STAT-AAS Determination of Cd, Pb, and Zn Leached from Turkish Glazed Ceramic Tableware

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INTRODUCTION

The ceramic pigments often used are known to be toxic and include compounds of lead, cadmium, chromium, and cobalt. Although these metals are not supposed to release into foods, this ultimately depends on the production quality and usage period of the dinnerware such as glass, porcelain, and plastic. Due to the high toxicity of Cd and Pb even at ppb levels, their control is of high importance for preventive medicine. Food and beverage contamination by heavy metals occurs either in a direct way or by contact with packaging materials which release contaminants (1-3). In other word, ceramic pigments that are known to be toxic include compounds of lead, cadmium, chromium, and cobalt (4-5). Lead compounds are used in three different ways in the dinnerware industry: as fluxes in glazes, as fluxes in fusing decorations to glazes, and as colorants in the glazes and decorations themselves. Colored, painted, and gilded porcelain dinnerware is commonly desired because of its aesthetic image. However, it should be remembered that colored paints are generally metallic and similar to ceramic pigments. The observed migration of metals is basically due to a chemical attack on the glaze surface by acid-base or complex reaction because ceramics possess too few free carriers to initiate electrochemical corrosion via redox reactions (6).

ABSTRACT

In the literature, slotted tube atom trap-atomic absorption spectrophotometry (STAT-AAS) has been successfully used for the determination of Cd and Pb at the ng g⁻¹ levels. In the present study, color-decorated dinnerware was exposed to different concentrations of acetic, citric, tartaric, and lactic acid as well as concentrated and 7-mol L⁻¹ nitric acid and yogurt. The extracted Cd, Pb, and Zn concentrations were determined by STAT-FAAS. The experiments indicated that there were differences in migration of citric/tartaric and lactic acid into foods as compared with acetic acid due to the strength of acidity. It was found that some porcelain plates released Cd (up to 0.084 mg dm⁻²) and Pb (up to 4.140 mg dm⁻²) which is more than the FDA limit of concentrations allowed (0.07 mg dm⁻² for Cd and 0.8 mg dm⁻² for Pb) by using 4% acetic acid.

Some metals such as Cd and Pb are considered to be toxic, while others such as Cu and Zn are nutritionally essential at lower levels, but can also be toxic and/or affect the toxicity of some toxic metals when certain limits are exceeded (7-10). Particularly, Cd and Pb produce adverse health effects in humans even at low concentrations and are toxic in all forms and in relatively small amounts. Briefly, Pb causes physiological, neurological, and growth problems in humans. The general assumption is that lead interacts with the function of enzymes, signal systems and membranes, probably by binding to cer-

tain sites of proteins (11). The U.S. Environmental Protection Agency (USEPA) has classified Cd and Pb as probable human carcinogens (Group B2) (12). The International Agency Research on Cancer (IARC) has placed Cd and Cd compounds in Group 1 (carcinogenic to humans), and classified inorganic Pb compounds as "probably carcinogenic to humans" (Group 2A), while Pb as "possibly carcinogenic to humans" (Group 2B) (13). The World Health Organization (WHO) established the provisional tolerable weekly intake (PTWI) of Pb as 0.025 mg kg⁻¹ body weight for all human groups (14).

In the 1980s and 1990s, extensive research had gone into the development of lead-free glazes (4-5, 15-18). However, lead glazes are still common on new dinnerware, especially on much of the ware imported from countries which includes China, Mexico, and Italy. After observing a large number of poisoning cases in the 1970s, the European Union decided to monitor dinnerware with regard to releasing lead and cadmium, and set the directive 84/500/EC, which fixes specific migration limits for ceramic articles (19-22). This directive regulates only the elements of lead and cadmium, although other toxic trace elements can leach and endanger public health, especially when colored glazes are applied. In order to test the conditions prescribed by 84/500/EC, migration experiments under different conditions such as the nature of the acid and contact time were conducted. Previous studies have shown that the release of lead and cadmium depends on the type of acid. Cer-

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tain acids present in food can even be more effective than 4% acetic acid (16-17, 23).

Current maximum allowable concentrations of leachable Pb range from 0.5 to 3.0 mg mL⁻¹ depending on the kind of dinnerware involved (22). For leachable Cd, the allowable concentrations range from 0.25 to 0.5 mg mL⁻¹ (24). These estimations are based on a plate with a 20 cm diameter, of 1.5 cm depth, and a volume of 471 mL, resulting in a food contact surface of 4.08 dm². A consumer, who eats a plateful of food into which the entire permitted amount of lead or cadmium has migrated, takes in approximately 3.2 mg Pb or 0.28 mg Cd. These results correspond to 0.8 mg dm⁻² for Pb and 0.07 mg dm⁻² for Cd. Accordingly, the permissible extracted Pb and Cd amounts with 4% acetic acid over a 24-hour period were limited by national and international authorities to 0.8 and 0.07 mg dm⁻², respectively (22, 25-26).

In the present study, the color-painted tableware was exposed to different concentrations of acetic, citric, tartaric, and lactic acid. Although data on the migration of elements by acetic and citric acid is abundant (16-17, 23), data on the migration of metals induced by tartaric and lactic acid mainly

occurring in contact with fruits and meals is difficult to find. Further, the dinnerware was also exposed to concentrated and 7 M nitric acid. Then, the extracted Cd, Pb, and Zn concentrations were determined by slotted tube atom trap-flame atomic absorption spectrophotometry (STAT-FAAS). The improvement in sensitivity by using STAT-FAAS is attributed to the increased residence time of the analyte atoms in the light path due to slower flame speed. The detail on the use of atom trap are given in Table I.

The dishes in this study were selected by a truly random method and are representative of dinnerware offered in the current Turkish market. The other goal of this study was to examine migration limits after food contact periods up to 24 hours.

EXPERIMENTAL

Instrumentation

A model ATI UNICAM 929 atomic absorption spectrophotometer, equipped with ATI UNICAM hollow cathode lamps, was used for the metal determinations. The optimum conditions for FAAS were applied as described in the manufacturer's handbook (Table I). A slotted tube atom trap (STAT) made from quartz (Quarzschmelze Ilmenau GmbH, Germany) was used to

enhance the sensitivity of FAAS. The applied conditions (Table I) for the quartz tube were taken from elsewhere (3, 27) and 30 ng mL⁻¹ of Pb and 3 ng mL⁻¹ of Cd were determined using STAT-FAAS.

Reagents

Unless otherwise stated, all chemicals used were of analytical reagent grade. Throughout the analytical work, doubly distilled water was used. All glassware (Pyrex®) was kept permanently full of 1 mol L⁻¹ nitric acid when not in use. Seven different concentrations of acetic, citric, tartaric, and lactic acid between 0.01–1.0% (0.01–0.02–0.1–0.2–0.4–0.5–1.0%) were used as the leaching agents. Furthermore, additional concentrations (2, 3, 4, and 5%) of acetic acid were used as the leaching agents for the same dishes.

Migration Procedure from Porcelain Dishes

Twenty-two overglaze-decorated porcelain plates were purchased at local markets and examined. These dishes are representative of porcelain generally used in Turkish households. The dishes were washed one by one in warm water with detergent and rinsed with Milli-Q™ water. Each of the objects was separately exposed to acetic, citric, tartaric, and lactic acid at concentrations ranging from 0.01% to 5.0% at a temperature of 22±2 °C and for different lengths of time.

For the extraction procedure, each porcelain sample was immersed separately in a 10-mL solution consisting of distilled water with acid, each containing a known concentration (0.01–0.02–0.1–0.2–0.4–0.5–1.0%) of the four acids (acetic, citric, tartaric, and lactic) mentioned above, and allowed to stand for two hours at a temperature of 22±2 °C. After removing the porcelain from the acid solution, the solution was evaporated, and the residue diluted

TABLE I
Instrumental and Operating Conditions for STAT and AAS

Instrument	UNICAM 929 FAAS
Atom trap	Quartz slotted tube
Diameter of tube	0.6 cm
Length of upper slot	0.7 cm
Length of lower slot	5 cm
Length of tube	12 cm
Height from burner	1.0 cm
Air/acetylene flow ratio	8 L/min
Wavelength	Cd 228.8 nm, Pb 217 nm, Zn 213.9 nm
HCL current	Cd 4.0 mA, Pb 7.5 mA, Zn 5.0 mA
Slit width	Cd 0.5 nm, Pb 0.5 nm, Zn 0.5 nm

with 2 mL with 1 mol L⁻¹ nitric acid. Then, the different parts of the same samples were exposed to 10 mL of acetic acid for different periods ranging from 2–24 hours at a temperature of 22±2 °C.

Use of Yogurt (natural lactic acid)

Different pieces of the same porcelain samples were also immersed to 10 mL of yogurt in Pyrex® vessels for various periods ranging from 2–24 hours at a temperature of 22±2 °C. After removing the porcelain pieces from the vessel, the yogurt sample was dried and ashed in Pyrex vessels as mentioned elsewhere (1-2, 28). After dry ashing of the ash sample by using concentrated nitric acid and hydrogen peroxide as described elsewhere (28), the final volume was completed to 2 mL of 1 mol L⁻¹ nitric acid.

Finally, the porcelain plates of different color, pattern, trademark, and quality obtained from local markets were immersed in 10 mL of 4% acetic acid solution for two hours at a temperature of 22±2 °C. After removing the plates from the solution, the clear solution was analyzed by STAT-FAAS. Each of the results given in the tables and figures are the average of three values obtained for the samples analyzed in triplicate.

RESULTS AND DISCUSSION

Analytical Performance

The calibration curves were linear at the concentration range of 3–300 ng mL⁻¹ for Cd, 30–3000 ng mL⁻¹ for Pb by using STAT-FAAS, and 0.2–2.0 mg L⁻¹ for Zn by FAAS. The equations of the curves are as follows:

$$Y = 0.31X + 0.2, R^2 = 0.9999, \text{ for Pb (30–400 ng mL}^{-1}\text{)}$$

$$Y = 3.13X + 0.3, R^2 = 0.9999, \text{ for Cd (3–100 ng mL}^{-1}\text{)}$$

$$Y = 270X + 2.0, R^2 = 0.9999, \text{ for Zn (0.2–2.0 mg L}^{-1}\text{)}$$

The relative standard deviations (RSD) for Cd, Pb, and Zn were 10%, 11%, and 11%, respectively, using seven replicate procedures. The levels of Cd, Pb, and Zn in the blank samples were 0.2 and 3.0 ng mL⁻¹ and 0.03 mg L⁻¹ with the standard deviation values of 0.06 and 0.3 ng mL using STAT-FAAS, and 0.004 mg L⁻¹ using FAAS only, respectively. Therefore, the limit of detection (LOD), calculated as 3σ of the reagent blank, was 0.18 and 0.9 ng mL⁻¹ for Cd and Pb and 0.012 for Zn. Further, the limit of quantitation (LOQ) was 3 ng mL⁻¹ for Cd, 30 ng mL⁻¹ for Pb, and 0.1 mg L⁻¹ for Zn.

Effect of Nature of the Acid on Migration

Unlike acetic and lactic acid, both of which are carboxylic acids, the tartaric and citric acids are bicarboxylic and tricarboxylic acids, respectively. This enables them to form the chelates: bidentate or tridentate complexes. The first formation constants of the complexes consist of these reagents, and the metals are as follows: for Cd: logK_f=3.98 for citric, 2.8 for tartaric, 1.7 for lactic, and 1.5 for acetic acid; for Pb: logK_f=6.5 for citric, 3.78 for tartaric, 2.40 for lactic, and 2.52 for acetic acid; and for Zn: log K_f=4.71 for citric, 2.68 for tartaric, 2.20 for lactic, and 1.50 for acetic acid. So, the formations of complexes are different depending on the acid species. Further, it can be stated that the main effect of migration is due to the quality of acidity. Due to the higher acidity constant of tartaric (K_{a1}:9.20x10⁻⁴ and K_{a2}:4.31x10⁻⁵), citric (K_{a1}:7.45x10⁻⁴, K_{a2}:1.73x10⁻⁵, and K_{a3}:4.02x10⁻⁷), and lactic (K_a:1.37x10⁻⁴) acid in comparison to acetic acid, a higher metal migration can be expected (see Figures 1-3). This explains, in part, the higher migration of the studied

three elements as seen. In addition, other concepts, such as solubility of the metals, also play a significant role. Although acetic acid is considered to be a harsh stimulant when compared with the foods selected, the conditions of use for the porcelain articles in contact with the food may in practice be harsher than the 24 hours at 22 °C conditions. Follow-up studies revealed an over-estimation of migration into acetic acid relative to foodstuff, although the products investigated only showed low levels of migration, and thereby established the suitability of acetic acid as a stimulant.

Effect of Acid Concentration on Migration

From Figures 1-3 it can be seen that the amount of migrated Pb continuously increases as the acid concentration increases. On the other hand, Cd and Zn remain steady after a concentration level of 0.5% for citric, tartaric, and lactic acid. Figure 4 shows that similar results were obtained for another plate sample immersed in acetic acid.

Effect of Contact Time on Migration

From Figures 5 and 6 it can be seen that the migrated metals do not generally change after four hours of contact time, except for Pb in one of the samples and in another for Cd. It can, therefore, be concluded that the interaction time depends on the porcelain decoration and the metal species in the glaze (Figures 5-7). Figure 8 shows that the migrated Pb increases continuously with an increase in interaction time, while Cd and Zn do not change after four hours in the leachate.

Migration of Metals From Different Porcelain Plates

Table II lists the amount of Cd, Pb, and Zn migrating into the

Fig. 1. Effect of nature of acid on migration of Cd from the same porcelain samples (Sample No. 22 in Table II).

Fig. 2. Effect of nature of acid on migration of Pb from the same porcelain samples (Sample No. 22 in Table II).

Fig. 3. Effect of nature of acid on migration of Zn from the same porcelain samples (Sample No. 22 in Table II).

Fig. 4. Effect of acetic acid concentration on migration of metals from the same porcelain samples (Sample No. 22 in Table II).

Fig. 5. Effect of time on migration of Pb from different porcelain samples with 4% acetic acid (Sample No. 2 in Table II).

Fig. 6. Effect of time on migration of Cd from different porcelain samples with 4% acetic acid (Sample No. 2 in Table II).

Fig. 7. Effect of time on migration of Zn from different porcelain samples with 4% acetic acid (Sample No. 4 in Table II).

Fig. 8. Effect of time on migration of metals from the same porcelain samples (Sample No. 22 in Table II) with yogurt.

TABLE II
Metal Amounts After Migration From Different Porcelain Samples by Various Acids (mg dm⁻²)
Standard deviations are lower than 15%. LOQ: Limit of quantitation.

Sample/Color No.	HNO ₃ , concentrated			HNO ₃ , 7M			Acetic acid, 4%		
	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn
1 Pink	<LOQ	0.054	0.007	0.002	0.049	0.014	<LOQ	<LOQ	0.007
2 Yellow	0.095	0.977	0.010	0.630	6.810	0.242	0.021	0.264	0.008
3 Blue	<LOQ	0.032	0.012	0.003	0.089	0.018	<LOQ	0.026	0.014
4 Gray	<LOQ	3.500	0.100	0.003	6.420	0.154	<LOQ	1.211	0.058
5 Pink	<LOQ	0.471	0.047	0.003	0.467	0.073	<LOQ	0.110	0.017
6 Yellow	<LOQ	0.063	0.007	0.002	0.027	0.008	<LOQ	<LOQ	0.008
7 Black,pink,yellow,green	<LOQ	0.231	0.022	0.005	0.510	0.013	<LOQ	0.331	0.018
8 Orange, yellow, blue	<LOQ	2.879	0.970	0.006	29.760	2.113	<LOQ	4.140	0.256
9 Green	<LOQ	0.007	0.007	0.002	0.020	0.010	<LOQ	<LOQ	0.007
10 Dark blue, yellow	<LOQ	0.112	1.142	0.008	0.430	0.660	<LOQ	0.157	0.480
11 Blue, green, yellow	0.089	0.095	0.420	0.024	0.384	0.420	0.002	0.380	0.300
12 Dark blue, yellow, green	0.023	0.082	2.700	0.010	0.500	2.730	<LOQ	0.056	0.463
13 Pink, yellow	<LOQ	0.011	0.038	<LOQ	0.084	0.039	<LOQ	<LOQ	0.011
14 Silver	0.021	0.500	0.030	0.060	1.660	0.070	0.010	0.240	0.016
15 Dark blue, yellow	0.004	0.080	2.740	0.007	0.156	2.650	<LOQ	0.037	0.792
16 Blue, brown	<LOQ	0.065	0.061	<LOQ	0.440	0.130	<LOQ	0.092	0.075
17 Green, brown	<LOQ	0.086	0.024	<LOQ	0.330	0.039	<LOQ	0.063	0.029
18 Blue, green	<LOQ	0.041	0.025	<LOQ	0.108	0.018	<LOQ	<LOQ	0.026
19 Blue, red,yellow,dark blue	0.017	0.007	0.014	0.022	0.220	0.039	<LOQ	0.030	0.020
20 Dark blue, dark red	0.002	0.910	2.740	0.027	22.070	6.300	<LOQ	2.183	1.210
21 Blue, green, pink, brown	<LOQ	0.088	0.019	<LOQ	0.187	0.033	<LOQ	0.098	0.017
22 Dark red	1.125	2.420	1.080	1.538	3.566	1.120	0.084	0.294	0.053

leachates after a 2-hour migration time in differently colored porcelain plates. Of the 22 ceramic dinnerware pieces purchased in individual patterns, three released Pb at a concentration of 4.14, 2.183, and 1.211 mg dm⁻² which exceeds the FDA limits (0.8 mg dm⁻² for Pb). As described in the Introduction section, the maximum allowable limits are based on a plate having a 20 cm diameter and 1.5 cm depth, with a volume of 471 mL and a food contact surface of 4.08 dm². A consumer who eats a plateful of food into which the entire permitted amount of lead or cadmium has migrated takes in approximately 3.2 mg Pb or 0.28 mg Cd, corresponding to 0.8 mg dm⁻² for Pb and 0.07 mg dm⁻² for Cd. As a result, the extracted Pb and Cd with 4% acetic acid within a 24-hour period is the limit allowed according to national and international authorities (22, 26). However, it should be noted that the provisional tolerable weekly intake (PTWI) of Pb and Cd was estimated by WHO (1993) as 0.025 and 0.007 mg kg⁻¹ body weight, respectively, for all human groups. For an adult person weighing 70 kg, these limits correspond to 0.25 mg Pb and 0.07 mg Cd per day. Thus, the limits given above of 3.2 mg Pb and 0.28 mg Cd for migrated values are higher than the regulatory values of 0.25 mg Pb and 0.07 mg Cd. It can be seen that this subject needs further re-consideration and requirements.

Nitric acid, unlike acetic acid, is an oxidizing agent and more effective than the latter in removing metal ions from overglaze-decorated dinnerware (4). All of the dishes that released Pb and/or Cd in acetic acid leaching tests also released the metals when tested with 7 M concentrated HNO₃. In most cases, the metal concentrations in the HNO₃ leachates were more often greater than in acetic acid leachates. Cadmium was released into 7 M HNO₃

from 18 of the 22 porcelain dinnerware plates. In 4% acetic acid, only four of the plates released Cd at the measurable concentration. In other words, the majority of the plates tested did not release Cd at the measurable concentration. Lead was released into 7 M concentrated HNO₃ from all of the 22 porcelain plates. In 4% acetic acid, 17 of these plates had released Pb at the measurable concentration. Zinc was released into 7 M and concentrated HNO₃ and 4% acetic acid from all 22 porcelain plates. As was to be expected, the Cd, Pb, and Zn concentrations in the final leachates of both 7 M and concentrated nitric acid were higher than in the 4% acetic acid.

Migration of elements is driven by attacking the hydrogen ions. Therefore, it is only logical that the release of metals grows with a larger number of hydrogen ions in the leaching agent and thus with a descending pH. A comparison between the diffusion of the entering hydrogen-bearing species and the diffusion of the outgoing alkali ions endorses the first step in defining the migration rate (29). Hence, the leaching rates will generally increase linearly with proton activity. It was found that the Cd and Pb concentrations in 7 M nitric acid leachates were at least two times higher in the 4% acetic acid leachates.

The metals Ni, Co, Zn, Fe, Cu, and Mn are all used in pigments to color the glaze used for ceramic articles in order to make the products more visually attractive. The metals can also have a functional role. For instance, green copper pigments used in combination with a glaze based on lead have been reported to result in a higher acidic solubility of the glaze. However, no harmonized international migration limits were established for the metals used in the glazing of ceramic articles. The estimated median intake of zinc from foods in

ceramic plates was found to be well below the UL. Thus, the contribution to the daily intake of zinc from ceramic plates (due to glazes dissolved by acids) is small compared to the intake, in particular, from animal food.

Further studies of metals migrating from dinnerware and packaging into foods are needed because there are clear differences between the migration into foods and into the acetic acid stimulant. Thus, the same plates (Sample No. 22 in Table II) were interacted with yogurt instead of acid (Figure 8). It was found that Pb migration increased with interaction time, but the official limit of 0.8 mg dm⁻² was not exceeded.

CONCLUSION

Although it is assumed that the Cd and Pb metals in porcelain plates do not release into food, it should be noted that this will depend on the production quality and usage period of the dinnerware. The set of migration values obtained in this study indeed confirm the assumption that lead and cadmium migrating from ceramic dishes into food are a potential health risk. For extraction of Cd, Pb, and Zn from plates, various acids (acetic, citric, tartaric, and lactic) were used as leaching agents to establish how much of these migrated into the acids. The experiments indicated that there are differences in the migration of Cd, Pb, and Zn depending on the strength of the acids tested (citric, tartaric, lactic, and acetic), as well as the differences in the formation constants between the acid anions and the metal cations. The main advantages of the STAT-FAAS method used in this study are improvement in sensitivity as well as less risk of contamination, high speed, and low cost. Thus, it can be said that STAT-FAAS is the best methodology for this type of study.

It was also found that some porcelain plates released Cd (up to 0.084 mg dm⁻²) and Pb (up to 4.140 mg dm⁻²) with 4% acetic acid, which is more than the FDA limit of concentrations (0.07 mg dm⁻² for Cd and 0.8 mg dm⁻² for Pb). After establishing 24 hours of interaction, it can be concluded that the leachable Pb content of many plates may exceed the FDA limit values of 0.8 mg dm⁻² and is enough to constitute a human health hazard. As a result, this study points to the fact that there are various toxic metals hazards associated with the use of new dinnerware.

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