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Migration of Lead and Cadmium from Ceramic Materials Used in Food Preparation

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Pottery containers and cooking utensils continue to cause metal contamination of foods in spite of warnings by health authorities of the need for caution when certain types of pottery are used in contact with food [(Shibamoto and Bjeldanes 1993; Watson 1995). Pottery used for cooking vessels is normally glazed to produce a non-porous, water-tight surface. The glass-like glaze of good earthenware and ceramics is produced by coating the surface with a carefully prepared frit and heating it to a high temperature in a kiln. The kiln, which contains salts of lead and other metals, is vitrified and forms a glass-like layer on the pottery surface. The glaze on properly made and kilned plates and dishes should normally be unaffected by food and should not release its lead and other metal components during cooking or standing. Unfortunately, some glazed pottery, especially of the craft and home-made kind, which has not been kilned at a sufficiently high temperature or has been made with poorly formulated frits, is capable of releasing toxic amounts of lead, cadmium and other metals into food (Belitz and Grosch 1985; WHO 1993).

Because of heavy metals leach from glazed ceramics, authorities in various countries have introduced regulations and guidelines with regard to the quality of such items. The Council of the European Economic Community has issued a Directive establishing limits for lead and cadmium leaching, under specified conditions, from ceramic materials (European Economic Community 1984).

To know if materials used are inert when they are in contact with food, analysis are necessary. Compounds in quantities liable to represent a risk for human health or liable to alterate the composition of food, must not be transferred to food by ceramic materials (Bureau 1995). Mainly two metals have to be studied in ceramic materials: lead and cadmium (Boudene 1986).

This paper presents a study of the release of metals by pottery used in the preparation of food. Analytical determinations are performed by AAS, according to the legislation (European Economic Community 1984). A study of a faster analytical method for the simultaneous determination of these metals was also carried out. Therefore, voltametry has been used. Polarographic methods can be used in the related technique of anodic stripping voltametry. A characteristic half-wave potential results for each metal and can

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be used for identification, while the height of the wave is related to the concentration. The technique is very sensitive and useful for the determination of heavy metals (Blanco, López and Cirugeda 1991; Reilly 1991).

MATERIALS AND METHODS

All reagents used were of analytical grade. Cd and Pb working standards were prepared by dilution of Cadmium and Lead stock solutions (1000 µg.L^{-1}) before use. A Shimadzu Model AA-646 AAS, and Cd and Pb hollow-cathode lamps (Shimazdu) were used. The settings on the instruments are shown in TABLE 1.

Table 1. Instrumental Operating Conditions.

Element	**Wavelength, Å**	**Slit Width, Å**	**Flame**
Lead	2833	1.9	Air-Acetylene
Cadmium	2288	3.8	Air-Acetylene

Voltametric measurements were made with a Metrohm Model 626 Polarecord in conjuction with a 663 VA Stand and a 621 Va-Timer (basic timer and control unit for stripping voltametry). A conventional three-electrode arrangement was used, consisting of glassy carbon rod as an auxiliary electrode, an Ag/AgCl/KCl(3M) double-junction electrode as an reference electrode and a Metrohm multi-mode electrode (MME) used in the hanging mercury drop electrode (HMDE).

Anodic stripping is a sensitive variation of the polarographic technique, especially suitable for metals as Cd and Pb.

After the preconcentration of the metal ions from the solution and amalgamation into a stationary hanging mercury drop electrode, the process is reversed by using a potential more negative than the reduction potentials of the metal being determined. The metals are stripped anodically, using a slowly increasing positive potential. The current recorded during stripping is directly related to the concentration of the metal.

Oxygen must be removed from the solution by bubbling with an inert gas, such as nitrogen, during analysis.

A study of the suitable conditions for the simultaneous determination of Cd and Pb was carried out. The following instrumental settings were used: initial voltage applicating, -700 mV; deposition time, 60 s with stirrer and 25 s without stirrer; scan rate, 10 mV.s^{-1}; pulse duration, 60 ms; modulation amplitude, 50 mV; pulse repetition time, 0.5 s; sensitivity, 2 nA/mm; Hg drop size, 0.52 mm^2. For the analysis of the samples, 20 mL of the sample were taken, adding drops of KCl, removing the oxygen by bubbling with nitrogen for 5 minutes, and making the metal determinations in the indicated conditions.

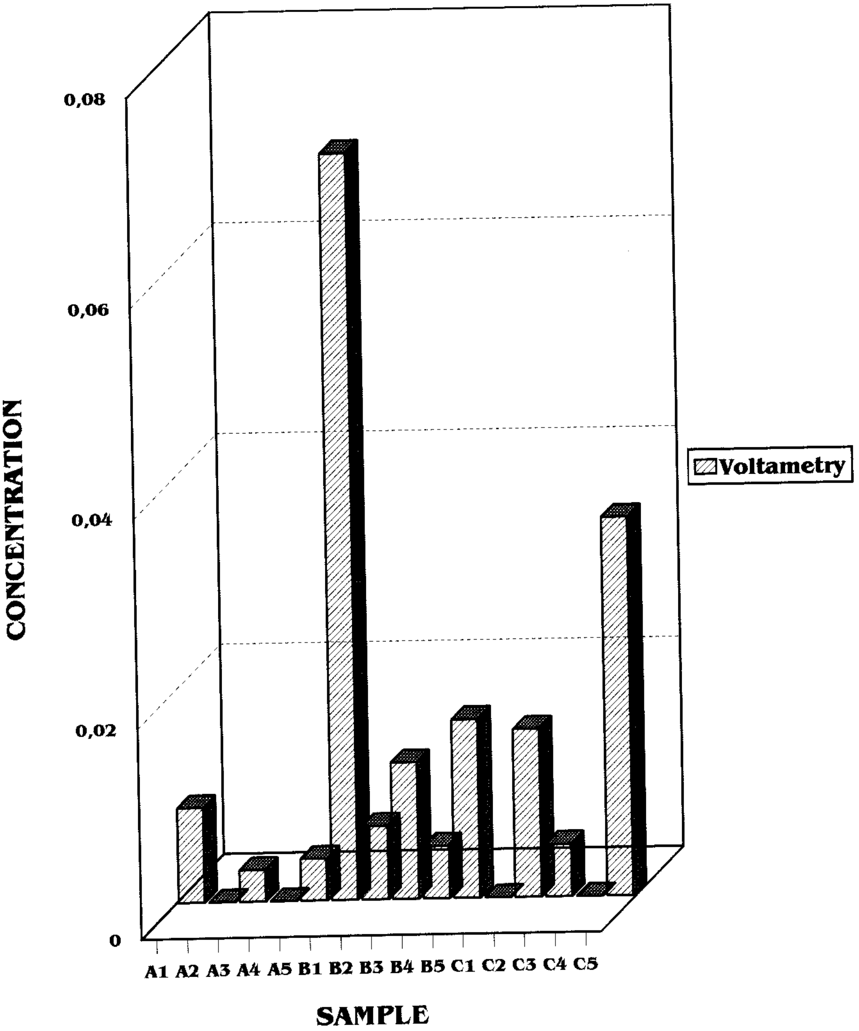

Figure 1. Cadmium concentrations (μg.L^{-1}) released by ceramic materials.

The metodology used for sample preparation takes into account the regulations and guidelines introduced by the Council of the European Economic Community. The method for testing the ceramic uses a 4% acetic acid solution to extract the toxic metals from the surface of the utensils. The experiment is made at 22 ± 2°C for 24 ± 0.5 hours. Samples were bought in different shopping centers that sell that kind of materials in A Coruña (NW Spain).

The *precision of the analytical method* was evaluated calculating the coefficients of variation of ten aliquots of a sample that were subjected to the procedure of analysis proposed. The coefficients of variation obtained were 2.99% for Cd and 1.85% for Pb.

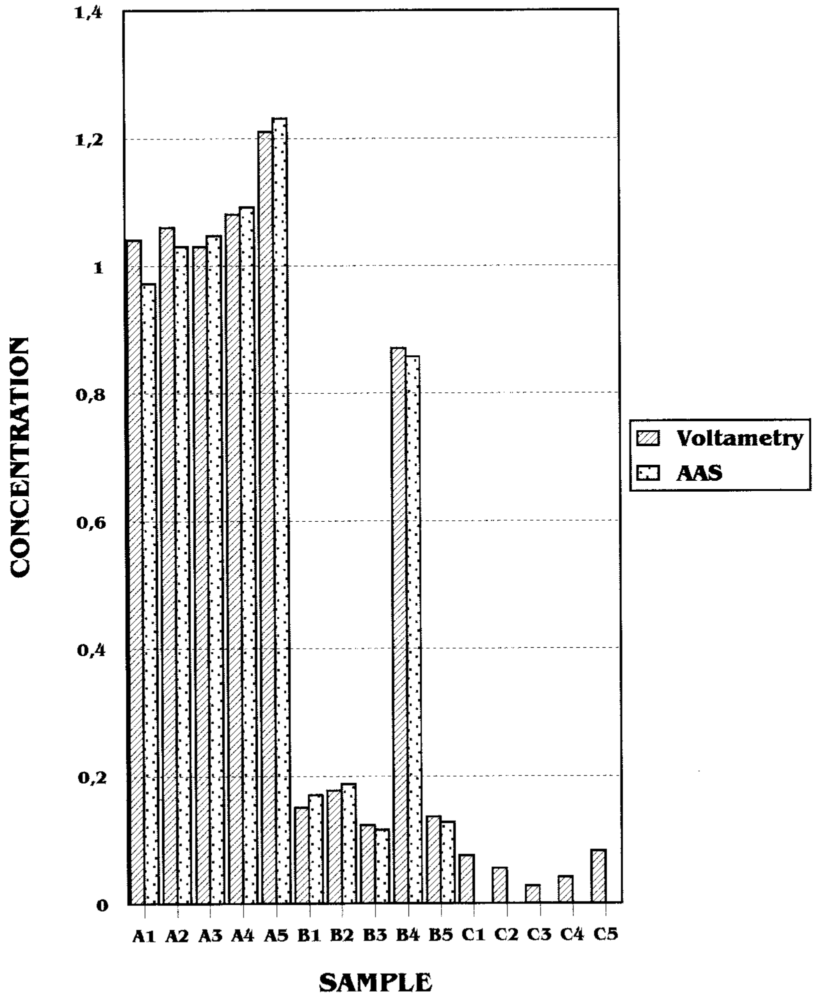

Figure 2. Lead concentrations (mg.L^{-1}) released by ceramic materials.

In order to investigate the *accuracy of the analytical method* for Cd and Pb determination, increasing quantities of a standard were added to different aliquots of the same volume of sample. We have obtained a good paralelism between the calibration and the addition curve:

Calibration curve (Cd): Signal(cm)=0.099+0.059[Cd]; r=0.999

Addition curve (Cd): Signal (cm)=0.0794+0.059[Cd]; r=0.999

Calibration curve (Pb): Signal(cm)=0.037+7.689[Pb]; r=0.999

Addition curve (Pb): Signal(cm)=-1.25.10^{-3}+7.337[Pb]; r=0.999

The *sensitivity of the method* was evaluated using the detection and quantification limits. TABLE 2 shows the obtained values.

Table 2. Limits of Detection (L.O.D.) and Quantification (L.O.C.) for Cadmium and Lead.

Metal	**L.O.D. (µg.L^{-1})**	**L.O.C. (µg.L^{-1})**
Cadmium	0.026	0.082
Lead	0.052	0.163

RESULTS AND DISCUSSION

The contact of some ceramic materials with food needs a complete absence of soluble heavy metals. A Directive of the Council of the EEC indicates the limits for Pb and Cd leaching, under specified conditions, from ceramic articles which are of 1.5 mg.L^{-1} for Pb and 0.1 mg.L^{-1} for Cd (European Economic Community 1984).

FIGURE 1 shows Cd concentrations in the samples, making the determinations by voltametry. Contents are lower than 0.02 µg.L^{-1}, except for samples C_5 and B_1 with 0.636 and 0.071 µg.L^{-1}, respectively. None of the samples reach the top level indicated by the legislation. A comparison with AAS was no possible because it was not possible to reach such low concentration levels.

FIGURE 2 shows Pb contents in the samples, being between 0.027 mg.L^{-1} and 1.21 mg.L^{-1}. None of the samples reach the limit indicated by the legislation. Results obtained are smaller than those found in the bibliography (Blanco, López and Rebollo 1986; Santos, Cirugeda, Cirugeda and Ancho 1988; Derache 1990). A comparison with AAS was no possible in samples C_1, C_2, C_3, C_4, and C_5 because it was not possible to reach such low concentration levels.

In order to estimate the *precision of the measurement*, the coefficient of variation of ten measurements of a sample was calculated as 8.97%, the mean value 2.17 µg.L^{-1}, and the standard deviation 0.1946 for Cd, and as 1.95%, the mean value 2.7 mg.L^{-1}, and the standard deviation 0.0527 for Pb.

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