ELSEVIER

0308-8146(95)00035-6

Food Chemistry 54 (1995) 245-249

0308-8146/95/$9.50

Leaching of lead from local ceramic tableware

Norita Mohamed,* Y. M. Chin & F. W. Pok

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

(Received 4 November 1994; revised version received and accepted 25 January 1995)

Ceramic tableware has long since been recognised as a source of lead poisoning. Locally available ceramic utensils (cups, bowls, sauce plates, cooking pots and spoons) were examined as possible sources of lead poisoning. The lead was leached out with 4% acetic acid stored in the samples at room temperature for 24 h. Overall, 54·7% of the sample items tested exceeded the US FDA maximum permitted lead release from earthenware. Of the sauce plates 83·7% exceeded the safety limit and released the highest levels of lead. The amount of lead leached out from the samples decreased with repetitive leachings and increased with temperature. Lead is also found to be leached into acidic foods such as thin soya sauce, tomato sauce and tamarind juice stored in samples of ceramic sauce plates for 24 h at room temperature.

INTRODUCTION

The toxicity of lead has been known for a long time (Chisolm, 1971). Lead poisoining can result from the continued daily intake of lead in amounts as little as 1 mg/day (Henderson & Andrews, 1975). Lead poisoning is a serious medical problem which can result in severe sickness and even death. Thus, it is important that steps are taken to prevent the ingestion of lead from all potential sources. The health effects attributed to lead are damage to the kidneys and liver and to the nervous, reproductive, cardiovascular, immune and gastrointestinal systems (Manahan, 1984). In children, lead has a particularly damaging effect on intellectual development. Lead also interferes with the manufacture of heme, the oxygen-carrying part of haemoglobin in red blood cells. As a poison, lead has its most profound effects on rapidly growing biological systems such as the foetus, infant and child (Lecos, 1987; Miller, 1988; Greely, 1991).

One source of lead is glazed earthenware pottery and ceramics. Cases of lead poisoning resulting from consumption of acidic beverages stored in glazed pottery have been reported (Whitehead & Prior, 1960; Beritic & Stahuljak, 1961; Harris & Elsea, 1967; Klein *et al.*, 1970; Henderson *et al.*, 1979). Lead oxide is a common ingredient in ceramic glazes because it improves the melting characteristics and their physical and chemical properties (Quon & Bell, 1980). Lead produces a smooth, deep satin gloss and trouble-free glazes and gives a lustrous glaze surface (Hamilton, 1977).

A glaze is a thin layer of glass fused onto the surface of clay ware. The glaze holds onto the clay by means of its physical grip on the clay form, but more importantly, by seeping into the surface of the clay and filling some of the open pores (Hamilton, 1977). Salts of other heavy metals such as cadmium, cobalt, chromium, and tin are also used to impart colour to ceramic products. A glaze is applied to ceramic wares and the products are fired at high temperatures. If the glazes are properly formulated, applied and fired, the lead salts are sealed into the glaze and are not extractable or leachable by food components that come into contact with the surface (Spielholtz & Kaplan, 1980; Krinitz & Hering, 1971). If not properly processed, the lead salts or heavy metals are readily extracted by acidic foods or beverages and more so at a higher temperature (Seth *et al.*, 1973).

Ceramic tableware, most examples of which are imports from China, are plentiful in the Malaysian market. There are also some produced by small local cottage industries. This paper reports the results of experiments to find the amounts of lead leached from locally available ceramic tableware (bowls, cups, spoons, earthenware cooking pots, sauce plates) as a function of temperature and number of extraction steps. The leaching of several other metals was also examined. At present in Malaysia, there are no safety limits for lead leached from ceramic ware. Thus, in this work, the safety limits set by the US Food and Drug Administration have been used as a guide.

MATERIALS AND METHODS

Apparatus

Quantitative analyses were performed with a GBC Model 903 atomic absorption spectrometer provided with Pb, Cd, Co, Cu, Ni and Zn hollow cathode lamps. The main instrumental parameters are summarised in Table 1.

---

* To whom correspondence should be addressed.

Table 1. Instrumental parameters

Element	Wavelength (nm)	Lamp current (mA)	Slit width (nm)	Flame type[a]
Pb	217·0	5·0	1·0	A–A
Cd	228·8	3·0	0·5	A–A
Co	240·7	6·0	0·2	A–A
Cu	324·7	3·0	0·5	A–A
Ni	232·0	4·0	0·2	A–A
Zn	213·9	5·0	0·5	A–A

[a] A–A, air–acetylene.

All glassware and polyethylene bottles used were soaked overnight with 2:3 (acid/water) nitric acid solution and then rinsed thoroughly with distilled water.

Reagents

All reagents were of analytical grade. All water used was deionised and distilled. Acetic acid solution (4%, v/v): 40 ml glacial acetic acid was added to 500 ml of water and then made up to 1 litre with water. Standard lead solutions: 1·5985 g of analytical reagent grade lead nitrate was weighed accurately. It was then dissolved in 4% acetic acid solution and diluted to 1 litre. The concentration of this lead solution is 1000 ppm. Concentrated nitric acid: ultrapure from BDH. 1000 ppm Co, Cu, Ni and Zn from BDH Spectrosol. 1002 ppm Cd, from Sigma Chemical Company.

Samples

Various types of glazed ceramic ware such as cups, soup bowls, sauce plates, spoons and earthenware cooking pots were obtained from the local stores for analyses.

Procedures

Choice of leaching agent

Standard tests for release of lead from ceramic ware involve an acetic acid solution as a leaching agent. The pH values of several local foods were compared to 4% acetic acid to ascertain that the acidity of the 4% acetic acid leaching solution proved to be an extreme condition in the use of the ceramic ware.

Leaching of lead into 4% acetic acid solution

The method used for the leaching of lead from the ceramic ware was a modified combination of the British standard procedure, BS 6748 (BSI, 1986) and that of the American Society for Testing Materials, ASTM C 738.81 (ASTM, 1982).

The samples to be tested were rinsed with distilled water and left to dry. They were filled with 4% acetic acid to within a level no more than 1 mm from the overflow point, measured from the upper rim of the sample and to no more than 6 mm from the extreme edge of a sample with a flat or sloping rim. The volume of acid required for each sample was recorded. The samples were covered with aluminium foil. (It was determined that no lead was leached out from the foil when pieces of foil were immersed in 4% acetic acid for a period of 24 h at room temperature.) The samples were set aside for 24 h at room temperature (30–32°C). After 24 h, the levels of the acetic acid in the samples were inspected and, if necessary, the samples were filled with fresh 4% acetic acid up to the original level. The leaching solution was then transferred to polyethylene bottles and analysed for its lead content by atomic absorption spectrometry. This procedure was repeated with fresh 4% acetic acid after each 24 h period, for seven consecutive days on five different sauce plate samples.

For the spoon samples, each sample was completely immersed in the minimum amount of 4% acetic acid in a beaker. The beaker was covered with aluminium foil. At the end of the 24 h period, the solution was analysed for lead.

Leaching of other elements

The 24 h leaching solutions for 14 sauce plates were analysed for lead, cadmium, cobalt, copper, nickel and zinc by atomic absorption spectrometry.

Effect of temperature on the leaching of lead

The effect of leaching at temperatures higher than room temperature (30°C) was investigated for sauce plate samples which were categorised according to the values of lead from the first leaching. Each category consisted of four samples. Each sample was placed in an oven at the designated temperature for 30 min. At the same time, enough 4% acetic acid solution was heated on a hot plate to the designated temperature. The sample was then filled with 4% acetic acid to the required level, covered with aluminium foil and returned to the oven for 2 h. After the sample was removed from the oven, it was left to stand for an additional 22 h at room temperature. After 24 h, fresh 4% acetic was added to the samples to restore the original level of acid in the samples. The leaching solution was then transferred to a polyethylene bottle before the determination of lead by atomic absorption spectrometry.

Effect of food stored in ceramic tableware

Samples of sauce plates of which the amount of lead leached out for the first time was already determined were chosen for this study. These sauce plates were filled with several acidic foods such as thin soya sauce, tomato sauce and tamarind juice for 24 h at room temperature. These food samples were then digested with concentrated nitric acid in a Teflon bomb at 120°C. The resulting clear solutions were transferred to 25 ml standard flasks, made up to volume and analysed for lead by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Choice of leaching agent

Table 2 shows that the acidity of 4% acetic acid solution

Table 2. pH values of local foods

Sample	pH
4% acetic acid	2·35
Lemon juice	2·90
Tamarind juice	2·55
Asam gelugor	2·40
Vinegar	2·40
Thin soya sauce	4·48
Tomato sauce	3·61
Laksa soup	4·74

is greater than the local foods that were tested. This suggests that the best choice for a leaching agent for the release of lead from the ceramic tableware is 4% acetic acid solution.

Leaching of lead

For the samples tested (cups, bowls, sauce plates, cooking pots and spoons), Table 3 lists the lead concentrations in 4% acetic solution stored in the ceramic ware for 24 h at room temperature (30°C). The spoon samples were immersed in a minimal amount of 4% acetic acid solution.

Under FDA guidelines (Gould *et al.*, 1990), the maximum permitted lead release from earthenware is 7 ppm (flatware, plates), 5 ppm (small holloware — cups, bowls) and 2·5 ppm (large hollowware — pots).

Overall, 54·7% of the samples tested exceeded the FDA safety limits. None of the cups tested released lead which exceeded the safety limit of 5 ppm. Only one bowl released more than 5 ppm. The glazed earthenware pots did not leach out detectable amounts of lead. Four of the five ceramic spoons tested released lead above 7 ppm. These spoons were decorated with coloured designs.

The samples which released the highest levels of lead were the sauce plates, 83·7% of which exceeded the limit of 7 ppm (between two and 50 times in excess). Like the spoons, these sauce plates had coloured patterns drawn onto them. On some of the samples, the leaching solution became coloured during the 24 h period due to the dissolution of the dyes used for the patterns on the plates. Definite decolorisation was noted in the plates and spoons even after the first leaching. Improper firing probably resulted in a loosely adherent glaze which is readily dissolved and decolorised by the acidic leaching medium.

Table 3. Distribution of ceramic ware samples with respect to the lead concentration in 4% acetic acid leaching solution after being stored in ceramic ware for 24 h at room temperature (30°C)

Type of sample	Range of lead concentration (ppm)				
	<1	1–50	51–100	101–200	>200
Cups	5	1			
Bowls	16	2			
Sauce plates	3	8	8	15	9
Cooking pots	3				
Spoons		5			

Table 4. Concentration of several elements leached out at room temperature

Sample	Concentration (ppm)					
	Pb	Cd	Co	Cu	Ni	Zn
1	165	0·1	0·3	0·1	—[a]	18·5
2	173	0·1	0·5	0·1	0·2	20·1
3	234	0·1	0·5	0·2	—	23·6
4	185	0·1	0·3	0·2	—	14·2
5	244	0·1	0·4	0·3	—	19·9
6	212	0·2	1·6	—	—	13·0
7	93·6	0·1	0·6	—	—	4·4
8	186	0·1	1·8	—	—	10·0
9	94·2	0·1	0·8	—	—	4·3
10	358	0·1	1·3	0·2	—	21·0
11	270	0·1	0·4	0·2	—	15·0
12	222	—	0·5	0·1	—	11·1
13	198	0·1	0·3	0·1	—	10·1
14	303	0·1	1·0	0·1	—	15·1

[a] —, below detection limit.

The sauce plates with similar patterns were found to release lead in varying amounts in the first leaching. These variations were probably due to differences in glaze formulations and the firing temperature used for each batch of samples or used by a particular manufacturer.

Table 4 shows the amounts of lead, cadmium, cobalt, copper, nickel and zinc leached out from 14 sauce plate samples. Significant amounts of zinc were leached out from the samples with lesser amounts of cadmium, cobalt and copper. The amount of nickel released was lower than the detection limit (0·06 ppm). Buldini had studied the action of a 4% acetic acid solution on a ceramic glaze containing lead, zinc and chromogenic oxides (Buldini, 1977, 1978). His results indicated that both copper and chromium oxides increased the release of lead and zinc. Cadmium, copper and iron(III) were leached at a higher rate than were cobalt(II), manganese(III) and nickel(II). Our findings are in line with Buldini's work. In fact, glazes from tableware must not be coloured with copper compounds as this greatly increases the solubility of lead in the glaze (Hamilton, 1977).

Repeated leachings from the same sample indicated that the amount of lead leached out decreased with each successive leaching (Fig. 1). The percentage of the ratio of the seventh to the first leaching varies between 0·3% and 33%. All samples except the one with the highest level of lead released, leached out lead below the maximum FDA permitted level, that is 7 ppm after the seven repeated leachings. With these repeated leachings, it was even more obvious that the colour and patterns on the samples had faded away.

These repeated leachings were made to simulate the multiple and continued use of these samples of tableware. The decrease in the amount of lead leached out might suggest that the samples become safe to use after a period of repeated use. However, there have been

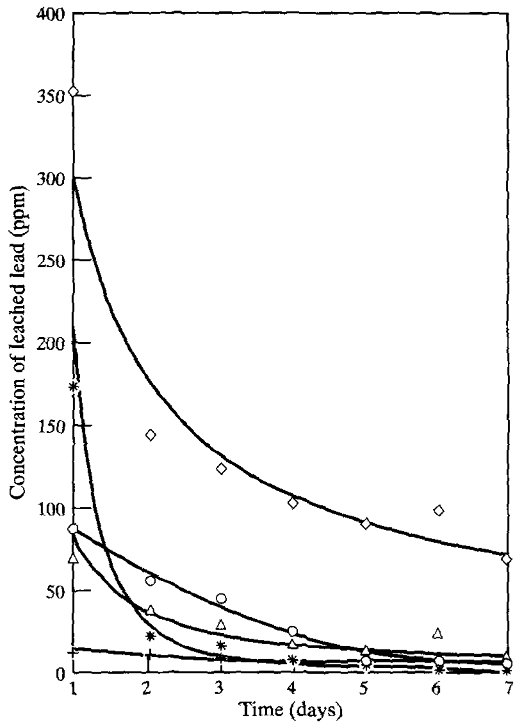

Fig. 1. Concentration of lead leached out as a result of repeated leachings.

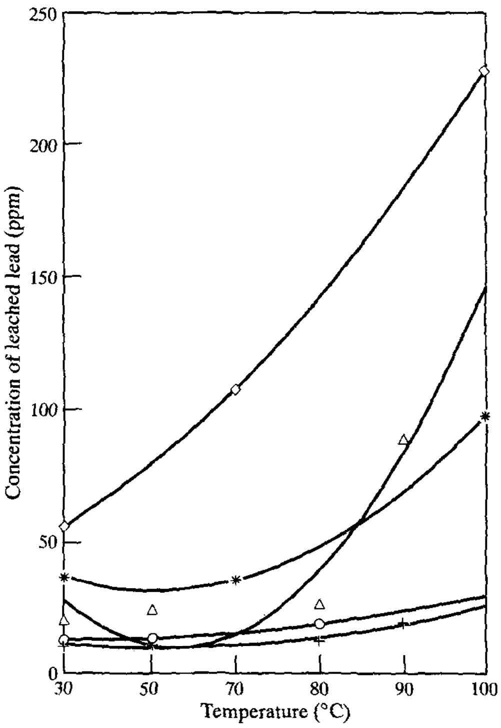

Fig. 2. Effect of temperature on the release of lead by 4% acetic acid.

findings which indicate single or multiple passive leachings or multiple dishwashings and scrubbings cannot reliably predict the future of lead release characteristics of glazes and decorations (Gould *et al.*, 1990). The lead-releasing properties can undergo changes as the glaze application on a ceramic item gets worn down. Therefore, a ceramic item which has been analysed to be lead-safe by its initial leaching may not be reliably free from excessive lead release throughout its usage (Gould *et al.*, 1990).

Effect of temperature on the leaching of lead

Figure 2 shows that the amount of lead leached out increased with temperature. These results support the concept that the release of lead from a glaze is a diffusion-limited, ion-exchange reaction. With such a mechanism, the lead released would remain in solution (Gould *et al.*, 1983).

Effect on food stored in ceramic tableware

Table 5 shows that foods such as thin soya sauce (pH 4·48), tomato sauce (pH 3·61) and tamarind juice (pH 2·40) leached out lead from the samples of sauce plates tested. The food samples which were not placed in the sauce plates contained no detectable amount of lead. These food samples were chosen due to their likeliness of being placed in such sauce plates tested.

Despite there being no safety limits for lead leached from ceramic ware in Malaysia, the Malaysian consumer must be made aware of this potential source of lead poisoning. The symptoms of lead poisoning might not even be diagnosed as lead poisoning. The samples that have been looked at in this investigation were ceramic tableware of a cheaper kind. However, being more expensive does not guarantee an item to be lead free. The FDA has recalled Italian ceramics, Italian designer handmade pottery dishes and Dutch ceramic teapots and pitchers due to the high levels of lead released (FDA, 1987*a*,*b*, 1988).

Table 5. Leaching of lead into food stored for 24 h in ceramic tableware

Sample	Concentration of lead
Thin soya sauce (μg/ml)	
Sauce plate 6	8·50
Sauce plate 7	13·4
Sauce plate 8	12·8
Sauce plate 9	18·9
Sauce plate 10	16·4
Sauce plate 11	17·0
Tomato sauce (μg/g)	
Sauce plate 12	38·4
Sauce plate 13	27·9
Sauce plate 14	31·7
Sauce plate 15	25·6
Sauce plate 16	32·2
Sauce plate 17	47·5
Tamarind juice (μg/ml)	
Sauce plate 18	6·0
Sauce plate 19	4·7
Sauce plate 20	11·7
Sauce plate 21	—[a]
Sauce plate 22	2·0
Sauce plate 23	1·0

[a] —, below detection limit.

REFERENCES

ASTM (1982). *Annual Book of American Society for Testing and Materials Standard* (Standard test method for lead and cadmium extracted from glazed ceramic surfaces. C 738-81). ASTM, Philadelphia, PA, pp. 757–9.

Beritic, T. & Stahuljak, D. (1961). Lead poisoning from lead glazed pottery. *Lancet*, **1**, 669.

BSI (1986). Limits of metal release from ceramic ware, glassware, glass ceramic ware and vitreous enamel ware. BS 6748, British Standard Institution, London, UK.

Buldini, P. L. (1977). Influence of coloring oxides on heavy metals release from ceramic glazes. *Bull. Am. Ceram. Soc.*, **56**(11), 1012–14.

Buldini, P. L. (1978). Influence of coloring oxides on the release of silicon and boron from ceramic glazes. *Bull. Am. Ceram. Soc.*, **57**(4), 430–1.

Chisolm, J. J. (1971). Lead poisoning. *Sci. Am.*, **224**(2), 15–24.

FDA (1987*a*). Ceramic teapots, pitchers recalled. *FDA Consumer*, **21**(7), 6.

FDA (1987*b*). Italian pottery recalled. *FDA Consumer*, **21**(8), 5–6.

FDA (1988). Ceramic ware recalled. *FDA Consumer*, **22**(6), 2.

Gould, J. H., Butler, S. W. & Steele, E. A. (1983). Release of lead and cadmium: comparison of two hot leach methods with a room temperature method, using specially glazed ceramic ware. *J. AOAC*, **66**(5), 1112–16.

Gould, J. H., Hight, S. C., Alvarez, G. H., Nelson, C. E. & Capar, S. G. (1990). Influence of automatic dishwashings and scrubbings on release of lead from glazed ceramic ware. *J. AOAC*, **73**(3), 401–3.

Greely, A. (1991). Getting the lead out of just about everything. *FDA Consumer*, **25**(6), 26–31.

Hamilton, D. (1977). Glazes. In *The Thames and Hudson Manual of Pottery and Ceramics*. Thames and Hudson Ltd, London, UK, pp 124–42.

Harris, R. W. & Elsea, W. R. (1967). Ceramic glaze as a source of lead poisoning. *J. Am. Med. Assoc.*, **202**(6), 544–6.

Henderson, R. W. & Andrews, D. (1975). Leaching extraction from aluminium. *Bull. Environ. Contam. Toxic.*, **13**(3), 330–3.

Henderson, R. W., Andrews, D. & Lightsey, G. R. (1979). Leaching of lead from ceramics. *Bull. Environ. Contam. Toxic.*, **21**(1/2), 102–4.

Klein, M., Namer, R., Harpur, E. & Corbin, R. (1970). Earthenware containers as a source of fatal lead poisoning. *New Engl. J. Med.*, **283**(13), 669–72.

Krinitz, B. & Hering, R. K. (1971). Toxic metals in earthenware. *FDA Papers*, **5**(3), 21–4.

Lecos, C. W. (1987). Pretty poison: lead and ceramic ware. *FDA Consumer*, **21**(6), 6–9.

Manahan, S. E. (1984). Environmental biochemistry and chemical toxicology. In *Environmental Chemistry* (4th edn). Brooks/Cole Publishing Company, Monterey, pp. 504–9.

Miller, R. W. (1988). The metal in our mettle. *FDA Consumer*, **22**(10), 24–7.

Quon, D. H. H. & Bell, K. E. (1980). Release of lead from typical Canadian pottery glaze formulation. CANMET report 80-7E, Ottawa, Canada.

Seth, T. D., Sircar, S. & Hasan, M. Z. (1973). Studies on lead extraction from glazed pottery under different conditions. *Bull. Environ. Contam. Toxic.*, **10**(1), 51–6.

Spielhotz, G. I. & Kaplan, F. S. (1980). The problem of lead in Mexican pottery. *Talanta*, **27**(11B), 997–1000.

Whitehead, T. P. & Prior, A. P. (1960). Lead poisoning from home-made wine. *Lancet*, **2**, 1343–4.