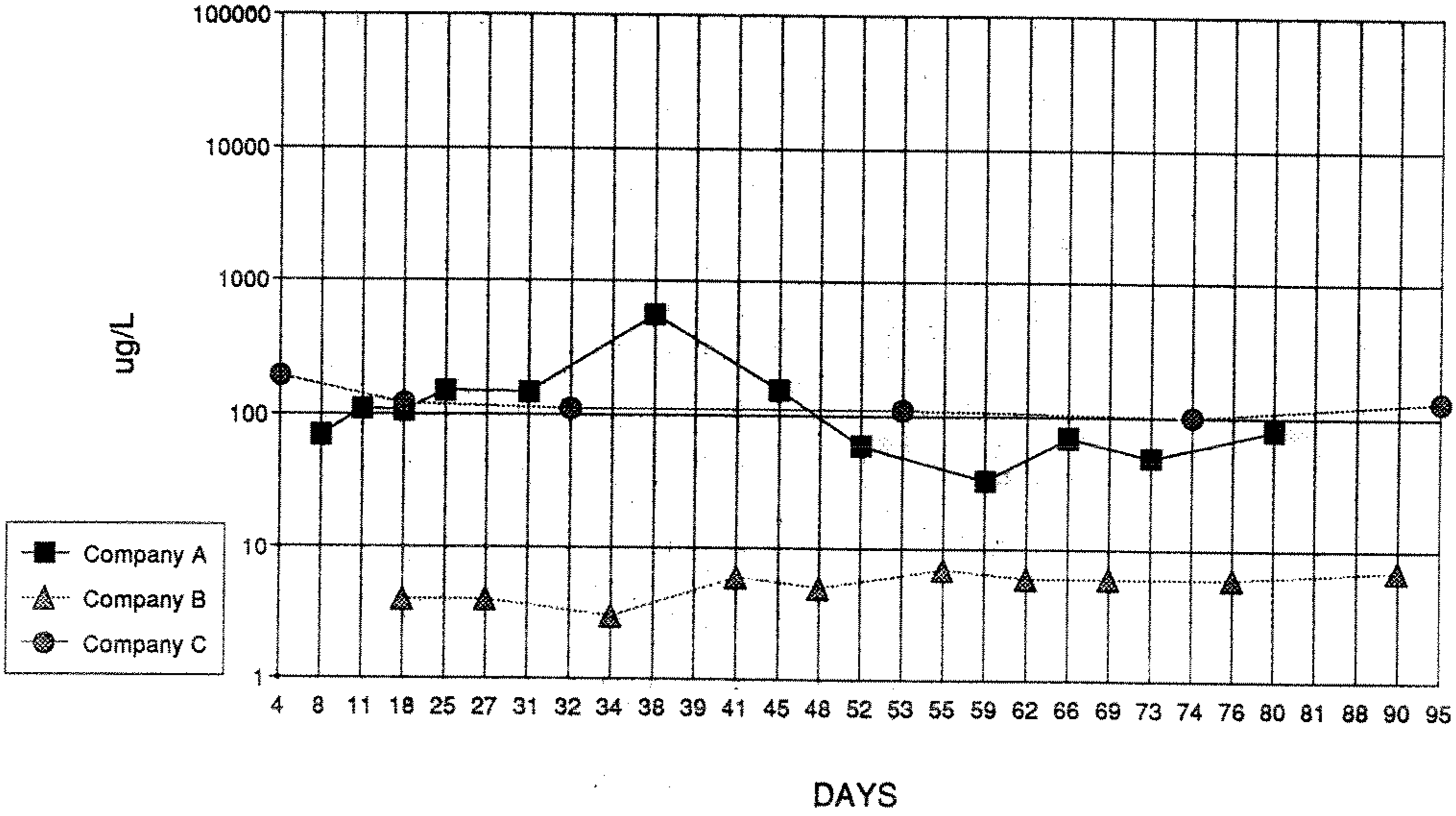


Figure 13

DWELL / DUMP TEST PROTOCOL

WATER TYPE 1 - LEAD

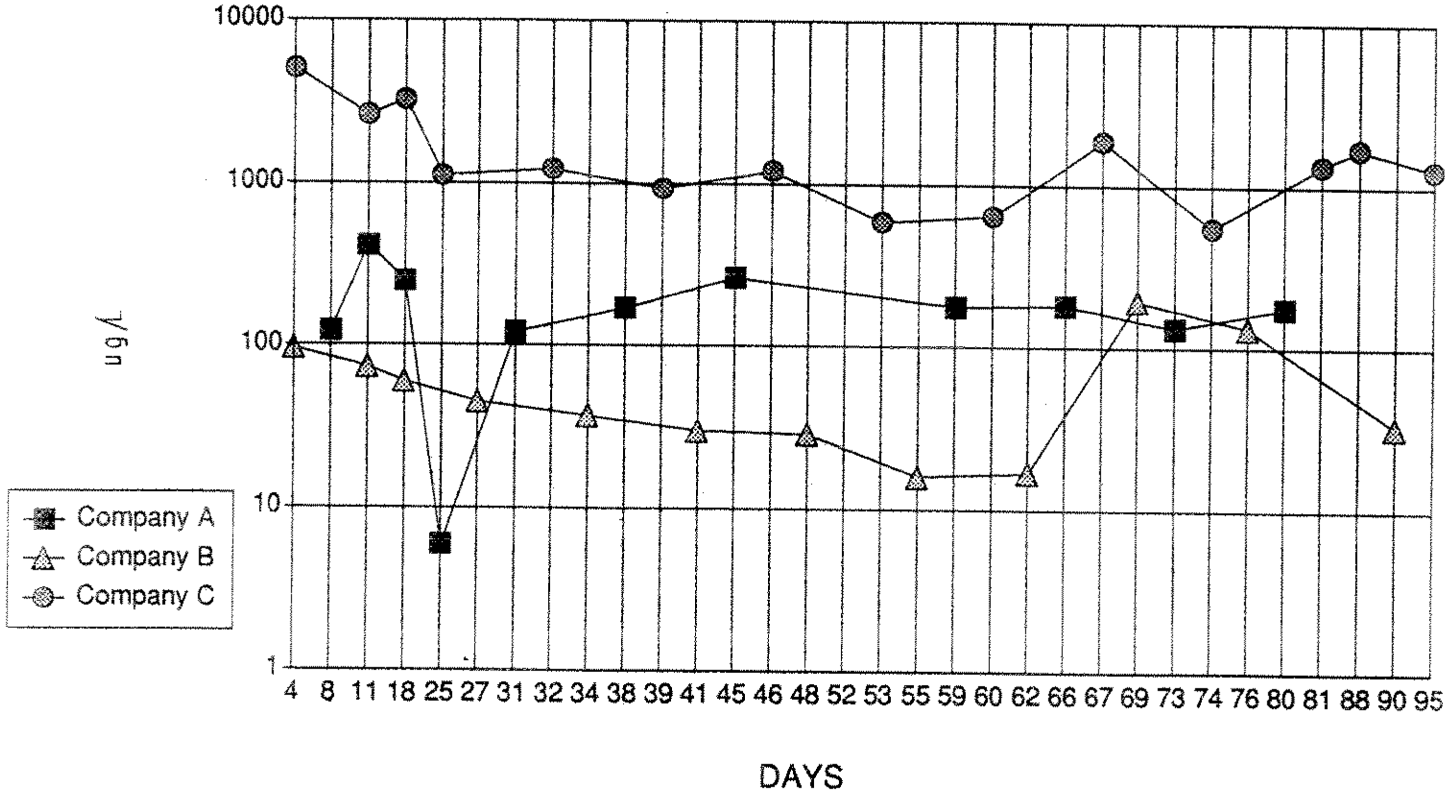


Figure 14

DWELL / DUMP TEST PROTOCOL

WATER TYPE 2 - LEAD

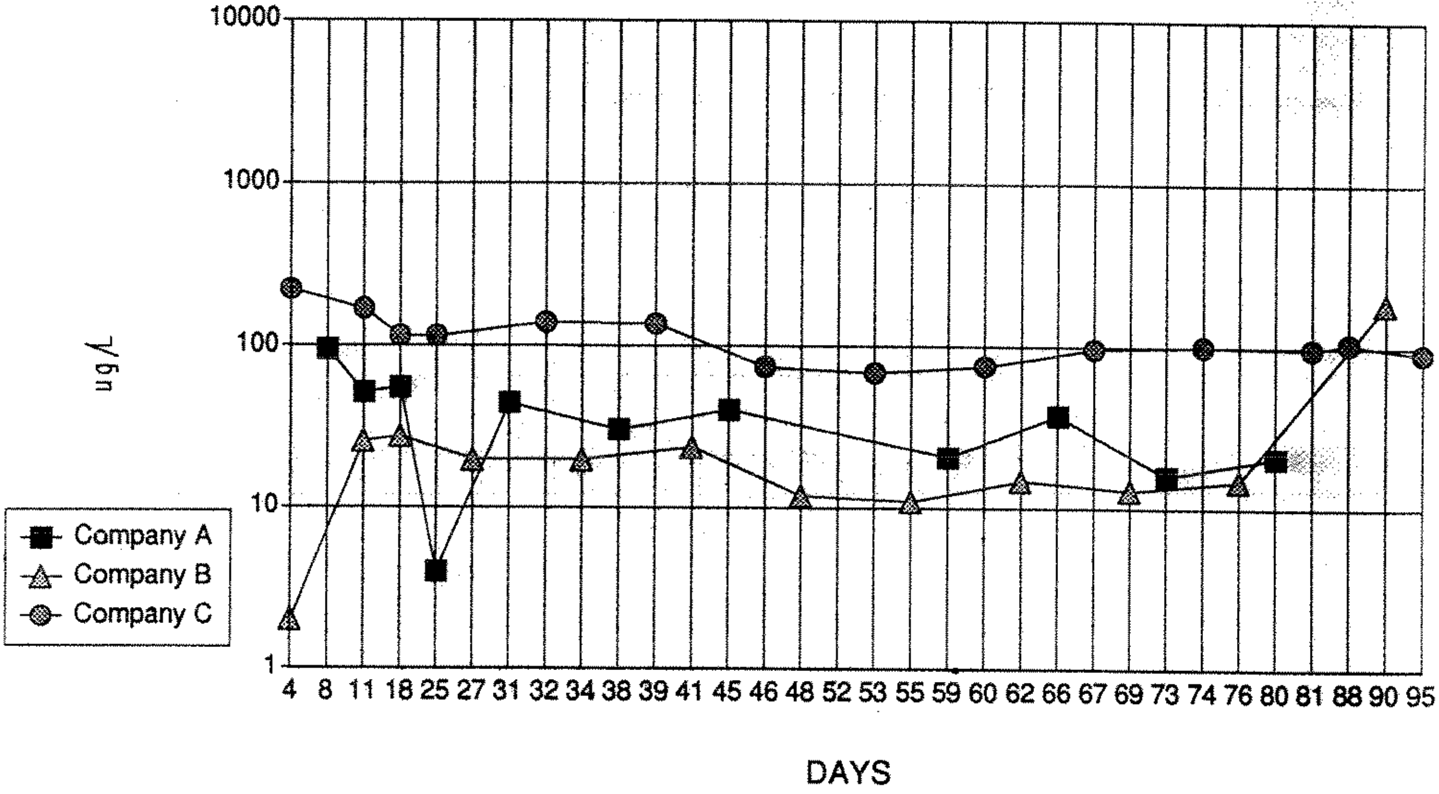
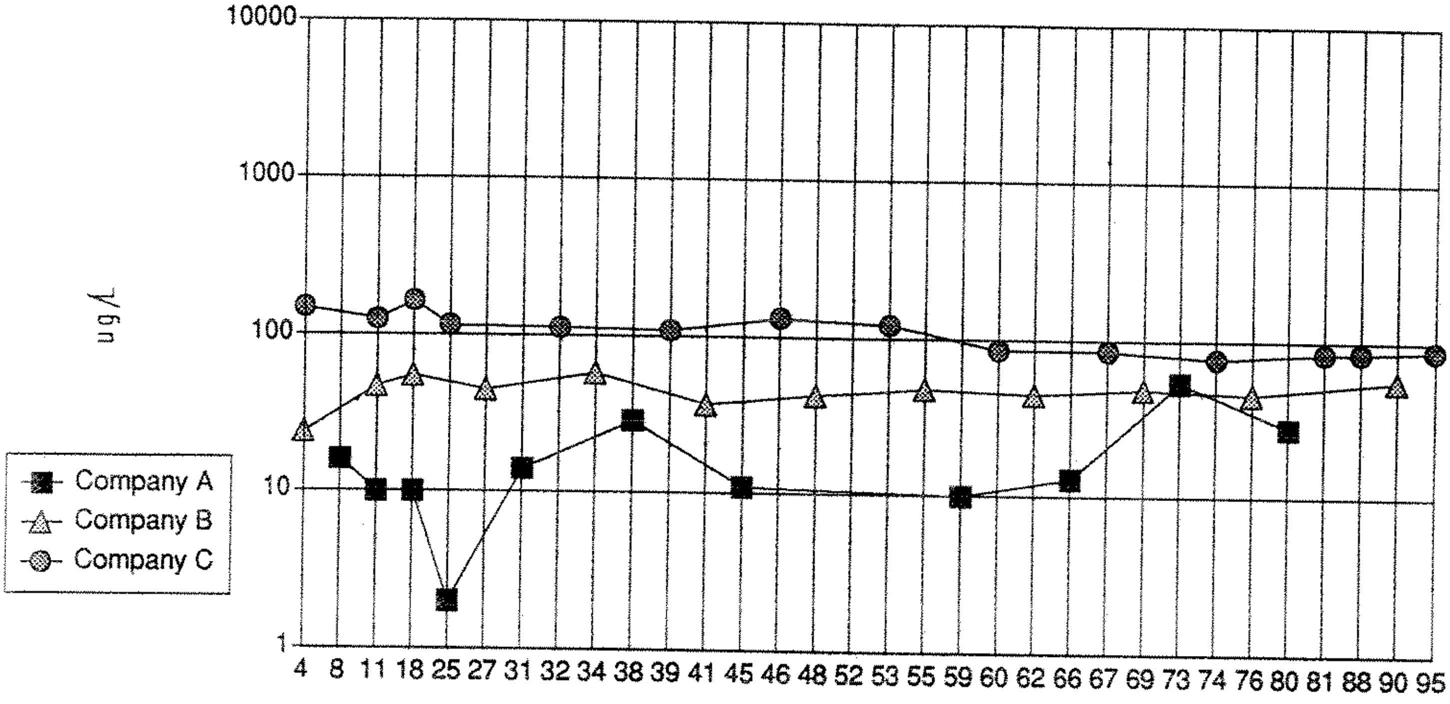


Figure 15

DWELL / DUMP TEST PROTOCOL

WATER TYPE 3 - LEAD



DAYS

Figure 16

DWELL / DUMP TEST PROTOCOL

WATER TYPE 4 - LEAD

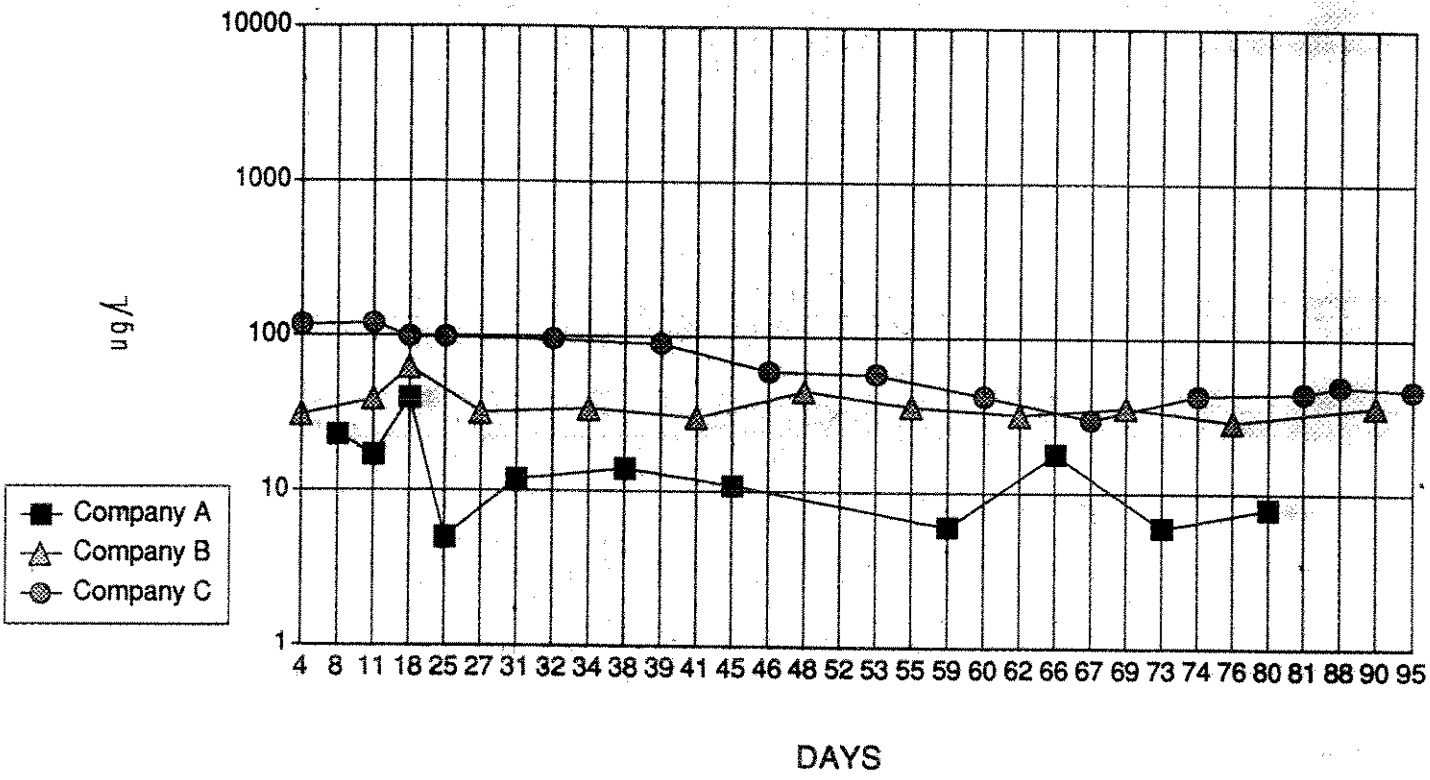


Figure 17

DWELL / DUMP TEST PROTOCOL

WATER TYPE 5 - LEAD

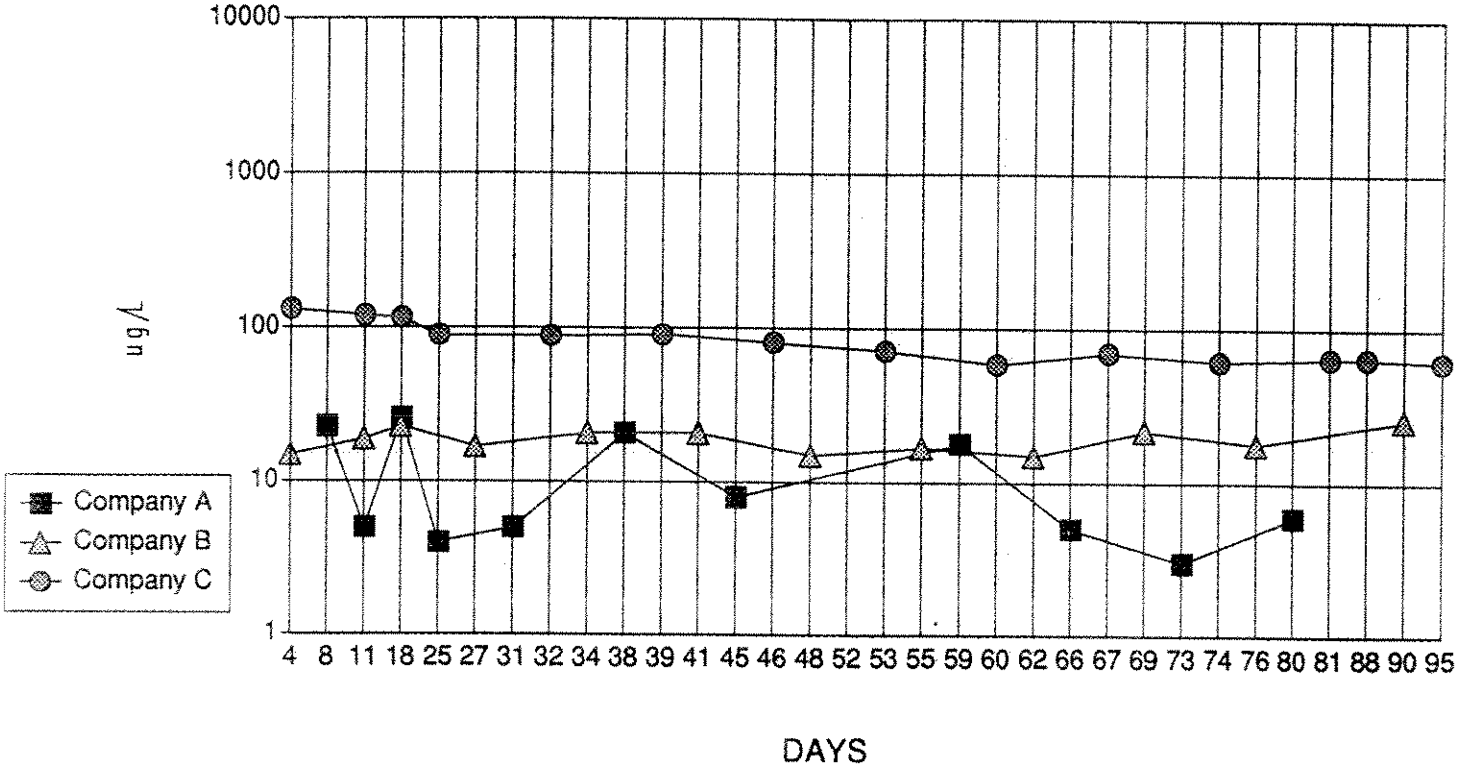


Figure 18

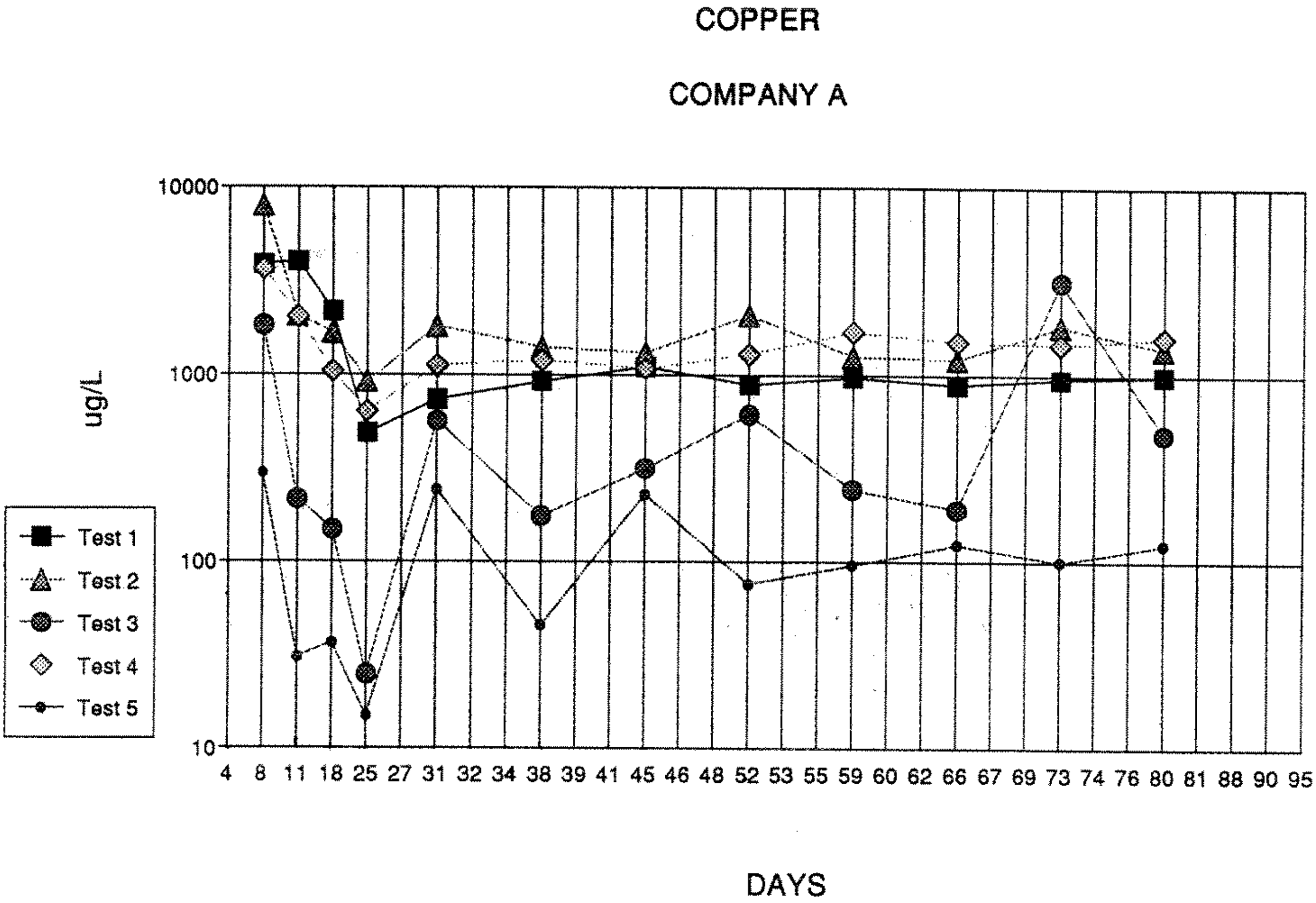

COPPER
COMPANY A
10000
1000
100
10
ug/L
Test 1
Test 2
Test 3
Test 4
Test 5
4 8 11 18 25 27 31 32 34 38 39 41 45 46 48 52 53 55 59 60 62 66 67 69 73 74 76 80 81 88 90 95
DAYS

Figure 19

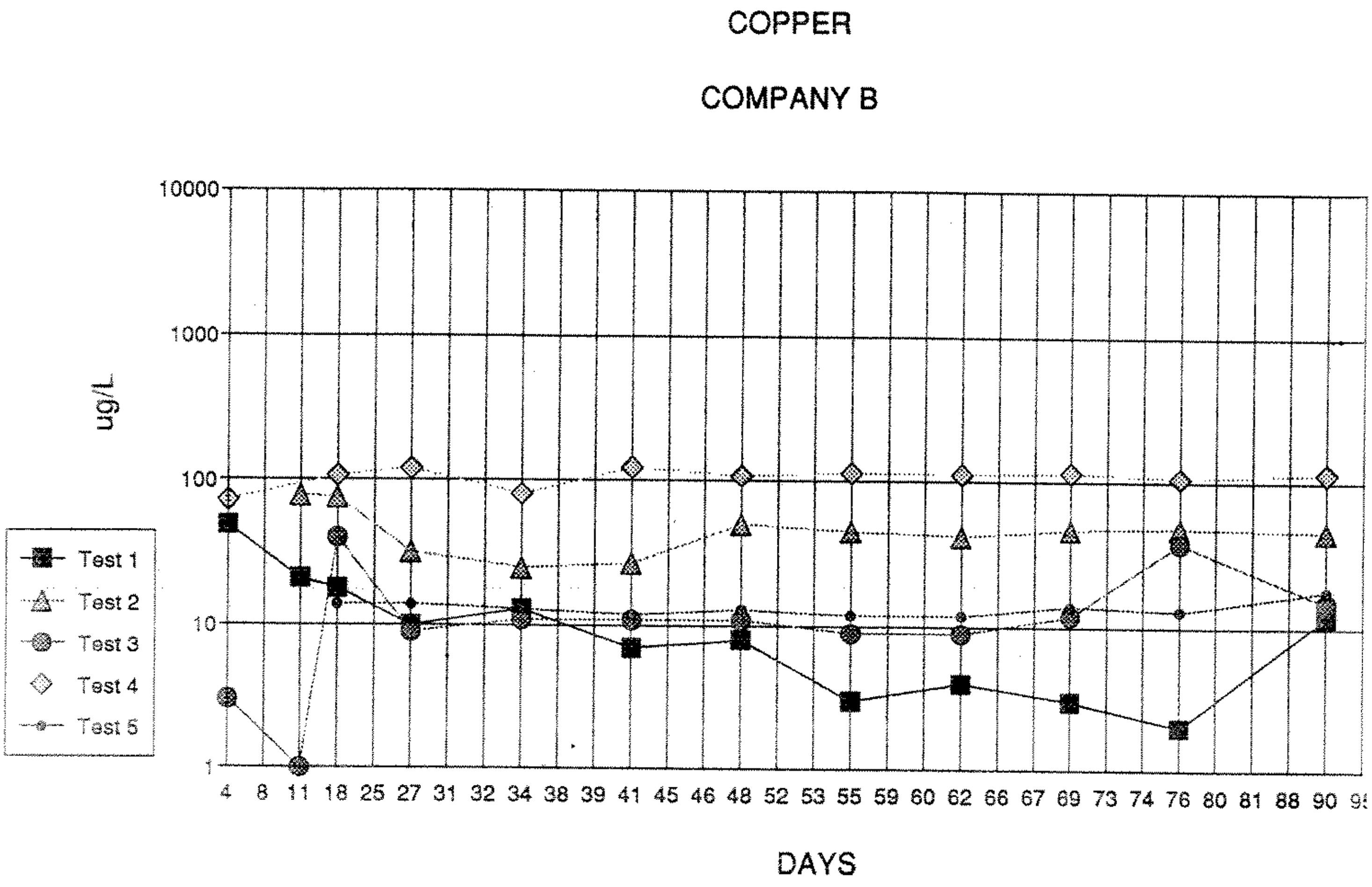
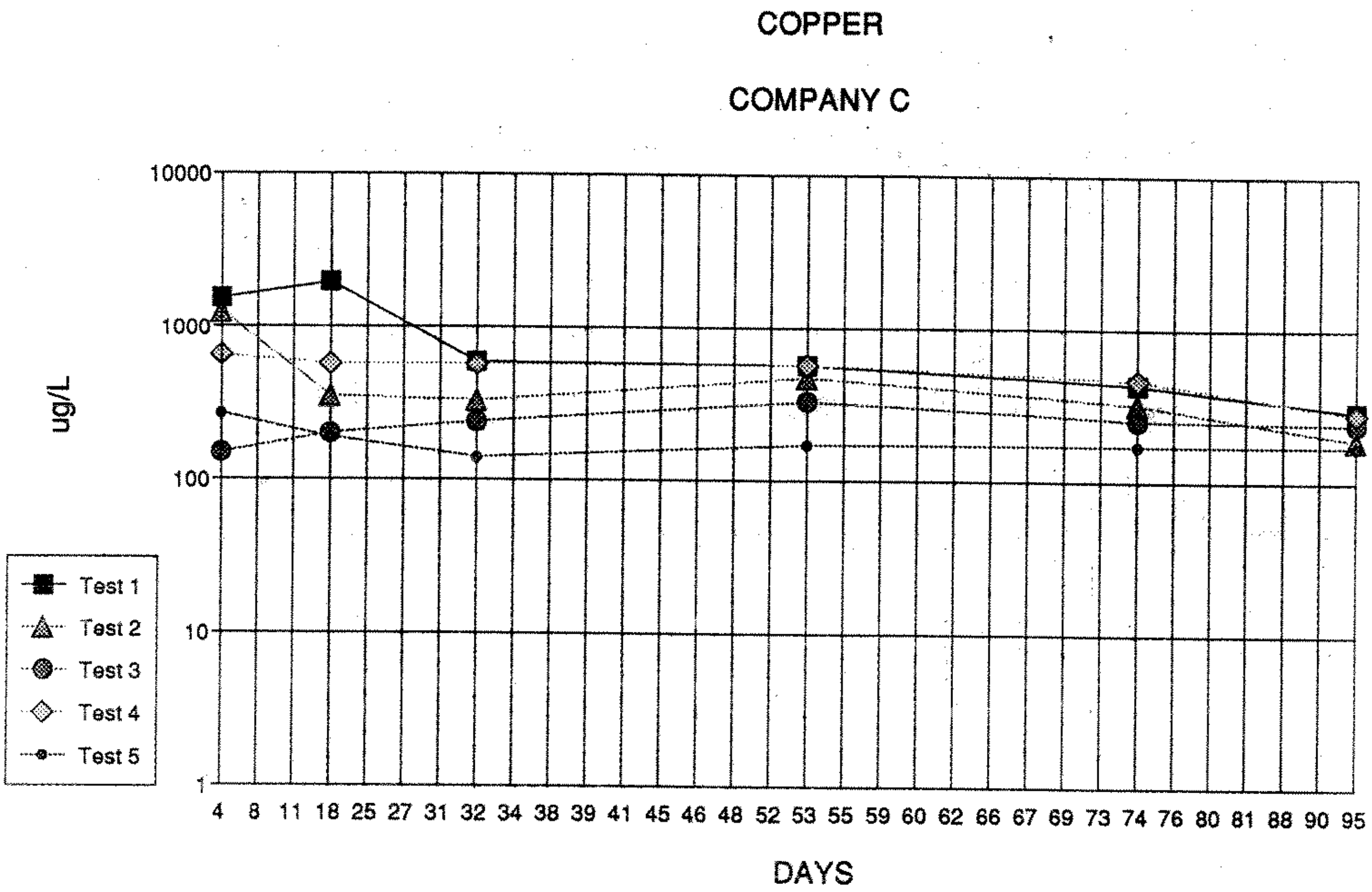

COPPER
COMPANY B
10000
1000
100
10
1
ug/L
Test 1
Test 2
Test 3
Test 4
Test 5
4
8
11
18
25
27
31
32
34
38
39
41
45
46
48
52
53
55
59
60
62
66
67
69
73
74
76
80
81
88
90
9
DAYS

Figure 20



COPPER

COMPANY C

Figure 21

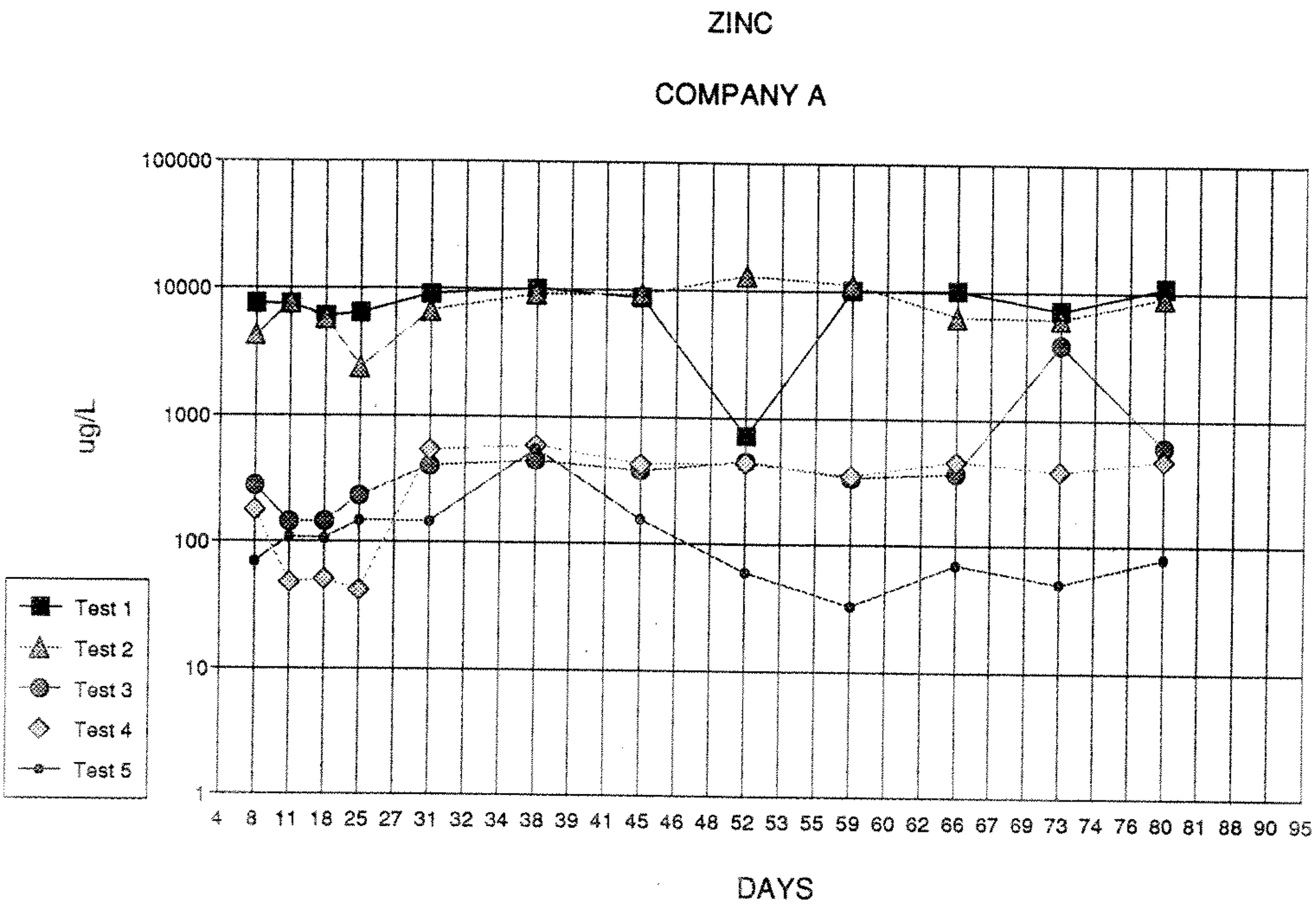

ZINC
COMPANY A
100000
10000
1000
100
10
1
ug/L
4 8 11 18 25 27 31 32 34 38 39 41 45 46 48 52 53 55 59 60 62 66 67 69 73 74 76 80 81 88 90 95
DAYS
Test 1
Test 2
Test 3
Test 4
Test 5

Figure 22

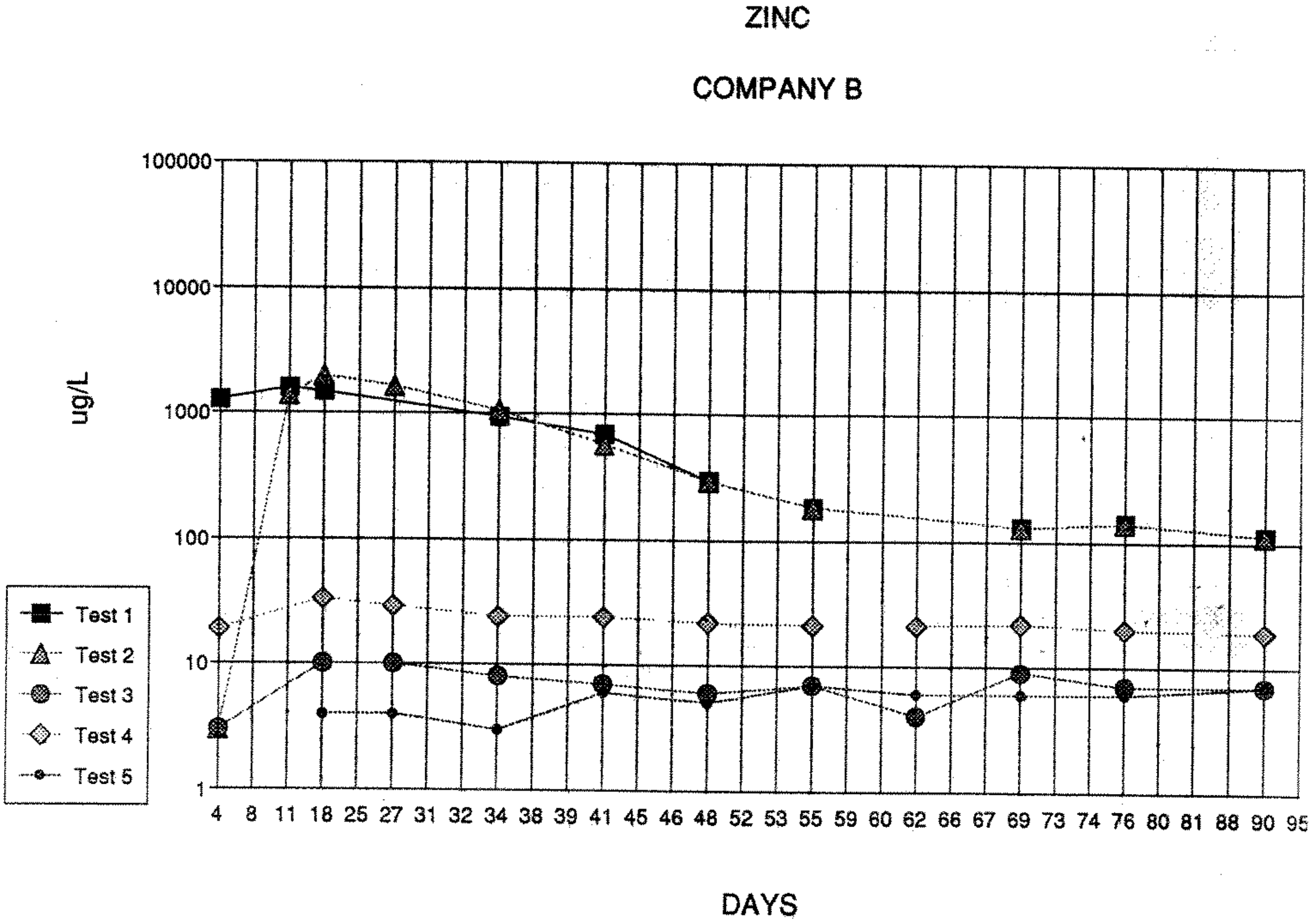

ZINC
COMPANY B
ug/L
100000
10000
1000
100
10
1
4 8 11 18 25 27 31 32 34 38 39 41 45 46 48 52 53 55 59 60 62 66 67 69 73 74 76 80 81 88 90 95
DAYS
Test 1
Test 2
Test 3
Test 4
Test 5

Figure 23

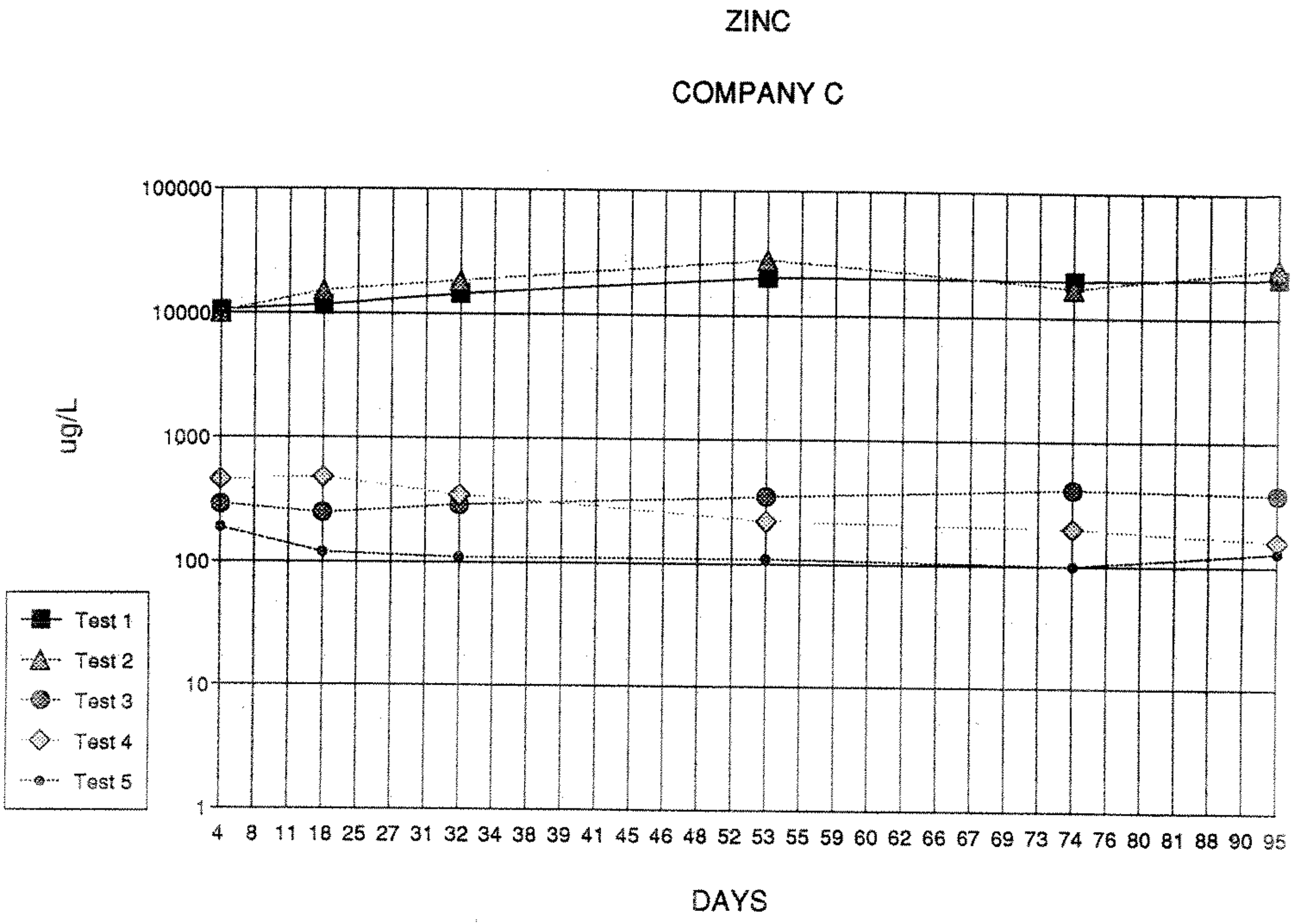

ZINC
COMPANY C
100000
10000
1000
100
10
1
ug/L
Test 1
Test 2
Test 3
Test 4
Test 5
4 8 11 18 25 27 31 32 34 38 39 41 45 46 48 52 53 55 59 60 62 66 67 69 73 74 76 80 81 88 90 95
DAYS

Figure 24

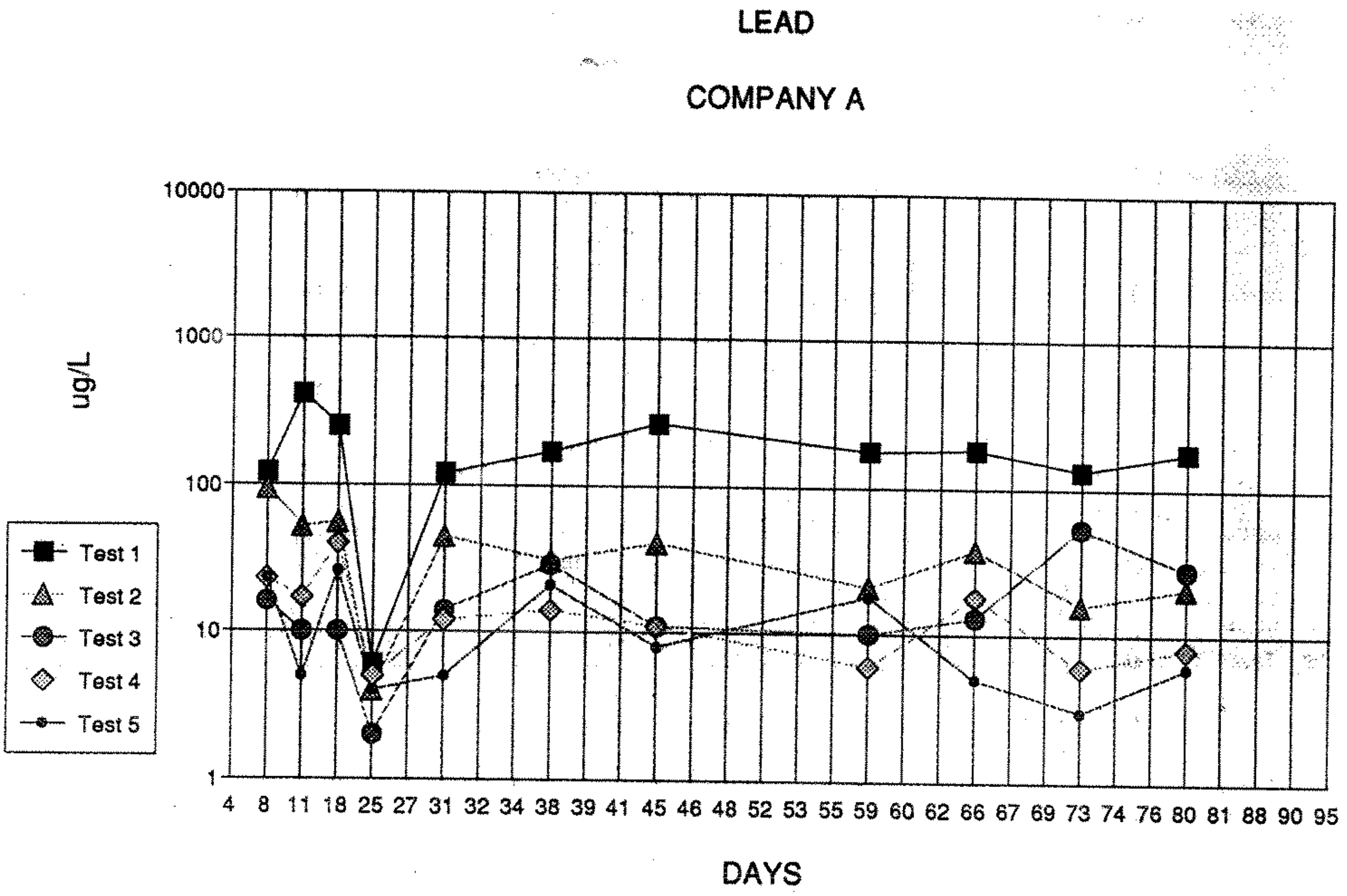

LEAD
COMPANY A
ug/L
10000
1000
100
10
1
4 8 11 18 25 27 31 32 34 38 39 41 45 46 48 52 53 55 59 60 62 66 67 69 73 74 76 80 81 88 90 95
DAYS
■ Test 1
▲ Test 2
● Test 3
◇ Test 4
• Test 5

Figure 25

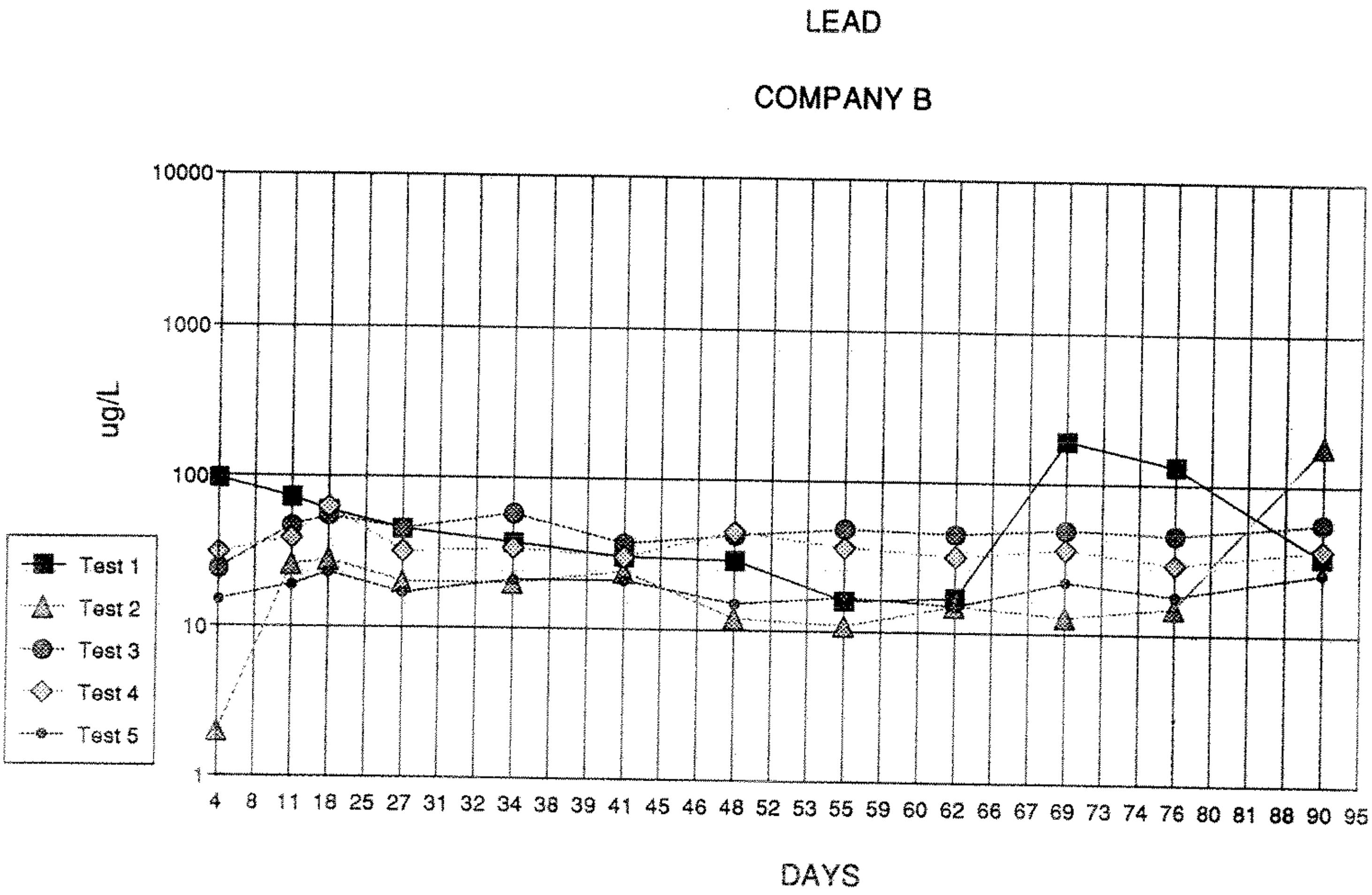

LEAD
COMPANY B
10000
1000
100
10
1
ug/L
Test 1
Test 2
Test 3
Test 4
Test 5
4 8 11 18 25 27 31 32 34 38 39 41 45 46 48 52 53 55 59 60 62 66 67 69 73 74 76 80 81 88 90 95
DAYS

Figure 26

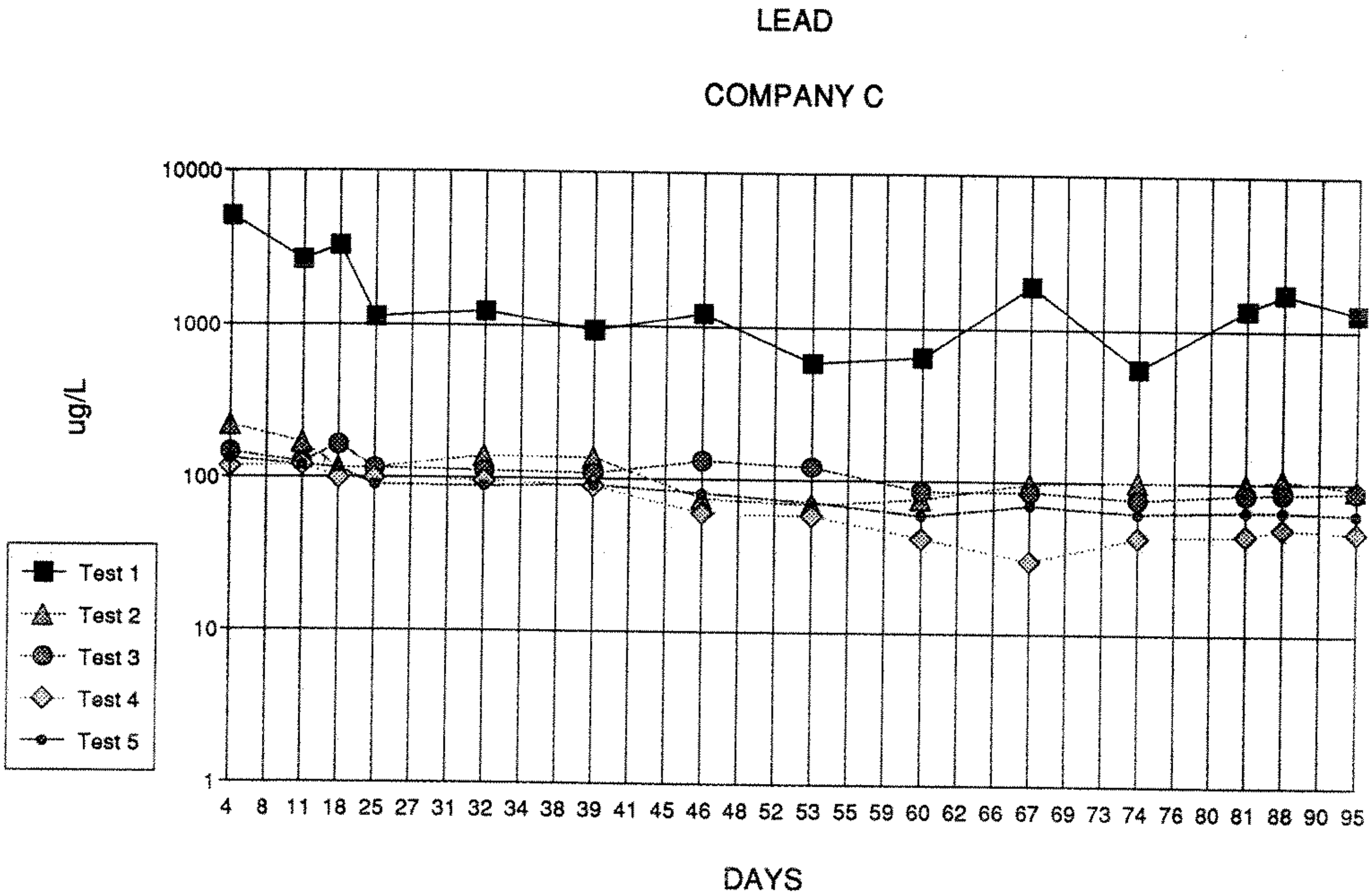

LEAD
COMPANY C
ug/L
10000
1000
100
10
1
4
8
11
18
25
27
31
32
34
38
39
41
45
46
48
52
53
55
59
60
62
66
67
69
73
74
76
80
81
88
90
95
DAYS
Test 1
Test 2
Test 3
Test 4
Test 5

Figure 27