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CERAMIC FOODWARE SAFETY

Sampling, Analysis and Limits for
Lead and Cadmium Release

Report of a WHO Meeting

Geneva, 8-10 June 1976

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WHO Meeting on Ceramic Foodware Safety

Geneva, 8-10 June 1976

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This Report can be obtained from the Food Additives Unit, World Health Organization, 1211 Geneva 27, Switzerland.

1. INTRODUCTION

The problem of lead and cadmium release from ceramic foodware requires effective means of control to assure the protection of the population against possible hazards arising from the use of improperly formulated, applied and fired glazes and decorations on ceramic foodware used for the preparation, storage, or serving of food and beverages. As a secondary consideration, the varying standards from country to country over the control of the release of toxic heavy metals from glazed vitreous surfaces or applied decorations present non-tariff barriers to international trade in these commodities. Accordingly, there is a need to establish internationally accepted methods of testing ceramic foodware for lead and cadmium release and to define permitted limits for the extraction of these toxic heavy metals.

Two practical considerations make it difficult to agree on effective means of control. In the first place, all test procedures are based on the use of simulative liquids in laboratory conditions, and the correlation with extraction in actual service use is as yet very inadequate. Secondly, there is a limit to what can practicably be achieved by the ceramic manufacturing industry working within a technology using lead and cadmium in glazes and colours.

Increasing awareness of the importance of heavy metal release from ceramic foodware was shown by the attendance of 130 participants, from 25 countries around the world, at the International Conference on Ceramic Foodware Safety which met in Geneva from 12-14 November 1974.

The following resolutions were unanimously adopted by the delegates to the Conference (1):

"It is the sense of the Conference that the term "ceramic" shall include ceramics, glass, vitreous enamels, and glass ceramics.

It is unanimously: **RESOLVED**, that:

1. The Conference recognizes the need to establish limits of lead and cadmium release and internationally accepted uniform methods of analysis to deal with ceramic foodware safety.
2. The Conference recognizes the need to establish a correlation between the extraction of lead and cadmium by food from ceramic foodware and a well-defined acetic acid extraction test.
3. The Conference recognizes the need for examining the extent to which lead and cadmium extracted from ceramic foodware contributes to the provisional tolerable weekly intake (2) of these elements.
4. The Conference recognizes the need to establish an educational programme to reach the industry, "Cottage Industry", art hobby potters, and teachers, with concise information on control of lead and cadmium in ceramic foodware glazes and decorations throughout the world.
5. The Conference recognizes the competence of WHO to determine the proper organizational path to deal with the above matters."

As a result of interest shown in and the importance attached to the subject, WHO convened a Meeting on Ceramic Foodware Safety in Geneva from 8-10 June 1976 to:

- i) review and recommend technical procedures for sampling, extraction and analysis of lead and cadmium released from ceramic foodware;
- and
- ii) establish limits of extracted lead and cadmium to protect the health of the consumer.

In addition, the meeting was to consider the further research needed to correlate the lead and cadmium absorbed by food substances from ceramics and its contribution to the body burden of lead and cadmium, with consideration being given to the variations in diets.

2. GENERAL CONSIDERATIONS

Although instances of acute lead intoxication due to glazed pottery have occurred, acute intoxication due to the absorption of lead and cadmium from ceramics does not constitute a widely spread world health problem. However, lower level, chronic exposure to lead and cadmium, may constitute a more general health hazard.

The problems of lead and cadmium release from ceramic foodware applies to dinnerware articles used for the serving or storage of foods and beverages as well as to articles used for the cooking and for storage of food. This problem has been known and investigated for at least fifteen years. In spite of the increased knowledge and awareness in this area, there remains an imperative need for education, surveillance and regulatory enforcement on a world-wide basis.

2.1 Different types of ceramic foodware

While the report refers to ceramic foodware, which is defined as including glazed pottery, vitreous enamelware and glass, it must be recognized that there are differences between these three types of utensils in terms of manufacturing technology, usage and the nature and magnitude of the potential health hazard. The Meeting was aware that the most important problem is improperly glazed pottery and that awareness has greatly influenced its discussions. The control of extractable metals in vitreous enamelware and glass is, in the light of available evidence, not as urgent or important and some countries may not wish to accord the same priority to their control as that for glazed pottery. However, if such controls are introduced at the same time, it is recommended that the testing and limits should be the same. Looking to the future, the possibility should be considered that further discussion or new evidence may point to the advisability of introducing some differences in the control details for the different materials, such as limits for another metal, reducing limits further on grounds of differences in usage or because there are no valid technical reasons for not doing so, etc.

Unglazed pottery presents a different problem due to the fact that it can permit the growth of pathogenic bacteria which potentially may constitute a more serious health hazard than that resulting from possible exposure to lead and cadmium. Thus the glazing of pottery does in practice confer a beneficial health effect in terms of better hygiene.

The report deals with utensils used in the home or eating establishments for the preparation, consumption and storage of food and beverages. It does not deal with articles used in food manufacturing industry or those in which food is sold. While it is desirable that such articles comply with extraction limits, no less strict than those for similar articles used in the home or in eating establishments, stricter hygienic standards may have to apply, such as statutory limits for contaminants in food for sale (it must be stressed that compliance with the extraction limits recommended in this report is not an alternative to compliance with such statutory limits for food).

2.2 Metals to be controlled

The Meeting agreed that there is need to control the release of lead and cadmium from ceramic foodware. The mechanisms of their release and their biological effects are outlined in Sections 3 and 4 respectively. The Meeting was aware of the fact that other metals are used in making glazes and can be extracted and that some of these metals are essential elements. However, on the evidence available at the present, including the consideration, there appears to be no need to control any other metals.

Furthermore, it was considered that introducing controls for these other metals is not only unnecessary from the health point of view, but it could actually be detrimental in dissipating effort and resources that would be much more usefully employed in controlling lead and cadmium.

2.3 Implementation of control measures

As regards the implementation of the recommended controls, which are intended to be applicable throughout the world, the meeting had to take into account the fact that local conditions and the systems that could be used to implement these controls can differ. For example, some countries would implement the controls at the manufacturing and importation stage, others at the retail sale stage. Still others could employ a combination of both.

2.4 Additional recommended measures

The Meeting felt that the control measures it recommended would deal with the situation in normal commercial sale of goods manufactured on both large and small scale. These measures would not, however, in themselves effectively control the hazard in certain other areas such as pottery as a hobby and "cottage industry". In these areas, the problem is more serious where raw lead or cadmium compounds are used in glazing (as against fritted materials) or when low firing temperatures are used, and the hazard is particularly serious when such ceramics are used for cooking or for storage of acidic beverages, such as wine or fruit juices.

It was considered that education and publicity, of the right kind and in the right quarters, is necessary to deal with these special problems, as well as certain forms of practical assistance such as providing advice and arranging for a supply of safe glazes. Before this can be done, it may be necessary to investigate the nature and extent of the problem, bearing in mind the possibility that this could vary considerably from district to district.

3. MECHANISMS OF LEAD AND CADMIUM RELEASE

It is well known that ceramic glazes may release lead and cadmium. However, the release mechanisms have been the subject of considerable research over the years. As far as lead is concerned, the release is a function of the stability of the silicate network in an acid medium. The stability is determined by the chemical constituents of the glaze, by the presence of network modifiers and by the temperature and acidity of the leaching solution.

As far as cadmium bearing glazes are concerned, the element is present in the two phases of the glaze, i.e. in the crystalline phase and the glassy phase. The crystalline phase is composed of cadmium sulfide or cadmium sulfoselenide. The glassy phase contains, in addition to the basic constituents, both lead and cadmium. Studies to date suggest that the release from the crystalline phase is dependant on the pH of the leaching solution, the light conditions in which the leaching is carried out, and the availability of oxygen in the leaching solution. Release of cadmium from the glassy phase is believed to be by mechanisms similar to that for lead. The mechanisms of lead and cadmium release are considered in greater detail in Annex I.

4. BIOLOGICAL EFFECTS OF LEAD AND CADMIUM

Excessive exposure to lead and cadmium can produce toxic effects. However, low levels of intake of lead and cadmium can be tolerated without adverse health effects. In arriving at what constitutes a tolerable intake, it is necessary to consider all sources of environmental exposures: air, water and food. The contribution of lead and cadmium from glazed ceramic ware is incremental to these environmental sources. More detailed discussion on lead and cadmium toxicity is described in Annex II.

5. DEFINITIONS AND SAMPLING

5.1 Definitions

In recommending the extraction limits, consideration was given to the way in which the differences in shape and use of the ceramic ware affect the potential hazard. For example, the term "flatware" is not used in its usual sense of including all plates, but is restricted to those that do not exceed 25 mm in internal height, thus in effect applying stricter limits to deeper plates such as soup plates and dessert plates. Other examples are the stricter limits for storage vessels (large hollow ware) and articles specifically designed for infants. The definitions of the different categories of ceramic ware are listed below:

Dinnerware: ceramic flatware and hollow ware used in the preparation, serving or storage of foods other than cookware.

Flatware: flatware consists of ceramic articles which have an internal depth, as measured from the lowest point to the horizontal plane passing through the upper rim, that does not exceed 25 mm.

Hollow ware: ceramic articles having an internal depth, as measured from the lowest point to the horizontal plane passing through the upper rim, greater than 25 mm.

Small hollow ware: hollow ware with a capacity less than 1.1 litre.

Large hollow ware: hollow ware with a capacity of 1.1 litre or more.

Items specifically designed for infant use: ceramic articles used for serving infant foods.

Cookware: glazed articles specifically intended to be heated by means such as steaming, boiling, braising, stewing, roasting or baking, in the course of the preparation of food or beverages. Examples of such articles are casseroles, bakers, roasters, souffles, percolators, slow cookers and saucepans.

5.2 Criteria for sampling

- 1) Dinnerware (includes flatware, small hollow ware, large hollow ware and items intended for infant use)

In selecting samples of dinnerware for determination of the lead and cadmium release rates, the following criteria should be employed:

The category posing the highest health risk to the consumer should be given priority. For example, in a set of dinnerware, hollow ware such as bowls, should be used for testing of lead and cadmium release rates.

Within each category of dinnerware selected for testing, the articles having the highest surface area/volume ratio in contact with foods shall be selected. Thus, the smallest bowl would be tested in preference to the largest. Further, the most highly coloured or decorated article within each category of dinnerware should be selected for testing.

- 2) Cookware

In selecting samples of cookware, the same criteria as for sampling dinnerware apply, except that cookware having a highly coloured interior (base and/or lid) should be given preference.

5.3 Sample size

- 1) Dinnerware

It is desirable to develop a system of control that is regarded as appropriate to its circumstances. Thus, when the consignment is large, it is recommended that six pieces from each lot be tested. Each of the six pieces should be identical in size, shape, colour and decoration. If the consignment is small, fewer pieces may be selected for testing.

- 2) Cookware

The size of sample selected for testing should be the same as for dinnerware (see above).

6. METHOD OF ANALYSIS

6.1 Preparation of test solution

A. Dinnerware (includes flatware, hollow ware and items intended for infant use)

1) Simulating solvent

- (a) Nature: the simulating solvent to be used in the extraction of lead and cadmium from ceramic articles used as food containers is a 4% by volume acetic acid solution.
- (b) Preparation of the solution: the 4% by volume acetic acid solution is obtained by adding 40 ml of glacial acetic acid to 960 ml of distilled water or water of equivalent quality. The solution should be freshly prepared from glacial acetic acid which has been stored in darkness.

2) Preparation of the samples

The sample must be clean and free from grease or other matter likely to affect the test.

The sample is accordingly washed at a temperature of about 40°C with a solution obtained from a liquid detergent.

The sample thus washed is first of all rinsed in tapwater and then in distilled water or water of equivalent quality.

It is then drained and dried either in a drying oven or by means of a new filter paper so as to avoid any stain.

After being cleansed in this way, the sample must be so handled that the surface to be tested does not come into contact with the hands of the person carrying out the test.

3) Filling

The level of the liquid must be within 5 mm from the overflow point as measured along the surface of the article.

4) Lighting

After being prepared in the manner described in Section 2, the sample is placed on a flat horizontal surface, filled as laid down in Section 3 with a 4% by volume acetic acid solution prepared as described in Section 1(b).

The lighting conditions during the test shall be as follows:

- (a) Lead extraction: when only the extractability of lead is tested, the article shall be covered with an appropriate means of protection and exposed to the usual conditions of illumination in a laboratory.
- (b) Lead and/or cadmium extraction: when the extractability of lead and/or cadmium is tested, the article shall be covered with a watch glass of a quality normally employed in chemical analysis laboratories and exposed to the following conditions of illumination for the full test period:

the room shall be illuminated solely with fluorescent lamps with a nominal colour temperature of 3 800 to 4 300°K. These lamps will have to be placed at a height of some 1.5m above the bench so as to give uniform illumination of approximately $1\ 000 \pm 10\%$ lux (3).

5) Temperature

An ambient temperature of $22 \pm 2^\circ\text{C}$ shall be maintained in the place where the test is being carried out.

6) Duration

The duration of the test will be 24 hours \pm 10 minutes, in the conditions set out in Section 4 (a) or (b), according to the type of test carried out.

B. Cookware

1) Simulating solvent

(a) Nature: the simulating solvent to be used in the extraction of lead and cadmium from ceramic articles used as cookware is a 4% by volume acetic acid solution.

2) Measurement of the effective internal volume

The ware shall be sufficiently clean (see 3) to ensure that a correct assessment of the effective internal volume can be made. In general the total internal volume shall be taken as being the effective internal volume. Where the vessel is supplied with a lid, e.g. casseroles, the effective internal volume shall be taken as the volume up to the plane on which the lid rests. The article is filled with water to the limit of the effective capacity, and the volume recorded as being the effective internal volume.

3) Preparation of the samples

The sample must be clean and free from grease or other matter likely to affect the test.

The sample is accordingly washed at a temperature of about 40°C with a solution obtained from a liquid detergent.

The sample thus washed is first of all rinsed in tapwater and then in distilled water or water of equivalent quality.

It is then drained and dried either in a drying oven or by means of a new filter paper so as to avoid any stain.

After being cleansed in this way, the sample must be so handled that the surface to be tested does not come into contact with the hands of the person carrying out the test.

The vessel is pre-heated to as close to 100°C as practical. It is then filled to two-thirds of its effective volume with boiling distilled water. The volume of glacial acetic acid necessary to result in a 4% v/v solution is added to the boiling water. The vessel will then be covered, using its own lid if

appropriate, in order to minimise evaporation. It should then be placed in contact with the source of heat and maintained at a temperature to ensure continuous but gentle boiling for two hours. In cases where significant evaporation occurs, more acetic acid (4% v/v) shall be added in order to ensure that the area of contact is not appreciably diminished. It shall then be removed from the source of heat and allowed to stand for a further 22 hours \pm 10 minutes, at room temperature, making a total time of 24 hours in contact with the acid.

The source of heat may be either an electric oven (preferably with fan-assisted circulation) or a heated liquid bath (such as glycerine). Where a liquid bath is used, the vessel will be immersed so that the acid test solution is approximately level with the bath liquid. It must be noted that the bath method can result in a greater refluxing and might be called for where such refluxing is desirable to test the lid. In the case of articles with a built-in source of heat (for example, slow cookers), that source of heat should be used.

The volume of the liquid remaining in the article after 24 hours shall be measured, and a sufficient acetic acid (4% v/v) shall be added to restore it to two-thirds of the effective internal volume. The measurement of the concentration of lead and cadmium shall be made on this restored volume.

If the article cracks or leaks during the test, the test shall be recommenced on a second sample. If the second sample leaks the outer surface of a third sample shall be sealed by coating with a suitable sealant, and the test again recommenced. Such a sealant is a silicone sealant diluted, before application, with toluene.

Recommended reference method of analysis

1. Sampling of the test solution for analysis

Prior to sampling of the test solution to determine the lead and/or cadmium concentration, the contents of the ceramic article to be tested are homogenized by an appropriate method for obviating any loss of solution and any abrasion of the surface of the article to be tested.

2. Method of analysis

The quantity of the lead and/or cadmium extracted by the solvent during the test is determined by the atomic absorption method with the aid of a flame spectrophotometer, the instrument having a sensitivity of at least one-tenth of the lowest limit fixed for the elements to be determined. This sensitivity is defined as the concentration of elements which gives rise to an absorption of 1%.

The determinations must be carried out in correspondence with the linear part of the instrument's calibration curve plotted by means of reference solutions. In the case of the concentrations of lead and/or cadmium in the test solution which lie outside the linear part of the calibration curve, prior dilution with 4% by volume acetic acid will have to be carried out in order to work with a concentration corresponding to the linear part of the calibration curve.

In order to plot the calibration curve, the reference solutions to be employed will have to be prepared prior to each calibration using concentrated stock solutions (at least 1 000 ppm for lead and 100 ppm for cadmium) which are diluted with freshly prepared 4% by volume acetic acid.

Prior to any calibration or analysis, a blank determination is carried out on a sample of 4% by volume freshly prepared acetic acid in order to take into consideration any quantities of lead and/or cadmium present in the glacial acetic acid and/or the water employed.

Other techniques may be used such as dithiozone or polarographic analysis.

The analysis of the solution should take place if possible within 8 hours of the end of the leaching period. This is because of a risk of significant absorption of lead and cadmium onto the walls of the storage container, particularly when they are present in low concentrations.

7. RECOMMENDED LIMITS OF RELEASE

After reviewing the current information on this subject, the Meeting agreed to recommend the following limits for the different types of ceramic articles. These articles should be tested according to the procedure in Section 6, "Methods of Analysis":

	<u>Lead (mg/l)</u>	<u>Cadmium (mg/l)</u>
Dinnerware		
Flatware	7.0	0.7
Small hollow ware	5.0	0.5
Large hollow ware	2.5	0.25
Items specifically designed for infants	2.5	0.25
Cookware	5.0	0.5

In recommending the limits set above, the Meeting wished to point out the following:

- (1) Because flatware should constitute a minimum source of lead burden from ceramic articles, limits for flatware (lead and cadmium) refer to the value obtained when the individual value of the piece tested are averaged.
- (2) All other limits are expressed in absolute maximum values, in that no individual unit comprising a sample may exceed these levels.
- (3) The limits for cookware are considered as provisional, since analytical data are lacking to support another figure. The Committee noted that additional data are required in order to better relate results to actual usage.

8. EDUCATION

Sufficient technology currently exists so as to enable the production of ceramic ware which will meet the recommended limits for released lead and cadmium. A great deal of this know-how has been published. Particularly useful documents are the International Lead Zinc Research Organization, Inc. Manual No. 1 - Lead Glazes for Dinnerware and the Proceedings of the International Conference on Ceramic Foodware Safety, 12-14 November 1974. These materials can be made available to all ceramics manufacturers throughout the world.

The smaller scale "cottage industries", and amateurs, present a unique problem in that they are generally not as well informed with respect to the proper technology to

prevent excessive lead or cadmium release. The meeting was informed that work was currently being done to produce easily readable and illustrated literature for distribution throughout the world.

The potential hazard of improperly glazed ceramic ware should be brought to the attention of publishers of books for hobby potters. Their attention should be drawn to the problems which may result from experimentation with glazes to be applied to potential food contact articles with the request that future editions be revised accordingly.

9. RECOMMENDATIONS

1. WHO should promote the adoption of the sampling methods, testing techniques, and limit values contained in this respect for the purpose of protecting health and harmonizing the regulations of all countries with respect to lead and cadmium release into foods from ceramic articles. National regulatory agencies should therefore institute effective programmes to implement the limits of release of lead and cadmium from ceramic foodware. Manufacturers should also be encouraged to establish effective quality control procedures to ensure the safety of their products prior to distribution for sale.

2. It is recommended that a series of educational materials be prepared and made generally available, explaining in a concise, simple manner the problem of lead release and the means of control. It is recognized that this material might be presented for audiences of varying skills and technical competence. Therefore, two levels of educational material should be developed: one of them relating to up-to-date information on the latest sophisticated technological advances in the control of lead and cadmium release from high-quality ceramic ware; the other for distribution to the "cottage industry" and the hobby potter in an easy-to-understand picture booklet, providing the rudiments of producing ceramic foodware with low levels of lead and cadmium release.

3. It is recommended that research be initiated or continued in the following priority areas:

- (a) development of a room-temperature procedure and limits adequately representing the extraction of lead and cadmium from cookware which are intended for use at high temperatures;
- (b) effects of light on cadmium release from ceramic foodware into food and simulated solvents;
- (c) development of simple screening tests for lead and cadmium release from ceramic foodware for use by "cottage industries", hobby potters and the like. The procedure would have to be available in kit form and should be easily used by non-scientifically oriented individuals;
- (d) determination of the most favourable conditions of composition and manufacturing techniques for stabilizing lead and cadmium in the structure of ceramic foodware for minimizing their release;
- (e) determination of the relationship between lead and cadmium uptake by food substances compared to the uptake by the solutions used in the recommended extraction methods;
- (f) the determination of the effect of factors encountered in service conditions, such as abrasion and detergent action, on the rate of extraction.

4. It is recommended that a future WHO meeting on ceramic foodware safety be convened, preferably in 1979, to consider:

- (a) educational materials intended to improve the quality of ceramic foodware, thereby reducing health hazards;
- (b) new test methods such as cookware tests at room temperature and simple screening tests, refined extraction of cadmium sulfide and more elaborate sampling and statistical methods.

REFERENCES

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2. WHO Technical Report Series, No. 505, 1972 (16th Report of the Joint FAO/WHO Expert Committee on Food Additives - Evaluation of Certain Food Additives and Contaminants Mercury, Lead and Cadmium)
3. HALPIN, M.K. et al. Report Ac# AC/MI/11/75, 1975. Institute for Industrial Research and Standards, Dublin, Ireland

ANNEX I

MECHANISMS OF LEAD AND CADMIUM RELEASE

The mechanisms for lead and cadmium release from certain types of ceramic foodware were described in the Proceedings of the International Conference on Ceramic Foodware Safety(1) as well as in the Report of the Institute for Industrial Research and Standards, Dublin, Ireland, by Halpin, M.K. et al.(2).

Lead migration

One of the important factors for the lead release from a glaze is the chemical composition of the glaze. With a properly designed colourless glaze, i.e. a glaze with a proper ratio of acidic to alkaline components, it is found that a typical hotel china glaze (cone 5) contains:

0.066 K ₂ O		
0.179 Na ₂ O	0.340 Al ₂ O ₃	
0.261 PbO	0.314 B ₂ O ₃	3.369 SiO ₂
0.494 CaO		

With this formula, the release of lead into an acetic acid test solution is a fraction of a part per million, i.e. very low compared to the limits generally accepted.

However, this picture may be disturbed by modification of the glaze composition. For instance, if for the purpose of colouring, a few weight per cent. of copper oxide are added, the lead release is considerably increased. On the contrary, the addition of acidic components, such as oxides of tin, zirconium and titanium (often used as opacifying oxides) has no adverse effect on the lead stability of glazes.

Certain low melting lead oxide glazes, i.e. glazes with a high ratio of lead oxide to acidic oxides, are especially sensitive to addition of alkali, for instance oxides of sodium, potassium and lithium. In this case, the lead release is found to increase with increasing radius of the modifying alkali ion.

Other factors affecting the lead release from glazes are the thickness of the glaze and the temperature and duration of the firing. Generally speaking, the thinner the glaze layer, the higher the firing temperature and the longer the duration of the firing, the greater is the probability of a low lead release. In addition, the atmosphere of the kiln is also of considerable importance.

A closer study of the very mechanism of interaction between a ceramic surface and the test solution has been made in the case of bulk glasses. Regarding the glass as basically a three-dimensional silicon dioxide network, to which a certain amount of modifying alkaline oxide (for instance lead oxide) is added, the mechanism of interaction with a test solution can be described as follows:

The process of lead leaching by acidic solutions implies that Pb-O-bonds are broken so that lead ions are set free and substituted by OH-ions in the network. If this lead leaching leaves a relatively undistorted silicon dioxide network, the dissolution of lead rapidly decreases with time. However, the leaching of lead from the surface layer results in a distorted network. The release will continue to a considerable extent, arising from deeper layers of the network. Therefore, one would expect the addition of modifying alkali oxides to the glass will decrease the stability of lead due to a weaker bonding within the distorted silicon dioxide network.

The most salient conclusion is that lead release from the glasses falls to low levels when the amount of modifying ions is less than about 0.7 mole per mole of silicon dioxide. This conclusion, if applicable to other glass systems more complex than the simple alkali-lead-silicate glasses studied, could prove to be valuable in the compounding of acid resistant lead glazes and glasses.

Cadmium migration

The history of cadmium pigments goes back to the last century. In Bohemia where the pigments were particularly admired, the brilliant cadmium yellow was described as "Kaiser yellow". Pure cadmium sulfide glasses are yellow, however, if increasing proportions of selenium are added to the glaze the colour changes from yellow to orange and finally to a brilliant red. As far as the designer of pottery decoration is concerned, the cadmium colours are important as they offer a range of colour which has considerable appeal in the market place.

The formation of the colour takes place on cooling the glass when cadmium sulfide or sulfo-selenide crystals precipitate out of the glass melt. X-ray diffraction studies have shown that the colour depends only on the chemical composition of the particular sulfo-selenide crystals and is independent of the size of the crystals. On the surface, therefore, of a cadmium glaze there are two phases present: (a) a glassy phase which in addition to other basic constituents contains lead and a small amount of cadmium, and (b) a crystalline phase of cadmium sulfide or cadmium sulfo-selenide. The results available in the literature suggest that the crystalline phase is liable to photo-oxidize to a soluble sulfate during test and in use.

In the leaching of the cadmium from glazes, it has been shown that the amount of cadmium released in the test with acetic acid is dependent on the intensity of the light, the duration of light during the test and the availability of oxygen in the test solution. Depending on these factors leaching carried out in light may yield many times the amount of cadmium compared with a test carried out in darkness. The release of lead is not affected by the light conditions during the test.

The present understanding is that if a leaching is carried out in darkness, cadmium and lead are released from the glassy phase. If a test is carried out in the light there will be not only release from the glassy phase but also release from the crystalline phase due to a photo-oxidation. The amount of cadmium released from the crystalline phase will be dependent on the light sensitivity of the colour. In the few years since the discovery of the effect, many relatively non-light sensitive colours have come onto the market.

As regards the release of cadmium from the crystalline phase in normal use, Halpin et al. have shown the release is affected by the presence or absence of oxidants or antioxidants in the beverage or other leaching medium. Significantly, however, it has been shown that even tap water can leach considerable quantities of cadmium from the sulfide phase of the glaze.

A test for cadmium in light therefore has certain advantages as it monitors the release from the crystalline phase and it monitors the light sensitivity of this phase.

Factors affecting lead and cadmium release into food

When considering the release of lead and cadmium into food, certain situations are of special interest because they are liable to give rise to a considerable potential intake of lead and/or cadmium:

1. The use of ceramic objects for cooking, serving and storage of beverages, liable to be consumed in greater amounts than foods.

2. Contact between ceramic foodware and food under extreme conditions:

- (a) exposure to food of a high temperature;
- (b) exposure to food of acidic foods;
- (c) storage of food for long periods.

Of these situations, it is the storage and subsequent intake of (acidic) beverages that has given rise to most of the known cases of acute lead poisoning from ceramic articles (3). However, the less extreme yet continuous exposure due to other types of contact between food/beverages and ceramic foodware should also be taken into consideration when attempting to control lead and cadmium release from ceramic objects into food.

General remarks on test solution compared to food acid attack mechanism

When the quality of ceramic foodware with regard to lead and cadmium release is assessed, an ideal test method would be to measure the release of lead and cadmium into all kinds of foods under normal use conditions.

However, taking into consideration the vast amount of different articles being produced, the great variety of foods potentially brought into contact with them, and the analytical difficulties, such a test is practically impossible. Consequently, it has become a common practice in many countries to use a simulating solution, generally 4% acetic acid, for the test procedure. This enables the test and analysis to be relatively simple and fast, thus making possible the testing of a great number of samples, both at the production level and in public control. It also gives a basis for comparison of the quality of the objects in relation to each other. However, it must be admitted that the extrapolation of such results to an estimate of heavy metal release - and intake - by contact with food is a difficult task and that the information obtained until now in this field is very limited.

In fact, as the fitness of ceramic ware for food use is decided by regarding the release of lead and cadmium by a test using a simulating solvent, it is mandatory for a precise estimation of the potential intake of lead and cadmium by practical use - and thus the importance to health - to know the link between release by the test and release during practical use. As for information available in the literature in this field, the situation is summarized in a report by Engberg and Bro-Rasmussen (4). Here, an attempt is made to compare the release of lead and cadmium from ceramic foodware into a test solution to the release into food under normal use conditions. Further, it has attempted to assess the potential weekly intake of lead and cadmium from this source, compared to the recommendations of FAO/WHO (5). However, more experimental work is clearly desirable in this field.

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ANNEX II

A. BIOLOGICAL EFFECTS OF LEAD

Exposure

Lead is an ubiquitous element in the biosphere. Therefore it will be present in the human body with the body burden depending on the level of environmental exposure.

In rural areas levels of lead in air are about $0.1 \mu\text{g}/\text{m}^3$ and in cities $1-3 \mu\text{g}/\text{m}^3$. Tobacco smoking may contribute to inhalation of lead. Estimates for absorption range from 25% to 50% of inhaled lead.

The lead concentration in municipal water is at the level of less than $0.01 \text{ mg}/\text{l}$. The WHO International Standards for Drinking Water suggest a tentative limit for lead of $0.1 \text{ mg}/\text{l}$ (1)(3). Assuming a daily consumption of 2.5 litres the maximum lead intake will be $250 \mu\text{g}$ per day.

Results of determination of lead in total diet indicate a daily intake of 200-300 μg per day. It is necessary to point out that approximately 10% of ingested lead will be absorbed.

Metabolism

Absorbed lead is transported primarily on the surface of the red blood cells and is distributed throughout the body. An equilibrium can be established between lead absorption and urinary excretion. Above a critical intake level, positive lead balance will appear. As an osteotropic element, lead will be stored in the skeleton. The total body burden of an adult is estimated to be 100-400 mg (about 95% in bones).

Recently mobilization of lead by chelating agents, as Ca EDTA has been used clinically for evaluation of lead body burden. In adults under normal lead exposure the blood lead level is less than $40 \mu\text{g}/100 \text{ ml}$ of whole blood.

Most of the ingested lead is excreted in the faeces which usually contain 0.22-0.25 mg lead per day. A very small amount is excreted in sweat. Urinary lead excretion is less than $0.1 \text{ mg}/\text{l}$.

Toxic effects

A sufficiently high exposure to lead will inhibit heme synthesis that is incorporation of iron into heme as well as inhibition of the porphyrin biosynthesis. As a consequence, the activity of ALA-dehydratase in the erythrocytes will be decreased, excretion of d-aminolaevulinic acid, coproporphyrin, uroporphyrin and porphobilinogen in urine will be increased; erythrocyte coproporphyrin, protoporphyrin and non-haemoglobin iron store will be increased.

Lead may cause haematologic changes such as an increase in the number of basophilic stippled cells and reticulocytes. Chronic exposure to higher levels of lead may cause anaemia, involving reduced haemoglobin, as well as the actual number of erythrocytes. Recently, an increase in urinary excretion of hydroxy-indolacetic acid was reported.

Renal damage, especially in children, due to chronic plumbism has been reported in some countries.

Exposure to higher concentrations of lead could produce acute poisoning, which is manifested in three main forms:

- (1) Abdominal colic and constipation represents the most frequent form;

- (2) Peripheral Neuropathy is in the second place by frequency. It is characterized by a motor involvement, particularly the extensor muscles of the hands, rarely of the feet. Sometimes neuropathy is combined with abdominal colic;
- (3) Lead encephalopathy is rarely observed in adults exposed to inorganic lead, but is more often seen in children. Signs include vomiting, irritability, drowsiness, stupor or coma. These symptoms can be followed by more serious sequelae: convulsive or behavioural disturbances, psychomotor impairments, learning difficulties, etc.

Although high lead intake has been reported to produce cardiovascular, carcinogenic, teratogenic and chromosomal aberrations, other reports have not confirmed such findings.

"Tolerable intake"

The Joint FAO/WHO Expert Committee (1)(3) recommended in 1972 a Provisional Tolerable Weekly Intake of lead of 3 mg per person equivalent to 0.05 mg/kg body weight. This level does not apply to infants and children. Any increase in the amount of lead derived from any one source (air, water, food) will reduce the amount acceptable for other sources.

B. BIOLOGICAL EFFECTS OF CADMIUM

Cadmium is a metal with an extremely long biological half-life in man. Even low exposure levels may cause in time considerable accumulation, especially in the kidneys.

Exposure

Food is the main source of cadmium intake. Daily intakes appear to be between 10-50 μg in some European countries and the United States of America, whereas in Japan the intake is higher. Cadmium may arise from various food containers such as cadmium-plated utensils and ceramic foodware.

The cadmium intake from water is low. The tentative limit set in the WHO International Standards for Drinking Water is 10 $\mu\text{g}/\text{litre}$ (2)(3). However, most municipal water supplies contain less than 1 $\mu\text{g}/\text{litre}$ and higher values may be due to contamination either from industrial sources and piping which may release cadmium. In Sweden, even near cadmium-emitting industries, cadmium content of drinking-water was not more than 1 $\mu\text{g}/\text{litre}$. Similar results have been obtained in Japan. The daily intake from water will usually contribute less than 5 μg .

Cadmium in water can influence levels in food: crustacea and shellfish from contaminated estuaries, and cereals irrigated with water containing cadmium may exhibit elevated levels of this contaminant. High levels of cadmium may also be found in certain target organs, such as the liver and kidneys of mammals.

The intake from inhaled air is low because the cadmium concentration is usually below 0.01 $\mu\text{g}/\text{m}^3$. However, areas close to cadmium-emitting industries have significantly higher levels.

Smoking may also contribute to intake. It has been estimated that the smoking of 20 cigarettes per day may cause the inhalation of 2-4 μg of cadmium. Assuming an absorption of 25%, this would add 0.5-1 μg per day to the body burden.

Metabolism

Less than 10% of cadmium ingested is absorbed. On the other hand, the body's uptake of inhaled cadmium depends on the particle size and solubility and on the pulmonary efficiency of the individual concerned. Respirable particles will be mainly deposited in the lower respiratory tract and may be absorbed to a high degree. With cadmium fumes the proportion may be 25%-50% and cadmium inhaled by cigarette smoke may similarly be absorbed to about 50%. With dusts, the evidence suggests the proportion may be somewhat lower particularly if they contain a high proportion of insoluble salts such as cadmium sulfide. Thus the main source of human body burden of cadmium is food.

Inside the body the cadmium at first circulates mainly in the plasma and accumulates primarily in the liver. The kidney is the target organ for cadmium, and after its initial accumulation in the liver it is transported, mainly in the erythrocytes to the kidney where it accumulates principally in the cortical tissue.

The low molecular weight protein metallothionein, and probably other similar low molecular weight proteins, has an important function in binding the cadmium and is believed to play a major part in its transport to the body. Metallothionein is produced in the liver and has a great avidity for certain metals including cadmium and may serve as a detoxification mechanism. Exposure to cadmium stimulates the production of metallothionein, a response which apparently limits manifestations of cadmium toxicity.

The urinary excretion of cadmium approximates 1-2 μg per day. The capacity of the healthy kidney to excrete cadmium is limited and any excessive intake will result in an increased body burden and in particular an increase in cadmium in the renal cortical tissue.

The body burden of cadmium in the adult is estimated to be 10 to 30 milligrams, there being a gradual accumulation with age to a maximum in middle life and possibly a slight decrease in the later years. Some 50% to 75% of this quantity is contained in the liver and kidneys, apparently in association with metallothionein. The renal concentration of cadmium is about 40 to 50 ppm, about one quarter the level at which renal damage is held likely to occur, viz. 200 ppm.

The slow excretion results in an extremely long biological half-life. Calculations have shown that assuming 0.005% of the total body burden is excreted daily, the biological half-life in the human body will be about 33 years, and assuming a daily excretion of 0.01% the half-life would be about 18 years. These figures agree with estimates of 10-30 years of other workers.

Toxic effects

1. Cadmium-related proteinuria and nephropathy

Prolonged exposure to cadmium gave rise to renal damage. The damage is manifest as a tubular proteinuria, the excessive accumulation of cadmium in the renal cortex leading to a decreased reabsorption of proteins in the proximal renal tubules and an increased excretion of low molecular weight proteins in the urine. At a later stage there may be glycosuria and aminoaciduria. The appearance of the proteinuria is accompanied by an increase in cadmium excretion in the urine and a decrease in the cortical cadmium content, and ultimately in the body burden of cadmium. Thus in cases with severe renal damage cortical cadmium concentrations well below 100 $\mu\text{g/g}$ are found, whereas in cases without proteinuria and no morphological kidney changes, levels of 150-450 $\mu\text{g/g}$ wet weight are recorded.

2. Itai-itai disease ("ouch-ouch" disease). In 1955 Japanese observers described among elderly women a previously unknown disease characterized by lumbar pain with myalgia, spontaneous fractures, skeletal deformities, and tenderness of bones to external pressure (3). Epidemiological studies showed high concentrations of cadmium and other metals in water and food in the endemic region.

While it is clear that the clinical phenomena of itai-itai disease are not those seen in recognized industrial poisoning, it has been suggested that the disease is a manifestation of long-term cadmium exposure modified by old age, borderline nutritional status, and the stresses of multiparity. The neuromuscular and skeletal signs similar to those observed in itai-itai disease had previously been described in a series of French industrial workers poisoned by cadmium in 1942 (1). Other similar manifestations in industrial cadmium workers have also been reported. Proteinuria is invariably present in itai-itai disease, and glycosuria and aminoaciduria are also common. Furthermore, the incidence of proteinuria and glycosuria was significantly higher among older women and men in the endemic area than in an equivalent control population, and the urinary excretion of cadmium was three times greater among the affected group. The renal manifestations of cadmium-related disease in Japan are therefore observed in both sexes, while the musculoskeletal phenomena (itai-itai) appear to be confined to elderly women. The role of cadmium as an etiologic agent of itai-itai disease remains uncertain.

"Tolerable intake"

The metabolic and toxicological effects of cadmium are difficult to assess in terms of dose-response relationships and decisions must be regarded as provisional.

The Joint FAO/WHO Expert Committee on Food Additives recommended in 1972 a Provisional Tolerable Weekly Intake of 400 to 500 μg per person.

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