REPORT ON LEAD IN CERAMICS: July 13, 1961

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Date: July 12, 1961

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Code for Identifying Glazes Tested During Investigation

Code	Company	Glaze	Color
Aa	Harker China Co., East Liverpool, Ohio		White
Ab	Hall China Co., East Liverpool, Ohio	A	White
Ac		B	White
Ad	Taylor, Smith and Taylor, East Liverpool, Ohio	1	White
Ae		2	Pink
Af		3	Wedgewood blue
Ag		4	Yellow
Ah		5	Light green
Ai		6	Blue
Aj		7	Mottled white
Ak		8	Mottled chartreuse
Al	The French Saxon China Co., Sebring, Ohio		White
Am	The Royal China Co., Sebring, Ohio	normal lead glaze	White
An		low lead glaze	White
Ao	Homer Laughlin China Co., Newell, West Virginia	11279	(Fiesta) yellow
Ap		14179	Yellow
Aq		14187	(Fiesta) turquoise
Ar		14421	Black
As		14553	Plum

THE EXTRACTION OF LEAD FROM GLAZED CERAMIC SURFACES

The occurrence of lead poisoning, from time to time, as the result of the use of certain types of glazed ceramic ware in the household, has led to several investigations of the extractability of lead from ceramic glazes. Certain cases of poisoning have been due to the use of ware in which the lead oxides had not been "fixed" properly, for one or more reasons, such as unduly low temperatures of firing, or insufficiently prolonged periods of firing, or the formulation of glazes without sufficient consideration of the problem of solubility. While responsible persons in the majority of potteries are aware of the technical and hygienic problems associated with the use of the lead oxides in ceramic glazes, and employ proper techniques for "fixing" the lead, no comprehensive investigation has been made of the extractability of lead from representative items of dinnerware in widespread use in the United States. Accordingly, the U.S. Potters Association has set out to obtain such background information by submitting to the Kettering Laboratory for testing, representative ware from a number of cooperating potteries. Another objective of the investigation was to devise or select a test to serve as a standard for future control purposes.

This report describes the methods and results of an investigation undertaken to determine the leachability of lead from tableware with accelerated, as well as some simulated, use tests.

Materials and Procedures:

Eighteen cups from each of thirty five different sets of glazed ware, as supplied by nine cooperating manufacturers, were supplied for testing. Each glaze was representative of a base glaze, containing the maximum content of lead, from which glazes of lower lead content could be prepared. In order to simulate conditions comparable to those of the contact of the ware with fruit juices, jams, and salads, hot acetic acid, in the concentration of 5 per cent, was chosen as the extraction agent in a severely accelerated test for the removal (in solution) of the lead in the ceramic glazes (Research Paper RP1196. Jr. Research of the National Bureau of Standards 22, 441, 1939). In this accelerated test, 150 ml. of boiling, 5 per cent acetic acid (prepared from DuPont Reagent Grade Glacial Acetic Acid) were poured into each of three cups chosen at random from each representative lot of ceramic ware (representative of a specific glaze). After standing for 0.5 hour, the cooled, dilute, acetic acid was rinsed into a polyethylene bottle, and the volume was adjusted to 200 ml. with distilled water. An aliquot portion of the acetic acid solution was then analyzed for its content of lead by a standard dithizone procedure, as used in the Laboratory (Cholak, J., Hubbard, D. M., and Burkey, R. E., Anal. Chem. 20, 671, 1948).

On the completion of the accelerated test, other cups from five of the lots which had shown the greatest loss of lead to the hot dilute acetic acid, were treated, in triplicate in each instance, respectively, with 150 ml. portions of 5 per cent cold acetic acid, boiling distilled water, boiling 0.3 per cent citric acid (prepared from Matheson, Coleman and Bell, Citric Acid A.C.S. Reagent Grade), and hot instant coffee, (i.e. 60 additional cups). The tests with the cold acetic acid, hot distilled water, and hot 0.3 per cent citric acid were carried out exactly as was the accelerated test with hot 5 per cent acetic acid. In the test with instant coffee, 150 ml. of boiling water were added to 4.5 grams of instant Maxwell House coffee in each cup. After standing for 0.5 hour, the cooled coffee was poured into a polyethylene bottle and the volume was adjusted to 200 ml. with distilled water. One half of the prepared solution was treated with sulfuric and nitric acids to destroy organic matter, and the sulfuric acid residue was then diluted with distilled water to a volume of 50 ml. for subsequent analysis for lead. The lead in the test materials was determined, in each instance, by analyzing, in triplicate, suitable aliquots of the solutions prepared for use in the testing program. The results are given in Table 6.

Results:

In Table 1 are listed the individual and the average concentrations of lead in parts per million (equivalent to mgs./liter) as extracted in the accelerated test with hot 5 per cent acetic acid. The glazes in this and in the other tables have been assigned an identifying code number for use with a master code sheet which is retained in the Laboratory.

The results obtained in the tests with cold 5 per cent acetic acid, the hot 0.3 per cent citric acid, the hot distilled water, and the soluble coffee, respectively, are tabulated in Tables 2, 3, 4, and 5.

In Figure 1 are charted the individual and the average concentrations of lead obtained by the repeated testing of cups of glaze Az with hot 5 per cent acetic acid.

Discussion:

Twenty two of the 35 glazes tested by the accelerated procedure with hot 5 per cent acetic acid were found, on the average, to release less than 0.077 mg. lead (0.50 ppm) per 150 ml. of dilute acid. Six glazes gave up lead at rates which yielded concentrations in excess of 1 mg. per liter of the dilute acid used as the extraction medium. From seven glazes, the concentration of lead extracted by hot 5 per cent acetic acid averaged between 0.5 and 0.99 mg. per liter of solution. Table 7 is of interest in that it lists the data for glazes divided into three general categories of color. Except for glaze Bb, which yielded up lead at an average concentration of 0.60 mg. per liter, the white glazes were responsible for levels well below 0.50 mg. per liter of hot 5 per cent acetic acid. As the color of the glazes deepened, the extractability of lead therefrom increased. Although equal numbers of glazes characterizing each designated color, were not available, it is obvious (Table 7) that the density of color is a factor in the extraction of lead from the glazes by the hot 5 per cent acetic acid. All of the nine deeply colored glazes yielded up lead in excess of 0.49 mg. per liter of hot 5 per cent acetic acid; six of them gave up to this solvent quantities which averaged more than 1 mg. of lead per liter. The five which yielded the highest concentrations were subjected to additional tests.

The results of the additional tests of the five glazes referred to above are shown in Tables 2, 3, 4 and 5. As may be seen in Table 2, all five glazes gave up less lead to the cold 5 per cent acetic acid than to the hot 5 per cent acetic acid. It is of interest to note that glaze Ba yielded more lead to the cold 5 per cent acetic acid than did glaze Az, which had shown the greatest loss of lead to the hot 5 per cent acetic acid.

Hot 0.3 per cent citric acid extracted appreciable quantities of lead from the five glazes. As in the case of the hot acetic acid, glazes Az and Ba were the most vulnerable to extraction of lead by citric acid, but their relationship to each other was reversed in the latter instance.

Hot distilled water extracted small quantities of lead from each of the five glazes. Glazes Az and Ba gave up lead at approximately the same rates (Table 4). Glaze Ao lost the most lead, the average of the three cups being 0.44 mg. per liter of water; one of these cups released lead at a rate of 1.05 mg. per liter of water. It should be recognized that 150 ml. of hot distilled water after standing for the standard time in a cup glazed with one of these five glazes would contain 0.003 mg. to 0.07 mg. of lead.

The five glazes employed in the simulated use tests lost significant amounts of lead to hot instant coffee. The concentrations of lead in the prepared coffee ranged from 0.35 to 2.22 mg. per liter. As in the accelerated tests, glazes Az and Ba lost the most lead, but again their vulnerability in this test was in the reverse order, as compared with the results of the accelerated tests. If 150 ml. is taken as the average volume of a cup of coffee, then the amount of lead ingested with instant coffee prepared in these cups would be 0.09 mg. in the cup glazed with Az, and 0.23 mg. in the cup glazed with Ba. The test with instant coffee simulates the actual use of the cups, and, therefore, the results are of considerable importance. The data recorded in Figure 2 shed further light on the extractability of lead during the repetitious use of the cups. The drinking of five cups of instant coffee prepared, repeatedly, in the same cup, starting with a new cup glazed with glaze Ba, and repeating the process five times successively, would result in the ingestion of 1.08 mgs. of lead. Similarly, the consumption of three cups of coffee prepared in ware covered with glaze Az would result in the ingestion of 0.14 mg. of lead. The determination of the rapidity with which extractable lead would decrease to a satisfactory level was not within the scope of this preliminary testing program, and the testing was discontinued, therefore, as soon as a decreasing trend was evident.

While cups in constant use, generally, would be expected to release lead at decreasing rates similar to those shown in Figure 2, glaze Az, under successive testing with hot 5 per cent acetic acid, yielded successively larger quantities of lead, as indicated in Figure 1. Glaze Az appeared to be decomposed by repetitive treatment with hot 5 per cent acetic acid, and each successive test, tended to yield a higher average concentration of lead than had its predecessor.

At the end of the 27th test, lead was being extracted at the average concentration of 27.5 mg. per liter, as compared to 7.3 mg. per liter in the first test with the hot 5 per cent acetic acid (Figure 1) (the lead in each 150 ml. portion increased from 1.09 to 4.11 milligrams). The action of cold 5 per cent acetic acid on glaze Az was not as severe as that of hot 5 per cent acetic acid, the trend of the results being in the reverse order (Figure 2).

Summary:

Six of thirty five glazes released lead to hot 5 per cent acetic acid to yield concentrations of lead in this extraction medium in excess of 1 mg. per liter (1 part per million). Seven other glazes released lead to produce solutions containing from 0.5 to 1.00 ppm lead. The deep colored glazes lost lead more readily than did the white or pastel colored glazes. Of the five glazes which suffered the greatest loss of lead in the accelerated test, four were classed as Fiesta ware (deep colors), and one was classed by us as a pastel or light color. Except for the orange or red colored Az glaze, the colors were yellow or shades of green. Hot 0.3 citric acid, cold 5 per cent acetic acid, and instant coffee prepared in the cups, also dissolved appreciable quantities of lead from the five glazes which yielded the largest quantities of lead in the accelerated test. Depletion tests involving the repeated testing of the same cups representative of the two glazes which had lost the most lead to hot 5 per cent acetic acid, revealed that one, glaze Ba, after releasing large quantities of lead initially, soon leveled off to a plateau at a much lower level. Glaze Az, on repeated treatment with hot 5 per cent a constantly increasing release of soluble lead by the glaze. The average concentration increased from the initial value of 7.3 ppm to 27.5 ppm in the 27th test.

The order of the extractability of lead in the five glazes differed appreciably, with respect to any one extraction medium, but it differed also under the influence of the different media. It is our opinion, therefore, that the use of a single solvent or extraction medium will not give an accurate indication of the facts with respect to the potential extractability of lead from glazes.

The colorimetric dithizone procedure is satisfactory from the standpoint of reproducibility, sensitivity and accuracy of analysis, for determining the concentration of lead released to the test solutions.

Recommendations for Testing:

Tests with at least three extraction media appear to be necessary to determine the probable extent of the release of lead from ceramic glazes under the conditions of use. In carrying out the test with any one extraction medium, a series of three cups from each glaze should be employed. A similar series should be tested with each of the following media, hot 5 per cent acetic acid, hot distilled water, and hot soluble coffee. In the event that the accelerated test shows an average concentration of lead of 1.0 ppm or more, it is suggested that the same cups be tested repeatedly with hot dilute acetic acid, in order to determine the trend in the loss of lead from the glaze. The same type of test should be applied to cups that release lead to hot water or instant coffee in excess of 0.1 mg. per liter of either of these media.

It is also suggested that the standard colorimetric procedure employing dithizone be adopted as the method for carrying out the lead analyses.

Recommendation as to the Development of a Specification for a Satisfactory Glaze:

It is suggested that the data obtained in this survey may serve as a basis for the establishment of a specification as to the degree of resistance to the solvent action of various extraction media that may properly be required. It may be, however, that additional information may be required before such a step can be taken. In any case, it would be advisable to explore the situation further with technical representatives of the producers of glazed table ware, in order to have the benefit of their experience in the consideration of the entire matter.

It is apparent that some of the ware that is in current use is unsatisfactory and should be excluded from general use through the operation within the industry of appropriate hygienic criteria. It is not so certain at this time just where the line should be drawn between obviously unsatisfactory and apparently satisfactory products of this type. Any attempt to formulate a standard in the present state of our knowledge of the practical facts would be premature and might have unfortunate consequences. In this connection the present report is regarded as confidential, and no information concerning it will be released until an opportunity has been offered for considering future action.

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Table 1

Solubility of Glazes in Hot 5 Per Cent Acetic Acid

(Accelerated Loss of Lead Test)

Glaze Code	Lead PPM			
	Cup #1	Cup #2	Cup #3	Average
Aa	0.09	0.14	0.11	0.11
Ab	0.02	0.02	0.04	0.03
Ac	0.05	0.20	0.20	0.15
Ad	0.04	0.05	0.06	0.05
Ae	0.23	0.20	0.20	0.21
Af	0.57	0.67	0.80	0.68
Ag	0.14	0.14	0.14	0.14
Ah	0.16	0.24	0.14	0.18
Ai	0.15	0.19	0.16	0.17
Aj	0.52	0.35	0.31	0.39
Ak	0.12	0.13	0.11	0.12
Al	0.14	0.10	0.22	0.15
Am	0.16	0.20	0.16	0.17
An	0.007	0.013	0.007	0.009
Ao	1.03	1.31	1.02	1.12
Ap	0.98	0.98	1.20	1.05
Aq	2.40	2.52	2.38	2.43
Ar	0.94	0.39	0.37	0.57
As	1.06	1.06	0.72	0.95
At	1.11	1.19	0.70	1.00
Au	0.24	0.17	0.16	0.19

Table 1, Page 2

Glaze Code	Lead PPM Cup #1	Cup #2	Cup #3	Average
Av	0.57	0.63	0.70	0.63
Aw	0.65	0.52	0.62	0.60
Ax	1.37	1.63	1.47	1.49
Ay	0.09	0.11	0.07	0.09
Az	7.95	7.90	5.80	7.22
Ba	4.70	4.70	4.40	4.60
Bb	0.62	0.62	0.57	0.60
Bc	0.06	0.13	0.18	0.12
Bd	0.14	0.12	0.17	0.14
Be	0.07	0.08	0.06	0.07
Bf	0.08	0.07	0.11	0.09
Bg	0.21	0.19	0.19	0.20
Bh	0.04	0.06	0.07	0.06
Bi	0.03	0.09	0.09	0.07

Table 2

Lead Leached Out of Glazes of Several Brands of Ceramic Cups by Cold 5 Per Cent Acetic Acid

Glaze Code	Lead PPM			
	Cup #1	Cup #2	Cup #3	Average
Ao	0.40	0.44	0.31	0.38
Aq	0.84	0.93	0.73	0.83
Ax	0.33	0.49	0.45	0.42
Az	0.76	0.63	0.55	0.65
Ba	2.56	2.13	2.39	2.36

Table 3

Lead Leached Out of Glazes of Several Brands of Ceramic Cups by Hot 0.3 Per Cent Citric Acid

Glaze Code	Lead PPM			
	Cup #1	Cup #2	Cup #3	Average
Ao	0.90	0.96	1.09	0.98
Aq	2.39	2.31	2.19	2.30
Ax	1.83	1.68	1.56	1.69
Az	2.04	2.76	2.76	2.52
Ba	3.36	5.60	5.40	4.79

Table 4

Lead Leached Out of Glazes of Several Brands of Ceramic Cups by Hot Distilled Water

Glaze Code	Lead PPM			
	Cup #1	Cup #2	Cup #3	Average
Ao	1.05	0.21	0.07	0.44
Aq	0.08	0.06	0.08	0.07
Ax	0.01	0.03	0.02	0.02
Az	0.12	0.26	0.08	0.15
Ba	0.14	0.05	0.13	0.11

Table 5

Lead Leached Out of Glazes of Several Brands Of Ceramic Cups by Hot Soluble Coffee

Glaze Code	Lead PPM			
	Cup #1	Cup #2	Cup #3	Average
Ao	0.35	0.36	0.36	0.36
Aq	0.61	0.52	0.51	0.55
Ax	0.36	0.33	0.35	0.35
Az	0.46	0.69	0.67	0.61
Ba	2.37	2.15	2.15	2.22

Table 6

Lead in Materials Used to Test Ceramic Glazes

Reagent	Lead PPM			
	Test #1	Test #2	Test #3	Average
150 ml. hot 5% acetic acid	0.000	0.000	0.000	0.000
150 ml. cold 5% acetic acid		not tested		
150 ml. hot 0.3% citric acid	0.000	0.000	0.000	0.000
150 ml. hot distilled water		not tested		
150 ml. hot distilled water + 4.5 g. Instant Maxwell House Coffee	0.009	0.005	0.007	0.007

Table 7

Summary of Losses of Lead by Various Glazes to Hot 5 Per Cent Acetic Acid

(Accelerated Test)

	Number of Glazes		
	Lead PPM		
	0-0.49	0.5-0.99	>1
White	15	1	
Pastel Colors	7	2	1
Deep Colors		4	5
Total	22	7	6*

*Six colored glazes showing greatest loss of lead in accelerated test.

Glaze Code	Color	Lead PPM >1.00
Ao	(Fiesta) yellow	1.12
Ap	Yellow	1.05
Aq	(Fiesta) turquoise	2.43
Ax	Melon	1.49
Az	(Fiesta) red	7.22
Ba	(Fiesta) light green	4.60

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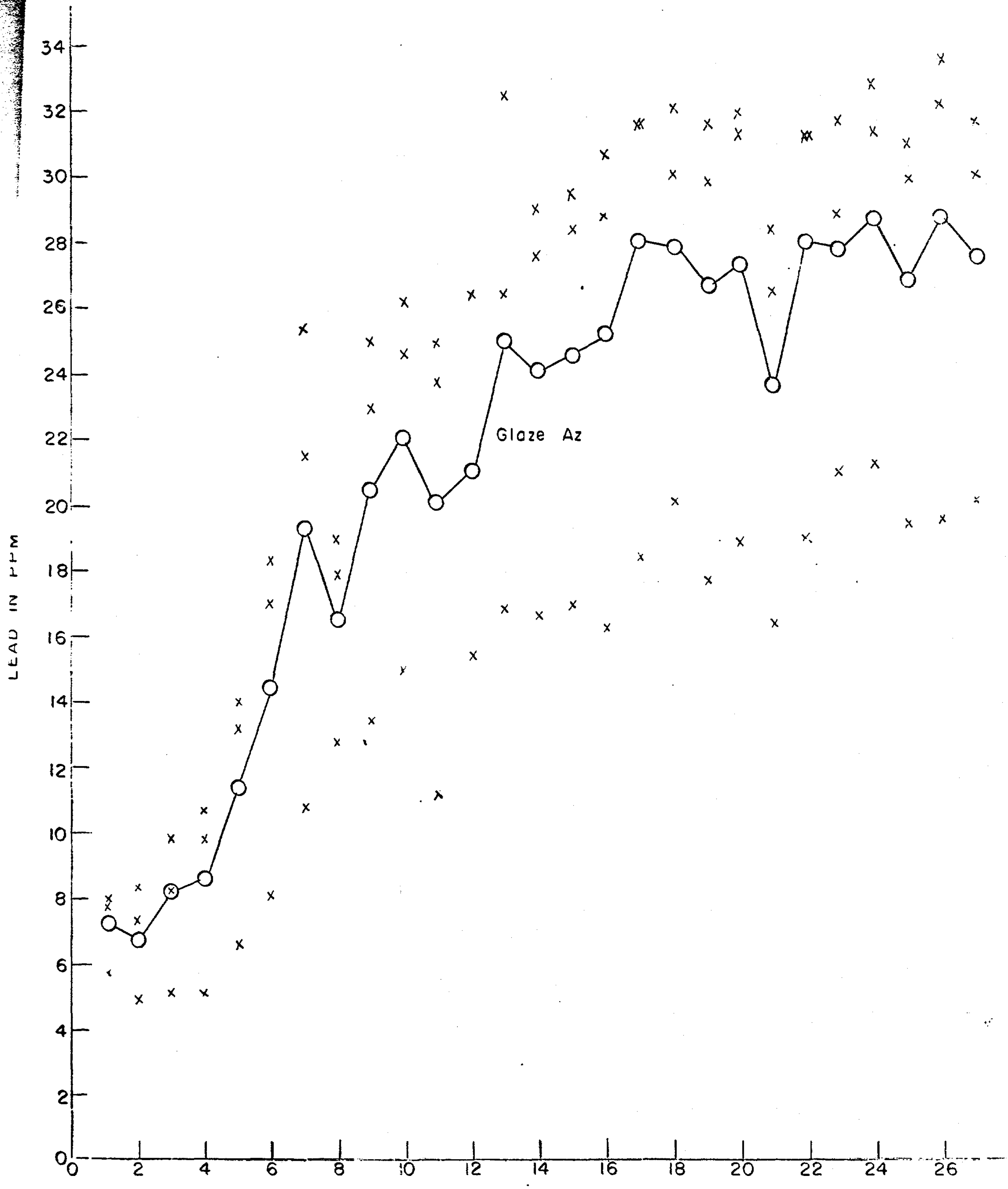

Figure 1.

LEAD EXTRACTED FROM CERAMIC GLAZE Az FOLLOWING CONSECUTIVE TESTS

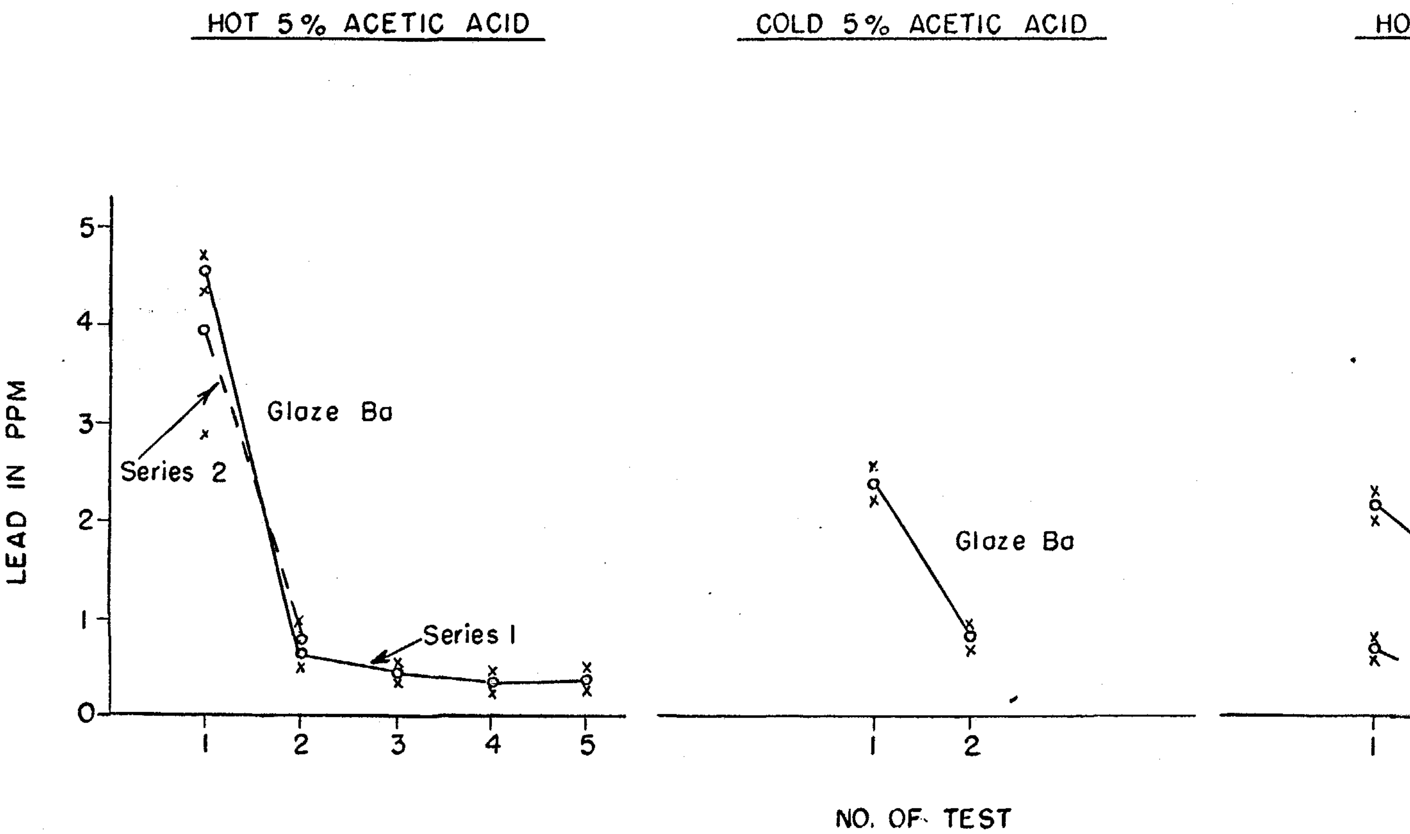

Figure 2.

LEAD EXTRACTED FROM CERAMIC GLAZES (Ba and Az) DURING CONSECUTIVE TESTS

EXTRACTIVE MEDIA.