

Dependence of Leachable Lead in Glazed Ceramics on Previous Treatment: Determination by an Improved Dithizone Extraction Method

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ABSTRACT

Fifty six samples of glazed ceramic ware (pottery, porcelain or china cups, plates, bowls, or pitchers) were analyzed for lead by the standard method of allowing the lead to leach into 4% acetic acid over a period of 24 hours at room temperature. The concentration of lead in the acid was determined spectrophotometrically following extraction from an alkaline cyanide solution into a toluene solution of dithizone. Five pieces (9%) were found to leach 7 or more parts per million, and an additional 14 pieces (25%) leached 1 or more parts per million. Analysis of several pieces showed that the amount of lead leached into acid was reduced by as much as three fold when immediately repeated, but the amount reached the original level if the piece was allowed to "rest" for several days before repeat determinations. This phenomenon was studied further, and the results indicated that leachable lead in glazed pottery was increased by time, temperature, and exposure to alkaline solution. Thus the repeated use of a dishwasher may cause dinnerware that had been previously "lead free" to leach lead on subsequent use with food. The effect of time of acid elution was also studied, indicating that the majority of lead is dissolved within one minute of addition of acid, with very slow increase over 24 hours.

INTRODUCTION

The ingestion of lead from glazed pottery can cause serious illness or death (Klein *et al*, 1970; Natelson and Fred, 1976; Bird, Wallace, and Labbe, 1982), and despite recent publicity it remains a problem, particularly in imported items (Burros, 1988). The standard method for determination of lead involves leaching the piece with 4% acetic acid for 24 hours (Spielholtz and Kaplan, 1980). My laboratory discovered several years ago that some imported children's juice cups that were purchased in the United States were capable of leaching dangerous quantities of lead into fruit juice.

The dithizone method for lead determination was modified for use in testing coffee mugs, cereal bowls, china, etc. that students and others have brought in over the past few years. In the course of repeated testing, it was found that if the piece was tested at least several days apart, similar quantities of lead were obtained, but if the piece was retested immediately, the quantity of lead leached was significantly less the second time. Further studies delineated some of the factors affecting the release of lead from glazed pottery.

MATERIALS AND METHODS

The acetic acid, ammonium hydroxide, potassium cyanide, dithizone, lead acetate trihydrate, hydrochloric acid, and toluene were reagent grade. The Beckman Acta CII spectrophotometer was used for absorbance determinations, with 0.25 mL microcuvettes and adapters. A Labconco constant temperature drying oven was used to heat the ceramic piece.

The analytical method was modified from Wilkinson (1970), which involved treating a neutralized acid digest of blood or urine with a buffer containing ammonium hydroxide, ammonium citrate, potassium cyanide, and sodium sulfite, extraction with a chloroform solution of dithizone, removal of the aqueous phase, washing the chloroform with an ammonium hydroxide-potassium cyanide solution, removing the aqueous phase, and determining the absorbance of the chloroform solution. Wilkinson's method was simplified by replacing the highly toxic chloroform with toluene, which yielded the color in the upper layer, and extracting directly from an ammonium hydroxide-potassium cyanide solution without washing.

For the determination of lead in ceramics the following procedure was used: Ten to twenty mL of 4% acetic acid was placed into the clean container to be tested, covered with aluminum foil to prevent evaporation, and allowed to stand for 24 hours at room temperature. 0.5 mL of the acetic acid eluate or blank solution of 4% acetic acid, 0.5 mL of standard solution containing 0, 1, 3, or 10 parts per million of lead in 0.1 M hydrochloric acid, and 0.5 mL of potassium cyanide-ammonium hydroxide (A) were successively added to 12x75 mm test tubes. The solutions were mixed with a Vortex mixer for 10 seconds. 0.5 mL of dithizone-toluene (B) was added, mixed with the Vortex mixer, let stand 5 to 30 minutes. 0.3 mL of the upper toluene layer was placed into a microcuvette, and the absorbance at 520 nM was recorded. Blanks without lead gave an absorbance of about 0.014 with freshly prepared dithizone, and about 0.06 with day-old reagent. The presence of lead gave an increased absorbance at 520 nM, with a molar extinction coefficient of 47120. For screening purposes the color of the upper layer was compared with standards containing 0, 1, 3, or 10 ppm lead. Zero lead gave a pale green color, 1 ppm pale pink, 3 ppm medium pink, and 10 or more deep pink. Samples were always analyzed twice, without and with 3 ppm added lead to ascertain that other substances leached by acid did not interfere with the color produced by lead.

The reagents were prepared as follows: A. 1 gram potassium cyanide was dissolved in a mixture of 50 mL concentrated (15 M) ammonium hydroxide and 50 mL distilled water. B. Dithizone, 3 milligrams was dissolved in 100 mL of toluene. 4% Acetic acid was prepared by dilution of glacial acetic acid with distilled water. 0.1 M hydrochloric acid was prepared by dilution of 85 mL concentrated (11.7 M) hydrochloric acid to 1 liter with distilled water. Lead standards; 100 parts per million (ppm, milligrams per liter) lead was prepared by dissolving 183 milligrams of lead acetate trihydrate in 1 liter of 0.1 M hydrochloric acid. This was diluted with 0.1 M hydrochloric acid 1:9 for 10 ppm, 3:97 for 3 ppm, and 1:99 for 1 ppm lead standards.

TABLE 1. Effect of Elution Time on Quantity of Lead. The cup was eluted with 0.1M HCl. Twenty ml of HCl were placed in the cup, and aliquots of 1 mL were removed at the times indicated and analyzed for lead as described in the text. The pitcher was successively eluted with water, 4% acetic acid (HAc), 0.1M HCl, and HAc. The items were gently swirled during the elution in the studies of 10 minutes or less, and were left still in longer elutions.

Item	Eluent	Time	Pb (ppm)
Cup	HCl	1 min	3.3
"	"	5 min	3.6
"	"	10 min	4.0
"	"	200 min	4.3
"	"	1400 min	4.9
Pitcher	water	1 min	0.7
"	"	10 min	0.7
"	HAc	1 min	12.3
"	"	10 min	12.3
"	HCl	1 min	4.0
"	"	10 min	4.2
"	HAc	1 min	0.6
"	"	2 min	1.1
"	"	10 min	1.3

RESULTS

Of the 56 ceramic items screened to date, 37 eluted less than 1 ppm lead, 14 eluted from 1 to less than 7 ppm, 4 eluted from 7 to less than 20 ppm, and one eluted over 20 ppm lead. Positive samples were distributed among domestic and imported products. No relationship between lead and appearance or color was noted, and in some cases two pieces of identical pattern contained widely varying lead. Thus a significant percentage of domestic, imported, and handcrafted ceramics contained potentially dangerous lead levels.

The effect of time of elution with dilute acid was studied, with key results shown in Table 1. An imported children's juice cup, and a handcrafted ceramic pitcher, both containing lead, were used in the study. Most of the lead is leached within the first minute of addition of acid. Successive elutions of the pitcher with water, acetic acid, HCl, and acetic acid indicated that water was ineffective, and that repeated elution gave smaller quantities of lead, regardless of eluent.

Repeated twenty four hour elution of several imported pieces showed that the second elution always gave much lower lead levels than the first. Further studies were carried out to determine the causes of the variation and to develop a procedure that would give reliable results in general screening. The same handcrafted ceramic pitcher used in the study of Table 1 was used for the study summarized in Table 2. In all of the experiments the pitcher was rinsed with deionized water, then the lead was eluted with 4% acetic acid for 1 minute. The studies were done serially according to the numbers in Table 2. After the initial test (No. 1), repetitions at least 24 hours apart gave comparable values (No. 2, 7, 11), but immediate repetitions of the elution gave much lower values (No. 3, 5, 8,

TABLE 2. Effect of prior treatment on quantity of lead. The pitcher was treated as noted, rinsed with deionized water, and lead then eluted with 4% acetic acid for 1 min. Experiments were done serially as numbered. When the absorbance was 2 the samples were diluted 10-fold and reanalyzed.

Number	Treatment	Pb (ppm)
1	none, initial analysis	12.3
2	none, 24 hr later	5.7
3	none, immediately reanalyzed	1.9
4	dishwasher detergent 30 min 46°	2.7
5	none, immediately reanalyzed	1.0
6	1M HCl 1 min 25°	0.4
7	none, 48 hr later	5.5
8	none, immediately reanalyzed	1.3
9	0.1M NaOH 10 min 25°	2.2
10	none, immediately reanalyzed	0.5
11	none, 48 hr later	5.4
12	none, immediately reanalyzed	2.1
13	none, immediately reanalyzed	1.4
14	none, immediately reanalyzed	1.5
15	157° C 24 hr	13.9
16	157° C 48 hr	20.3
17	none, immediately reanalyzed	3.9
18	none, immediately reanalyzed	3.0

10, 12-14, 17-18). Immediate treatment with dishwashing liquid (No. 4), or sodium hydroxide (No. 9), caused an increase in lead. The greatest increase in lead, however, followed heating in a constant temperature oven at 157 °C for 24 or 48 hours (No. 15 and 16).

DISCUSSION

A simplified method for screening of ceramics for lead is described, based on the method of Wilkinson (1970). The toxic chloroform was replaced by toluene, and the number of extractions was reduced to one. The method described here has been used for several years to screen domestic and imported ceramic ware brought in by students and other interested parties. Of the 56 samples of ceramics examined, 5 (9%) were found to leach 7 or more ppm lead, indicating the continued appearance of dangerous products. At present the action level of the Food and Drug Administration for detaining imports is 2.5 ppm for large hollowware, 5.0 ppm for small hollowware, and 7.0 ppm for flatware (Food and Drug Administration Compliance Policy Guides, 1980), but a much lower level (0.1 ppm) has been proposed (Federal Register, 1989).

Analysis of several pieces showed that the amount of lead leached into acid was reduced by as much as three fold when immediately repeated, but the amount reached the original level if the piece was allowed to "rest" for several days before repeat determinations. This phenomenon was studied further, and the results

indicated that leachable lead in glazed pottery was increased by time, temperature, and exposure to alkaline solution. Thus the repeated use of a dishwasher may cause dinnerware that had been previously "lead free" to leach lead on subsequent use with food. The effect of time of acid elution was also studied, indicating that the majority of lead is dissolved within one minute of addition of acid, with very slow increase over 24 hours. A cup or pitcher may thus elute dangerous quantities of lead even if it is used for a very short time to contain acidic fruit juice.

Spielholtz and Kaplan have shown that the quantity of lead that is leached from glazed ceramic was critically dependent on the temperature of firing (heating process leading to vitrification of the surface). Thus a change in firing temperature of a given glaze formulation from 850° to 1250° C resulted in over a thousand fold decrease in leachable lead (Spielholtz and Kaplan, 1980). We had found that different china pieces of the same pattern eluted widely different quantities of lead; presumably they were made at the same factory but fired at different temperatures.

Our studies indicated that only a small quantity of lead in the glaze was leachable at a given time, and after a period of days, or treatment with heat or alkali, an additional quantity of lead in the bulk of the glaze became available for leaching. Previous studies have shown that the combined heat and alkali from mechanical dishwashing increased the leachable lead (Natelson and Fred, 1976). The greatest quantity of lead was obtained by heating the ceramic ware for 24 hours at 157° C, before elution with dilute acid. The time of elution by acid is not critical, since the quantity of lead eluted in one minute is comparable with that eluted in 24 hours.

The method described here has also been used to analyze pewter ware. Very high levels of lead have been found in some pewter, but in other cases ions were eluted that interfered with the chelation of lead ion with dithizone. The interfering ions in pewter were not explored further, and the method requires modification for use with pewter.

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