Ç.Ü. Sosyal Bilimler Enstitüsü Dergisi, Cilt 15, Sayı 1, 2006, s.165-170

HEAVY METALS LEACHING FROM, LOW TEMPERATURE GLAZED TURKISH TRADITIONAL CERAMIC WARES

Yusuf Ziya HALEFOĞLU,
Çukurova University
Arts Faculty,
Department of Ceramics,
yhalefoglu@cu.edu.tr

Hunay EVLİYA,
Çukurova University
Faculty Of Sciences and Letters
Department of Chemistry
hevliya@cu.edu.tr

Nergis KILINÇ
Çukurova University
Arts Faculty,
Department of Ceramics,
nkilinc@cu.edu.tr

ABSTRACT

Ceramic pottery has long been recognized as a source of lead poisoning. Lead, copper, chromium, zinc and other heavy metals are found to leach from the glazes of some Turkish poorly-fired glazed pottery in concentrations high enough to result serious health hazards. Poorly-fired ceramic ware with a lead-based glaze can release lead to food, in particular to acidic foods such as tomato sauce salsa. Under acidic conditions, leaching of level heavy metals is maximum. Samples of ceramic ware were purchased from ceramic producers. Locally available ceramic wares (sauce plates, pitchers, pithos) were examined as possible sources of heavy metals. The heavy metals have been leached from the ceramic pottery samples filled with 4% acetic acid at room temperature for 24 hours. The values significantly exceed the limits allowed by United States Food and Drug Administration (FDA) regulations for a 24-h leaching test. Hence, the use of such ceramic ware may constitute a serious health hazard to the users.

Key Words: Ceramic ware, ceramic glaze, lead, heavy metals, acidic food.

DÜŞÜK SICAKLIKLARDA SIRLANMIŞ, GELENEKSEL TÜRK SERAMİK ÜRÜNLERİNDEN AĞIR METALLERİN SALINIMI

ÖZET

Geleneksel seramik ürünleri (çömlek, seramik saklama kapları, güveç kapları) kurşun zehirlenmesinin en önemli kaynaklarından biridir. Kurşun, krom, çinko, bakır ve diğer ağır metallerin, sırlanmış seramik ürünlerin düşük sıcaklıklarda pişirilmesinden dolayı, yüksek konsantrasyonda çözünmesi sağlık açısından çok ciddi sorunlara neden olmaktadır. Düşük sıcaklıklarda sırlanmış bu ürünlerde, özellikle asidik yiyeceklerin saklanması kurşun çözünürlüğünü artırmaktadır. Asidik durumlarda kurşun çözünürlüğü maksimum düzeye çıkmaktadır. Bu çalışmada kullanılan örnekler seramik atölyelerden satın alınmıştır. Bu ürünlere States Food and Drug Administration (FDA)'da belirtilen, 24 saatlik % 4'lük asetik asit testi uygulanmış ve Atomic Absorbsiyon Spektroskopisi ile metal konsantrasyonları tespit edilmiştir.

Anahtar Kelimeler: Seramik, sır, kurşun, ağır metal, asidik yiyecek.

1. Introduction

Glazed ceramic ware is traditionally and widely used in Turkey for conservation of foodstuff. Ceramic ware are made of common clays mixed with small amounts of light burned clays and fired in traditional furnaces at temperatures not much higher than 800-900 °C. The fired items are then covered with wet glaze and refired at approximately 900-1000 °C. Glazes are applied to clay-based ceramic products to provide a shiny generally smooth surface and to seal the clay (Belgiad, J.E., 2003). Lead also allows the glaze to melt and flux easily, besides increasing the bond between glaze and substrate (Oecd,1994). The glaze and the ceramic body are not heated enough to cause them to fuse and no glassification or vitrification occurs. Since the late eighteenth century, certain ceramic glazes have been recognized as potential sources of dangerous lead release when used with acidic food or alkaline foods. Since 1970s, attention has been focused on the use of lead glaze and the tendency of lead leaching from the glaze into the food. This tendency towards leach ability depends on several factors, including glaze composition, firing conditions, pH, temperature, and physical properties of food and duration of contact. Furthermore, when colored glazed are used, basic compounds of lead, cadmium, chromium, zinc, both copper and other heavy metals are present. They present a potential health hazard to ceramic pottery makers and consumers, since they can be leached from the glaze (Belgiad, J.E., 2003).

Previous investigations have reported the release of lead from lead-glazed the ceramic dinnerware. Colorants used in glaze contain the same kind of pigments used in ordinary oil and water colors; hence they contain basic compounds of lead, chromium, zinc and copper. These studies have shown a clear correlation between the uses of the lead-glazed ceramic ware for cooking and/or conservation and elevated blood lead levels (Belgiad, J.E., 2003).

In many countries, authorities for possible release of lead and other toxic metals have monitored lead-glazed ceramic ware. For instance, the FDA has fixed the maximum allowable concentrations of leachable lead range from 0.5 to 3.0 μg/ml depending on the type of dinnerware.

Besides lead - which is the major heavy metal that can be leached from glazed ceramic ware- chromium, zinc, copper and other heavy metals were detected in many kinds of glazed ceramic ware and may constitute a health hazard if such utensils are not used properly (Sheets, R.W., 1997).

Until now, pitchers, pithos and other kitchen utensils made of glazed ceramic ware are widely used in Turkey for the preparation and storage of a large variety of foodstuffs. The purpose of this study is to investigate the leachable lead and other heavy metals from glazed ceramic ware that was purchased from the Turkish ceramic producers. Acid-leaching tests have been carried out to determine whether the use of glazed ceramic ware may have a human health hazard risk to the Turkish people.

This study describes the levels of lead and other heavy metals released from the ceramic ware into the acid foods, such as tomato paste or salsa.

2. Materials and Method

2.1. Sample Collection

6 ceramic pottery (ceramic ware) have been purchased from a manufacturer in Gaziantep, situated in South East Anatolia. The manufacturer has been in production since 40 years. The samples have been selected randomly. Before starting the chemical analysis, all potteries have been washed with a commercial dish washing detergent, rinsed with distilled H_2O and air dried.

3. Experimental

Samples of pottery (ceramic ware) were subjected to acid leaching tests to investigate the release of heavy metals. Extraction with 4% acetic acid has been realized for a period of 24 hours at 22 ^oC according to Turkish Food Codex (Turkish Food Codex, 2001).

Leaching tests of glazed-ceramic ware involve either filling or dipping each ceramic pot into 4% CH_3COOH solution allowing it to stand 24 hours. Then, acetic acid solution is decanted and aliquots taken for analysis. Extraction was repeated twice for each experiment and analysis have then been performed. Lead and other heavy metals were analyzed according to the method of FDA. The leachable heavy metals, Pb, Cr, Zn and Cu have been analyzed with Atomic Absorption Spectrophotometer (Perkin Elmer Model 2380) with a graphite furnace using a chemical modifier and instrumental background correction. Concentrations in leached metal solutions are calculated using calibration curves and linear least squares regression.

This method is applicable to food-contact surfaces of silicate-based materials (ceramic ware, glazed ceramic, decorated ceramic ware…) and is capable of determining lead concentrations greater than approximately 0.0005-0.002 μg/ml, depending on instrument design.

4. Results and Discussion

For added safety, the FDA recommends the use of acidic conditions (4% acetic acid) to test the ability of heavy metals leaching from glazes. The use of more acidic conditions (6N HNO_3) resulted in a considerable increase in lead leaching. Since such extreme conditions are unlikely to occur for foodstuffs, the FDA test uses 4 % acetic acid, which is much closer to the actual situation. For this reason we adopted the FDA procedure for leaching lead and other heavy metals and no other pH conditions were tested (Belgiad, J.E., 2003). Results of the 24-h acetic acid leaching tests are given in Table 1-4.

Poorly-fired ceramic ware with a lead-based glaze can release lead into food, particularly when acidic foods such as tomato sauce or salsa are used. Under acidic conditions, leaching of heavy metals is found to be maximum.

Glazed ceramic ware is traditionally and widely used in Turkey for conservation of foodstuff, an example is ceramic pitchers or pithos for salsa. Tomato salsa is commonly used in Turkey and its pH is 1.45. This is highly acidic; therefore, heavy metals may be releasing easily from the ceramic pitchers in which tomato salsa is stored.

Table 1. Concentration of Lead

Sample No	Pitchers (μg/ml)	Pithos (μg/ml)
1	7.1	11.7
2	8.3	12.5
3	8.1	10.6
4	4.3	13.5
5	5.7	10.6
6	8.4	10.1

As seen in Table 1, the lead concentrations change within 7.1 to 8.4 in pitchers and the results are larger in pithos, this is most probably a result of the size of the pitcher and the pithos. These results exceed the allowed limits given in Table 5 tremendously.

Table 2. Concentration of Chromium

Sample No	Pitchers (μg/ml)	Pithos (μg/ml)
1	7.80	2.30
2	8.50	3.10
3	8.00	2.00
4	8.10	2.50
5	7.90	1.10
6	8.10	2.30

Table 3. Concentration of Zinc

Sample No	Pitchers (μg/ml)	Pithos (μg/ml)
1	2.90	1.20
2	2.80	3.10
3	3.00	3.30
4	3.10	3.50
5	3.00	2.10
6	3.00	2.30

Table 4. Concentration of Copper

Sample No	Pitchers (μg/ml)	Pithos (μg/ml)
1	3.90	2.80
2	3.70	2.10
3	3.70	2.30
4	3.90	2.20
5	3.70	2.10
6	3.80	2.00

FDA is in the process of reducing the standards for acceptable levels of lead in ceramic ware. The regulations are given in Table 5.

Table 5. Standards for acceptable levels of lead in ceramic ware according to FDA

Ceramic Wares	New Regulation (μg/ml)	Old Regulation (μg/ml)
Plates, Flatware	3.00	7.00
Small Pithos	2.00	5.00
Cups, Mugs	0.50	2.50
Large Pithos	1.00	2.50
Pitchers	0.50	5.00

When ceramics are used normally, it is unlikely that the maximum possible lead amounts are taken up daily or even life long. However, if sour (acidic) foods, in particular, are stored for longer periods in heavy metal-permeable ceramic containers, the amount of lead released may reach critical levels.

Lead and other heavy metals are toxic in relatively small amounts. Lead produces physiological and neurological effect in human and severe lead poisoning can lead to coma or death. Even very low blood-lead levels in children can produce significant, long-term effects that include permanent neurological damage (Sheets, R.W., 1998). FDA is in process of reducing the standards for acceptable levels of lead in ceramic ware. Besides chromium, copper and zinc are very toxic heavy metals. All of them produce acute and chronic effects on human. Chromium, copper intoxications initially manifest the symptoms diarea and vomiting. They may lead to liver and heart damage, kidney and circulatory failure. At low doses over a longer

period, they go hand in hand with non-specific symptoms like exhaustion, headaches and neurological disorders. Chromium, copper accumulates in the body and can cause serious health effects such as lung disease, kidney damage, and lung cancer. Exposure to cadmium, even at low levels, may also have serious effects on the fetus, infants, and young children.

5. Conclusion

In Turkey, no special regulations concerning the amount of lead -leached from glazed ceramic ware- exist. There is no warning concerning the amounts of possible lead release in ceramic kitchenware. Hence high lead level in acidic food conserved in ceramic ware is critical for human health. Except lead and cadmium, FDA has not set limits for permissible concentrations of heavy metals leached from glazed ceramic ware.

It is concluded that regular use of such glazed ceramic ware for food conservation could present a health hazard. Glazed ceramic ware may be a potential source of toxic lead levels when used with acidic foods.

The results of this research work reveals that severe control of the possible release of heavy metals from lead glazed ceramic ware must be realized immediately.

REFERENCES

[1] ARAB-ABOU, A. A. K., 2001. Release of lead from glaze-ceramic ware into foods cooked by open flame and microwave, Food Chemistry 73, pp. 163-168.

[2] BELGIAD, J. E., 2003. Release of heavy metals from Tunisian traditional ceramic ware. Food and Chemical Toxicology 41, pp. 95-98.

[3] MOHAMED, N., CHIN, Y. M., POK, F.W., 2000. Leaching of lead from local tableware. Food Chemistry.

[4] SHEETS, R. W., 1997. Extraction of lead, cadmium and zinc from over glaze decorations on ceramic dinnerware by acidic and basic food substances. The Science of the Total Environment 197, pp. 167-175.

[5] SHEETS, R. W., 1998. Release of heavy metals from European and Asian porcelain dinnerware, The Science of the Total Environment 212, pp. 107-113.

[6] SHEETS, R. W., 1999. Acid extraction of lead and cadmium from newly-purchased ceramic and melamine dinnerware, The Science of the Total Environment 233, pp. 233-237.