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COMMISSION
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Directorate-General
for Social Affairs

Health Protection
Directorate

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June 1975

STUDY ON INFORMATION ALREADY AVAILABLE IN THE LITERATURE ON FOOD CONTAMINATION CAUSED BY LEAD AND CADMIUM IN CERAMIC HOUSEHOLD CONTAINERS

PREPARED FOR
The Commission of the European Communities

by Åse Engberg and F. Bro-Rasmussen
National Food Institute,
2860 Søborg,
Denmark

This report represents the views of the authors and not necessarily those of the Commission

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REFACE

This report was prepared at the request of the Health Protection Directorate of the Directorate General for Social Affairs of the Commission of the European Communities, Luxembourg.

Among the subjects treated in this report a comparison is made between national legislations and a proposition for a proposal of directive of the Council of the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with food (limitation of extractable quantities of lead and cadmium).

In the meeting of the Division Removal of Technical Barriers of an Industrial Nature of the Directorate A - Movement of foods of the Directorate General of Industrial Market held in Brussels on 6 June 1975, the National Experts present examined the report prepared by Åse Engberg and F. Bro-Rasmussen: "Study on information already available in the literature on food contamination caused by lead and cadmium in ceramic household containers".

The Experts recommended that this document be circulated to National Representatives and other bodies and organizations interested.

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of 6 June 1975 in Brussels

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N O T I C E

In the following study, emphasis has been given to a comparison of existing or proposed national regulations of EEC member countries, as such have become available to the authors, partly in their capacity of national experts to the EEC working group on Lead and Cadmium Releases from Ceramic Surfaces.

The use and interpretations of such regulations, proposals etc. is solely the responsibility of the authors.

As a standard for comparison, methods and test limits have been chosen, which were considered by the said working group in document XI/422/74 during the time of the study, i.e. the period May-September 1974. Since then a final proposal for a harmonized directive has been presented by the EEC-commission to the Council through document R/112/75 or COM(74)2173 of 18. december 1974. A recalculation of all study data in the light of this document has been made and may be found in the format of a listed Appendix to the report.

The authors wish to express their gratitude for the support given by the EEC Commission, Health Protection Directorate which initiated and made the study possible. The interest and assistance in supplying additional information from the side of the chairman and from individual members of the EEC working group is also greatly acknowledged.

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Chapter 1

1. I N T R O D U C T I O N.

1.1 Frames of the study.

In the request for this study from the Health Protection Directorate of the Commission of the European Communities, the frames of the present work have been defined as follows:

a) Investigation into the relation between the present danger of food contamination from ceramic household containers, bearing in mind the conditions in which they are used, and the quality of ceramic surfaces, assessed by methods of analysis at present used by the community member states.

b) Attempt to assess contamination of humans based on Acceptable Daily Intake.

1.2 Sources of information.

In the attempts to meet these requirements, information has been searched along the following lines:

a) An EDB-literature search was made, covering Chemical Titles through the years 1962-1967, and Chemical Condensates (alias Chemical Abstracts) from 1963-1974.
b) A manual cross reference search was based on these primary sources.
c) A request for unpublished information was sent to selected official laboratories and institutions in each of the Community member states.
d) Some information from industrial laboratories was used, namely from Féderation Europeenne des Industries de Porcelaine et de Faience (F.E.P.F.) and the Degussa Farben I.G., Germany.
e) Results of experimental work at the National Food Institute, Denmark were reviewed. Only parts of these results have been published earlier.

The information thus obtained has been used in the following way:

1.3 Study performance.

Stage 1: Evaluations of test methods for simulative extractions (cfr. Chapter 2).

The analytical test methods on lead and cadmium extractability from ceramic surfaces differ widely between the countries in which regulations are already established. A comparison of these methods must therefore necessarily involve evaluations of those parameters which are of importance for the extraction rates of lead and cadmium during the tests and which are significant for the effect of both the test liquid and of the food. The dominant parameters in this context are:

a) the acidity of the test solution
b) the temperature
c) the duration of the test and
d) eventually the light conditions.

Stage 2: Comparison of different European test procedures (Chapter 3)

In the light of the varying effects of the individual test parameters, the different national test procedures (legislative, recommended standards or proposals under consideration) are investigated. Focusing on the attempts to harmonize such procedures, it is hereby emphasized to evaluate the individual methods against a common model of comparison. For this purpose, a choice has been made of the preliminary proposal for a harmonized EEC-method, which was presented in the spring of 1974 to a working party of experts under the Directorate General for the Internal Market of the Commission of the EEC (Doc. XI/422/74).

With the present, nearby confusing situation of many different methods in use, such a framing of the discussion is felt to be of utmost importance. As an intermediate outcome of the study, this comparison is concluded in an estimate of the relative degree of restriction imposed on ceramic ware by the different test methods, all measured towards the degree of restriction given by the model for comparison.

Stage 3: Collected information on quality of marketed ceramic ware in Europe (Chapter 4).

In this section of the study, a review is made of some national surveys of ceramic utensils which have been presented during the later years. Although much of such surveying has been based on selected - often suspected - specimens of ceramic-ware, they will usually pinpoint the most important quality problems connected to ceramic surfaces, and they may disclose trends or special problems which are found common for the surveys.

Here, the different types of ceramic surfaces (plain, decorated, enamelled etc.) are treated separately, their behaviour during the tests is examined and a concluding attempt is made to estimate the impact of a common test method, viz. the selected EEC working-group method, on the survey results.

As an integral part of this examination, it is for each of the surveys further attempted to evaluate the possible consequences of an eventual lowering of the limits below those of the EEC working-group method.

Stage 4: Characterisation of food as the receiving medium for migrating lead and cadmium (Chapter 5).

The ultimate aim of the study is to relate the extraction of lead and cadmium in simulated test procedures to the corresponding potential migration into food. In this context special attention has been paid to the acidity of food.

Stage 5: Available information on experimental studies on migration into food (Chapter 6).

Having evaluated these parts individually, the study proceeds to discuss the direct information which is available on the comparability of simulated tests and practical food exposure. The results from direct experimental comparisons are reviewed, and an attempt is made to evaluate the contamination of food which may be expected from such containers, utensils etc. for which the release of lead and cadmium corresponds to the limits under discussion.

Stage 6: Assessment of potential total food contamination from ceramic surfaces (Chapter 7).

Such levels of contamination, when added op from typical situations of daily eating habits, may be taken as representative estimates of the potential migration loads on the diet concerned. When these estimates are compared to the provisional, tolerable daily intakes as they are established by FAO/WHO expert groups, it is the assumption of the study, that the best possible evaluation is thereby achieved on the degree of food protection which is obtained from the given set of regulating limits.

Stage 7: Supplementary review on ceramic ware as cause of lead poisoning etc. (Chapter 8).

Finally, in order to study the circumstances, which have so far been involved in actual cases of lead poisoning etc. from the use of ceramic utensils, a supplementary review on case stories described in the literature is included.

1.4 Follow-up of the study.

This study has been made parallel to the work of the EEC-Commission working group of experts from which group some sources of information have been drawn or - through the kind assistance of individual members - made available. An important part of this information, of course, is the drafted working-group document (Doc. XI/422/74) to which has already been referred above. Although only of a preliminary nature, this paper has been the arbitrarily chosen standard of comparison and has thereby become intimately connected to the numerical results of the study.

Towards the end of 1974, i.e. after the termination of the study period, however, a proposal for a directive was prepared by the EEC-Commission and presented as the final version for the Council (R/112/75-COM(74)2173). Among the changes and amendments introduced by this version the following deserve special mentioning:

A) A formerly considered provision of a 100% higher limit value for the first extraction out of two has been abandoned. As far as can be judged from the observations of the present study, this change is especially of significance for overglaze decorated ware, for which it will in many cases introduce a 50% reduction of the decisive limit.

B) An originally considered hot test procedure for cookingware is replaced by a 24 hour cold test, at the same time reducing the numerical value of the limit to 50%.

C) As a new concept, the final proposal introduces a special set of provisions for so-called "children's tableware", thereby acknowledging the special needs of protection for this age-group.

These changes will evidently be of significance for the degree of protection and safety connected to the risk of migration of lead and cadmium which is ultimately imposed by a harmonized Community directive. However, in the context of the present study and its adopted set of calculations, only the first mentioned (A) above) will give a direct impact on the calculated results of the report. The second (B),above) gives rise to principal considerations concerning the correspondence between test procedure and practical use. Formally, however, it will not be of significance for the concluding results.

To conclude the present study, a supplementary study has therefore been made:

<u>Final stage</u>: Recalculation of study data based on the final version of a proposal for EEC-directive (Appendix).

Based on the detailed provisions of the final version of the EEC Commission proposal a full recalculation of the study data has been made. To avoid interference with the adopted presentation of the study this has been attached as an Appendix to the study. In a few individual cases recalculations are given together with appropriate technical comments, and as a matter of convenience, in the original text an editorial remark has been added referring to the Appendix, whenever the final directive proposal has imposed a change of the study calculations.

Chapter 2

2. Regulations and test methods in the EEC countries.

Objects with ceramic surfaces normally used for household utensils include the following types:

1) Ceramic products such as earthenware, faience, majolica, stoneware and porcelain,
2) Ceramic enamels for metal-coating and
3) Glassware.

For the time being, the quality of such surfaces with regard to release of lead and cadmium is assessed in the countries within the EEC by the methods of simulative extraction which are shown in table 1. In this table is included for comparison the extraction conditions found in the EEC working group document XI/422/74.

It is noted that several of the regulations or proposals, including the test considered by the working group, are limited to ceramic surfaces of the abovementioned type 1, avoiding enamelled metals and glassware. Consequently, the present work will mainly be concentrated on the surfaces of type 1. Only in a few cases, where enough information has been available, the enamels and glassware will be treated.

It is observed that differences between the national regulations exist for all parameters of interest. The legislative character of the regulations, the kind of metals involved, the concentration and temperature of the test solution (though in all cases, acetic acid solutions are used), the duration of the test and finally, the limits for permissible release of lead and cadmium. It is mentioned that other parameters (not mentioned in table 1) such as definitions of hollowware versus flatware, filling heights during extraction etc. may exist and vary considerably. Some of them may be of a certain interest in special cases, but they will not be treated in the present work.

2.1 The character of the national regulations.

3 countries (Denmark, Italy and Western Germany) have legislative regulations in force. While the Danish legislation is rather new (1972), the Italian and German legislations are considerable older. Because

able 1: Current European, standards etc. on ceramic ware tests.

ountry	Type of surface	Character of regulation	Metals	%Acetic acid	Temp. °C	Duration	Limit Pb	Limit Cd	Remarks
elgium		None							
enmark	1,2,3	Legislation 1972	Pb,Cd	4	100	3 x ½h	3mg/l 0.6mg/dm²	1mg/l 0.2mg/dm²	Hollowware Flatware
ance		None							
eland	1	Standard 1973	Pb,Cd	4	16-23	24h	7mg/l	0.5mg/l	Tableware
aly	1,2	Legislation 1962	Pb	1	Room	24h	0 (defined by det.limit of method)		
		Considered for revision	Pb,Cd	3	40 100-120	3x24h 3x½h	10mg/l 3mg/l same	0.5mg/l 0.2mg/l same	1st att.) Tableware 3rd att.) same Cooking ware
xembourg		None							
etherlands	1,2	Leg.proposal 1974	Pb,Cd	3	40 100	3x2h 3x2h	0.3mg/dm² same	0.02mg/dm² same	3rd attack Tableware 3rd attack Cooking ware
ited ngdom	1	Standard 1972	Pb,Cd	4	19-21 120	24h 2h+22h	20mg/l 7mg/l 2mg/l 7mg/l	2mg/l 0.7mg/l 0.2mg/l 0.7mg/l	Flatware: Hollowware 1 ltr.) Table- Hollowware 1 ltr.) ware Cooking ware
Germany	1,2	Leg.1887	Pb	4	100	½h	0		
	1	ALAC-proposed standard	Pb	4	22±2	24h	(1.5mg/dm²)(Status of limit not clear)		
C mmission x)	1	Working-group consideration, XI/422/74	Pb,Cd	4	22±2 120 22±2	(2x)24h 2h+22h 10x24h	5mg/l 1mg/dm² 5mg/l 5mg/l	0.5mg/l 0.1mg/dm² 0.5mg/l 0.5mg/l	Hollowware) Tableware Flatware) Ovenware Storage vessels
						Remarks: Decisively valid for 2nd attack 100% higher limits for 1st attack			

x) Cfr. Appendix

of their zero limits for lead and the lack of limits for cadmium, however, they are presently under consideration for revision in the two countries. A Dutch proposal for legislation has been reported as being nearly finalized. In the United Kingdom and Ireland, preference has been given to recommended standards rather than to legislative measures.

2.2 Concentration of acetic acid test solution.

Apart from the 1% solution prescribed by the Italian legislation from 1962, the acetic acid concentrations usually chosen are 3% or 4% (in 2, resp. 4 countries).

The basis for choosing the 3% acetic acid seems to be an assumption that 3% acetic acid forms an azeotropic mixture with water, which is then considered preferable, especially for hot tests. This assumption, which is supported by the information in the Handbook of Chemistry and Physics (cfr. 54th ed., 1973-74), has not found confirmation elsewhere. Thus, investigations on the acetic acid/water system made by Gilmont et al. (1944) and Conti et al. (1960) show no azeotropic behaviour of the system at all (cfr. also Beyersdorfer, 1973). The boiling point of the mixture of acetic acid and water is smoothly increasing from 100° - 118°C when the concentration of acetic acid is raised from 0 - 100%.

Consequently, the claimed advantage of a 3% acetic acid in stead of the 4%, which is favoured by the majority of countries inside and outside the EEC, seems to be unjustified.

It is interesting to note the findings of Peco (1972) and Krinitz et al. (1973), that the variations in extractive power of acetic acid within the ranges 1 - 4% and 4 - 5%, respectively, are actually very limited, if not without significance in connection with lead extraction.

Using 12 pairs of identical vessels of overglaze decorated porcelain, Peco finds an average difference in lead release of ÷0.02 mg/litre (from ÷0.6 to +1.0) between 1% and 4% acetic acid extractions. The range of lead releases in these 12 doublet samples was from 0.1 - 7.8 mg/litre in the 24 hr/4% - tests.

In another series of 11 doublet samples of faience and majolica objects the range was 0.5 - 19.8 mg/litre. Here, the average difference between 1% and 4% extraction results was ÷0.61 mg/litre (from ÷4.8 to + 1.5).

Similarly, Krinitz et al. (1973) finds for 18 identical ceramic test cups:

	5% acetic acid		4% acetic acid	
	0.5 hr	24 hr	0.5 hr	24 hr
Lead release(mg/l)	23.6	101.9	24.1	92.9
Range	17.2-36.8	72.8-167.4	15.9-28.1	64.5-122.4
Standard deviation	4.2	26.8	2.9	16.0

Thus there are hardly any significant differences between 4% and 5% acetic acid, as far as extractive power is concerned.

This practical lack of dependence of the acid strength is probably due to the rather moderate variation of the hydrogen ion concentration. pH is only decreasing from 2.78 - 2.48 when the acetic acid concentration is increased from 1% to 4%. A further reduction, however, of the acid concentration may be expected to give rise to a decrease in the extractive power. At least, the extractive power of pure water is markedly lower. This is f.i. shown in the results published by Engberg (1972), where boiling extraction with water for 1 hour is compared to 4% acetic acid for ½ hour resulting in ratios of 0.005 - 0.75 between these two systems.

In connection with the latter experiments, it is especially noted that the ratio was highest for objects with a relatively low lead release.

As for the connection between cadmium extraction and acetic acid concentration, no data have been found in the literature.

2.3 Temperature of test solution and sample.

With minor deviations, the test temperatures which are in use or proposed within the Community are centered around 20°C, 40°C and 100°C, i.e. a range which may be expected to influence the extraction rates of metals greatly.

Theoretically, the release of lead and cadmium from ceramic surfaces may be regarded as chemical reactions for which the reaction velocity is determined by the activation energy in accordance with the classical "rule of thumbs" by van't Hoff. This would mean that the rate of release expectedly would be doubled for each temperature rise of 10°C, assuming a "normal" order of magnitude for the activation energy.

In practice, however, other processes as f.i. diffusion may be involved. Such processes could also be temperature dependent, but most probably then to a much lesser extent. Dependent on whichever of these processes is the decisive, wide variations can therefore be expected and this is also experienced in experiments on lead extraction from various types of ceramic surfaces.

Temperature dependence of lead release

For overglaze-decorated ware, several sources of information are available concerned with the temperature dependence of the lead release by acetic acid extraction. As examples should be mentioned the following direct comparisons of test at 100°C during 1.5 hours and at room temperature (i.e. 20° - 25°C) during 24 hours between which the theoretical ratio after the van't Hoff rule should be from 12 (25° - 100°C) to 16 (20° - 100°C):

1) Beyersdorfer (1973) tested 3 ceramic overglaze colours and 4 glazes without coloured pigments with the following results:

	Pb-Abgabe		
	Farbe 1	Farbe 2	Farbe 3
A: 22°C/24h - mg/dm^2	0.14	0.18	0.20
B: 100°C/1.5h-mg/dm^2	0.34	0.33	0.31
Ratio B:A	2.43	1.84	1.55

	Fluss 1	Fluss 2	Fluss 3	Fluss 4
A: 22°C/24h - mg/dm^2	0.08	0.04	0.04	36
B: 100°C/1.5h-mg/dm^2	0.22	0.13	0.09	95
Ratio B:A	2.75	3.25	2.25	2.63

It is seen that the ratios between hot and room temperature extractions are 1.6 - 2.4 for the ceramic colours, and from 2.3 - 3.3 for the unpigmented glaze mixture. While these sets of values are most certainly not significantly different, they are both considerably lower than the theoretically expected values mentioned above.

2) Engberg (1973) reports for overglaze decorated surfaces that lead release ratios between the Danish test and the 24hr/room temperature test are in the range 1.1-9.0. Six out of 8 ratios were between 1 and 3:

mg Pb/l at 25°C	10.0	3.35	3.55	0.20	0.29	8.0	21.7	0.09
Ratio: $\frac{\text{mg/l at } 100^{\circ}\text{C, 90 min}}{\text{mg/l at } 25^{\circ}\text{C, 24 hrs}}$	1.1	1.1	1.7	1.8	2.8	2.9	5.2	9.0

Thus, in these two reports from different sources there is a good agreement that the ratio between hot and cold temperature lead release typically is within the range 1.5 - 3.0. In one case, only, out of 8, Engberg (1973) found a value of 9, approximating the theoretical ratio of 12.

As far as the intermediate temperature-range is concerned, the Food Inspection Service at Haarlem, The Netherlands (1974) has examined 13 x 2 samples of decorated ware at 40°C for 3 times 2 hours in comparison with 20°C for 24 hours. Theoretically, these two procedures should be equivalent when the effects of temperature and test duration are both taken into consideration. In practice, the examination of the 13 pairs of results for onglaze decorated ware showed an average ratio of 1.12 (range: 0.31 - 2.0) between the 6 hours/40°C and the 24 hours/20°C procedures, i.e. on the average rather near to the theoretical equivalence.

For the conclusion, this means that there is indication of a fairly good agreement between the theory and practice as far as these overglaze decorations are concerned, when only a temperature range around and a little above room temperature is considered. As this, however, is overlapped by a lowered temperature dependence in the temperature range from 20° - 100°C, it seems well justified to interpret the over-all information as the result of a low activation energy - or a rather loose binding of lead and cadmium in the overglaze decorations.

For plain ceramics, the temperature dependence of lead release is illustrated in a few direct experiments, only.

Engberg (1972) finds for 7 cases that the ratios between lead releases at 100°C for 1.5 hours and at 25°C for 24 hours varies as follows:

mg Pb/l at 25°C	225	44	24.8	2.6	0.87	0.43	0.043
Ratio: $\frac{\text{mg/l at } 100^{\circ}\text{C, 90 min}}{\text{mg/l at } 25^{\circ}\text{C, 24 hrs}}$	0.44	1.1	1.5	2.2	5.4	9.3	10.0

These results clearly demonstrate that the temperature dependence increases with decreasing lead release, approximating the theoretical ratio value of 12 in cases of very small release. In the three cases for which the releases were great - and in fact, well above any regulatory limits - the ratios are near to 1, i.e. for such objects the impact of a boiling test for 3 x 30 minutes is practically equivalent to a 24 hours storage at room temperature.

The data of Krinitz (1973) and Peco (1972) which have alreadv been quoted, fit rather well into this pattern:

Krinitz finds as the average for 2 x 18 identical cups a lead release of 102 mg/litre at 22°C and of 83 mg/litre at 60°C (both extractions for 24 hours). The corresponding ratio between high and low temperature extractions is 0.81. This indicates a practical independence of the temperature of the lead release from these cups. As they are characterized by a very soluble lead glaze, this is in good accordance with Engberg's findings above.

It should be mentioned that after the first 30 minutes in Krinitz' experiments, a ratio of 2 was established, which indicates that a higher activation energy was required to loosen the lead from the surface during the initial part of the test period. However, the factor of 2 is still much lower than the factor of 8 which in this case would be expected, if the rate of liberation was determined by the velocity of a "normal" chemical reaction.

Peco (1972), in his experiments with 6 pairs of faience objects, finds a ratio of 2.7 between averages of lead releases at 40°C with 3% acetic acid and at 20°C with 4% acid. This ratio should be compared with a theoretical ratio of 4 and therefore points in the same direction as the other experiments, namely an often lower practical temperature dependence than theoretical. The observation that, in this case, the relative deviation from theory is less pronounced than above is already well-explained by the fact that Peco's faience objects were of a relatively good surface quality, i.e. with low lead releases (cfr. Engbergs results above).

It is also in Peco's experiments interesting to note that in a second 24 hour extraction, the ratio between averages at 40°C and at 20°C was 2.8, while at the third extraction it had risen to 4.4. During these three tests the lead releases decreased from 4.4 mg/litre through 3.5 mg/litre to 1.4 mg/litre (all at 20°C). Therefore, here again a decrease in lead release is connected to an increase in the temperature dependence.

The Food Inspection Service at Haarlem (1974) has investigated 8 x 2 different plain ceramic objects, at 40°C for 3 x 2 hours, respectively at 20°C for 24 hours. As mentioned earlier, the releases of lead should "theoretically" be equivalent. The following ratios are found:

Object type	1	2	3	4	5	6	7	8
mg/l at 24 hours, 20°C	28.6	13.1	9.2	8.2	5.2	2.6	1.7	1.0
release ratio $\frac{6h40^{\circ}C}{24h20^{\circ}C}$	0.57	1.05	0.80	1.26	0.78	1.1	2.76	2.08

It is noted that the average ratio, theoretically being 1.0, is found to be 1.30 (range 0.57 - 2.76), and that the regularity in the rise of temperature dependence with diminishing lead release is not so clearly demonstrated for this narrower temperature range as for the abovementioned range of 25 - 100°C.

Conclusively about the influence of temperature on the lead release from different types of ceramic surfaces, it can be generalized that a rather low degree of dependence is found in cases of overglaze decorated ware and of plain ware which is characterised by high lead releases, while on the opposite a more pronounced temperature dependence, approximating theoretically expected values, is typical for plain surfaces with low lead releases.

Temperature dependence of cadmium release.

Only a few sources of information are recorded on this question. At the Danish National Food Institute, Engberg (1972) compared the cadmium release from 3 pairs of objects by 3 x 30 minutes extraction at 100°C and by 24 hours followed by 96 hours at 25°C as follows:

Samples (enamelled iron)	Release of cadmium (in mg/litre)		
	3x30min,100°C	24 hrs,25°C	96 hrs,25°C
Dish, orange	4.95 (2.32x)	2.13	0.66
Dish, yellow	6.25 (2.98x)	2.10	1.09
Bowl, orange	9.95 (1.31x)	7.58	3.27

The ratios between hot and cold (24 hr) test results are indicated in parantheses and it is seen that thev are similar to those found for lead release from overglaze decorated porcelain.

As far as the temperature range 20° - 40°C is concerned, the Food Inspection Service at Haarlem (1974) has compared the cadmium release from 8 double samples of onglaze decorated ware at 40°C for 2 x 3 hours with the release from 8 doublet objects at 20°C for 24 hours. In this case, the ratio of high to low temperature release was 1.09 (ranging from 0.28-1.87), which is nearly equal to the ratio of 1.00, predicted theoretically. Here again, the results are closely corresponding to those found in connection with lead releases.

2.4 Duration of test

Most commonly, a 24 hour test period is prescribed for tableware. Exceptions are the Dutch proposed regulations which suggest 3 x 2 hours test with the 3rd extract as the decisive, and the Danish regulations prescribing 3 times 30 minutes with the total amount of lead from the three extracts as basis for evaluation.

In order to assess the release of lead by continued practical use, it is found useful to consider the change in released amounts of lead and cadmium as it develops in a series of subsequent extractions. This is done in the following two tables (table 2 and 3) which summarize results from a number of different sources. Evaluating this data, at least two observations seem to be justified:

1) There are considerable variations in the release versus time-relationship according to the types of surfaces, and

2) there are considerable variations in this relationship, when comparing the hot method on the one side and the cold extraction methods on the other.

For lead, when considering the hot test only, it is seen from table 2 (A) that there is a reasonably constant release throughout the 3 extractions of the decorated surfaces and of the plain surfaces with elevated lead releases. This is measured in terms of second and third extraction rates, both related to the released lead in first extract. Varying in the range from 0.75 - 0.94, these ratios are on the average sufficiently near to 1.0 to indicate that the releases into second and third extract are of the same order as the release into the first extract.

For lead crystal surfaces and for plain ceramic glaze surfaces with a low lead release, the situation is different. Here, there is a significant, often sharp, drop in lead release from the first extract to the second and third.

Turning to the cold extraction methods (3 x 24 hrs at room temperature or at 40°C) a practically opposite pattern is exhibited by the results in table 2. Although a certain decrease in the rate of lead release in 3 consecutive extractions can be seen for both types of objects, such decreases are most pronounced for surfaces with relatively loose binding of the lead, i.e. the onglaze decorated ware and the plain surfaces with high releases. The more constant or only moderately decreasing releases are in this case found for plain surfaces with a low lead release.

Table 2:
Time-relationsship of lead release in 3 concecutive extractions

(A_1=Pb in 1st extract; A_2=Pb in 2nd extract; A_3=Pb in 3rd extract)

A) Hot extraction (100°C/3 x 30 min/4% acid) (Engberg, 1972)

	Plain surfaces		Onglaze decorated		Lead crystal
Number of objects	17	15	4	7	9
Total release, i.e. $A_1+A_2+A_3$ (mg/l)	0-3	3-30	0-3	3-30	0-7
Ratio $A_2 : A_1$	0.54	0.94	-	0.87	0.23
Ratio $A_3 : A_1$	0.45	0.75	-	0.82	0.17

B) 40°C extraction (3 x 24 hr/3% acid) (Sampaolo, 1973)

Number of objects	15	17	1	16
First release, i.e. A_1 (mg/l)	0-1	1-232	0-1	1-673
Ratio $A_2 : A_1$	0.74	0.64	0.51	0.26
Ratio $A_3 : A_1$	0.69	0.61	0.51	0.19

C) 40°C extraction (3 x 2 hrs/4% acid) (F.I.S., Haarlem, 1974)

Number of objects	8	12
Total release, i.e. $A_1+A_2+A_3$ (mg/l)	1-29	1-19
Ratio $A_2 : A_1$	0.28	0.30
Ratio $A_3 : A_1$	0.19	0.21

D) Room temperature extr. (2 x 24 hrs/1% acid) (Peco, 1973)

Number of objects	17	9
First release, i.e. A_1 (mg/l)	1-23	1-10
Ratio $A_2 : A_1$	0.55	0.38

Table 3:
Time-relationsship of cadmium release in 3 consecutive extractions.

(A_1 = Cd in 1st extract; A_2 = Cd in 2nd extract; A_3 = Cd in 3rd extract)

A) Hot extraction (100°C/3 x 30 min/4% acid) (Engberg, 1972)

Number of objects	Plain enamelled iron surfaces (7 objects)	Decorated faience and procelain (6 objects)
Total release, i.e. $A_1 + A_2 + A_3$	3 - 16 mg/l	1 - 10 mg/l
Ratio $A_2 : A_1$	0.29	0.85
Ratio $A_3 : A_1$	0.24	1.22

B) 40°C extraction (3x 24 hrs/3% acid) (Sampaolo, 1973)

Number of objects	Plain ceramics (5 objects)	Decorated faience and porcelain (6 objects)
First release, i.e. A_1	0.2-100 mg/l	0.2-17 mg/l
Ratio $A_2 : A_1$	0.48	0.23
Ratio $A_3 : A_1$	0.40	0.18

C) 40° extraction (3 x 2h/3% acid) (F.I.S., Haarlem, 1974)

Number of objects	Decorated Faience and porcelain (8 objects)
Total release, i.e. $A_1 + A_2 + A_3$	0.07-1.29
Ratio $A_2 : A_1$	0.70
Ratio $A_3 : A_1$	0.36

These observations seem to support the conclusion, that surfaces of a more rough or soft character (which is often typical for overglaze decorations or for plain surfaces of a simpler quality) are rather susceptible to penetration by hot acid. New surface-layers may be uncovered from one ectraction to another and the leachability can be maintained in subsequent hot acid treatments.

For the lead crystal and for the plain ceramic glazes of low solubility, the surfaces may better be characterized as smooth and/or hard. Here, the first hot extraction seems to remove a loose surface layer of lead constituents. During the following extractions, it is probably more difficult for the hot acid to penetrate through the surface layer, and the release of lead will be found decreasing.

In a similar set of explanations concerning the cold test conditions, the cold acetic acid is less aggressive and operates mainly by removing the loosely bound surface layers of lead. Consequently, the release can be expected to decrease for all types of objects, although at a greater rate, the looser the binding. This is in accordance with the observations that the most rapid decrease is found for overglaze decorated surfaces; intermediate values are connected to plain surfaces with elevated or high lead releases (i.e. more than 1 mg/litre in first extract) and the slowest decrease is found for plain surfaces of good quality.

For cadmium (cfr. table 3), a similar difference in surface resistance is observed by hot extraction between plain (red, orange and yellow) enamelled iron surfaces on the one hand, i.e. a pronounced decrease of cadmium release, and decorated faience and porcelain surfaces on the other hand, i.e. a nearly constant rate of release in three consecutive extractions.

In room temperature extractions, the repeated cadmium releases also follow the pattern described for lead: The less aggressive cold acid removes the loose surface layer with the first extract, whereafter the releases decrease in the second and third. This is especially pronounced in the cases of decorated porcelain.

When evaluating the quality of ceramic surfaces, these observations on the metal release *versus* time-relationships should be borne in mind, especially when food "extraction" is simulated: In order to avoid an introduction of fundamental differences between the release patterns by the simulated test and by practical usages, the test temperature which is chosen should not deviate from the normal use range more than is practically needed for the different types of objects.

2.5 Light conditions.

It was discovered by Carroll & Halpin (1973) that the release of cadmium into test solutions is often strongly dependent on light conditions. From the summary and foreword of their report AC/M1-11/73, the following is quoted:

"The release of cadmium into acetic acid solutions from glazed ceramic ware has been found to be dependent on the light conditions in which the tests are carried out. Extractions using acetic acid are widely used in National Standards to set limits on the amount of lead and cadmium which can be leached from ceramic glazes.

The release of lead is not affected by the light conditions. The amount of cadmium released is dependent on the illuminance and the period of exposure to light during the extraction. The effect also occurs if the acetic acid is replaced by other organic or inorganic acids as the leaching solution.

The extraction of cadmium was also found to take place when water was used as the leaching solution.

Two types of release of cadmium would appear to occur, the first which is independent of light, and the second type which is believed to be due to the photo-oxidation of cadmium sulphide or sulpho-selenide. The latter reaction is inhibited by the addition of an antioxidant to the leaching solution. Oxidising conditions will enhance the release of cadmium.

The implications of the results are important and twofold (a) present tests procedures are inadequate in that light conditions are not taken into account when specifying the experimental conditions of the test and (b) light sensitivity can affect the release of cadmium from glazed ceramic ware into the foodstuffs with which they may come into contact. The former could be resolved by incorporating light conditions into test procedures. The latter must be considered in conjunction with the overall toxicology of cadmium release from glazed ceramic articles."

For the cadmium release tests which are reviewed in this report, the light conditions are generally not specified. This means that a general reservation towards the possible influence of this factor on the results is necessary. The importance of the effect for releases into food has not been evaluated, but of course, the reservation must also cover the results reviewed for cadmium release into food.

Chapter 3

3 Comparison of the EEC proposed directive with national regulations and standards.

In the following paragraphs, an attempt will be made to evaluate the degree of restriction which is imposed on ceramic products by established limit values and test methods in the individual EEC-member states in comparison with limits and methods as they are presently considered by the EEC working group.

A comparison of this kind is necessarily most complicated, when all the important parameters which have already been discussed are to be taken into consideration simultaneously. And with due reference to the variabilities which have also been noted, its empirical nature should be emphasized.

It is found, however, to be a most needed and useful guideline for the further studies, and it will be limited to such objects, which are usually classified as "holloware", this being the most important group from the point of view of protecting the food against migrated metals. Two groups of holloware will be dealt with separately, namely: 1) Tableware and 2) Cookingware (including oven- and kitchenware).

3.1 Tableware, lead release.

In the EEC-working document the limit of permissible lead release is 5 mg per litre in a 24 hr./22°C/4% acetic acid test.

This limit is attached to the second extraction as the decisive, thereby allowing for a decreasing release from the 1st extraction, for which a supplementary limit of 10 mg per litre is proposed.x)

In comparison, the national regulations and standards are as follows:

Denmark.

The Danish legislation prescribes a limit of 3 mg lead per litre in a 100°C/3 x 30 minutes test with 4% acetic acid. The practical release under these circumstances is on the average (deviating,

x) Cfr. Appendix

of course, for various types of surfaces) about 3 times higher than under the conditions considered by the EEC working group. Transforming the Danish numerical limit to the conditions of the latter, this therefore implies that the Danish limit is 5 times more restrictive, when the second and decisive extraction is considered. Dealing with the supplementary provision suggested for the working group, viz. the 1^{st} extraction limit, the Danish limit is in the order of 10 times more stringent.

Italy.

The Italian proposal for new national legislation (Sampaolo,1973) suggests a limit which is valid for the 3^{rd} extract with a value of 3 mg lead per litre in a 40°C/24 hrs test with 3% acetic acid. It is further provided, that the release by the first extraction does not exceed 10 mg/litre.

In this case, a low temperature range is involved and - as has been seen in the discussion above - a transformation to the EEC testconditions will be justified on the basis of the theoretical temperature dependence. Thus, in view of the temperature difference of 1.8 x 10°C, the limit by the 1^{st} extraction could be evaluated as about 4 times more restrictive than the EEC working group limit of 1^{st} extraction, although these are numerically equal.[x)]

Comparing on the same basis, the Italien decisive limit of the 3^{rd} extract against the corresponding limit of the 2^{nd} extraction in the EEC working document, it is seen that these are not numerically equal, and the Italian limit can be judged as in the order of 7 times more stringent than that of the working group. In this connection, it is noted that the difference between releases in the second and third extract are small compared to the differences between first and second extract.[x)]

Ireland, United Kingdom and Western Germany.

In these countries a 7 mg per litre limit for lead is prescribed for the first extract in a 20°C/24 hours test with 4% acetic acid. (In Germany, this is expressed in a surface area migration limit, namely 1.5 mg per dm^2, which, however, is approximately equivalent

x) cfr. Appendix

to 7 mg per litre for hollowware).

By first sight, this is a 40% higher (milder) limit than the limit considered by the EEC. As however, room temperature test conditions in most cases favour a decrease (cfr. table 2; average ratio: $A_2 : A_1 \sim 0.25 - 0.74$) in lead release and the EEC working group considers its limit as attached to the second extract, it seems more justified to evaluate these national limits as being equivalent to or a little stricter than the limit of document XI/422/74.[x)]

Netherlands.

Under consideration for national regulations is a 0.3 mg per dm^2 limit for the 3^{rd} extract of a $40^{\circ}C$/2 hours test with 3% acetic acid.

From the Dutch experimental reports (F.I.S., Haarlem, 1974 - cfr. also table 2) it is seen that on the average, the release into the 3^{rd} extract is 21% of the release into the 1^{st}, and it is 13% of the total release into three extracts. Based on the assumption of a temperature dependence in accordance with theory, therefore, the Dutch limit for the 3^{rd} extract could be transformed to a first extract limit of about 2.3 mg/dm^2 under the conditions considered by the EEC, which is fairly near to equivalence with 10 mg per litre.

Dependent on the pattern of decrease by consecutive extractions, the limits under consideration in the Netherlands may therefore be slightly milder than or equivalent to those of the EEC working group.[x)]

3.2 Cookingware, lead release.

The EEC working document prescribes a hot test: extraction with 4% acetic acid for 2 hours at $120^{\circ}C$, followed by cooling for 22 hours. The limit for lead in connection with this procedure is 5 mg per litre. For the first extraction, however, a 10 mg/litre release is tolerated as is the case for tableware.

x) Cfr. Appendix.

Denmark.

The Danish cookingware regulations are identical to those mentioned for tableware, i.e. a limit of 3 mg per litre in a 100°C/3 x 30 minutes test with 4% acetic acid.

In theory, this is a test which is about 40% less severe than the test considered by the EEC, and with an attached limit, which correspondingly is 40% lower. As the working group test provides for the possibility of a second extraction, it is recalled that hot tests are most often connected with only moderate decreases in lead release, and the Danish regulation can therefore in this case be evaluated as only slightly different in its degree of restriction.[x)]

Italy.

The proposed Italian legislation prescribes an extraction for 3 x 30 minutes at 100°C or at 120°C for cookingware, using 3% acetic acid. This is a procedure which is at least 5 times less severe, judged by the lengths of the extraction periods. However, one of the limits (10 mg/l for 1st and 3 mg/l for 3rd extract) is also somewhat lower. For practical purposes, therefore, the limit considered in Italy in this field can be evaluated as being about 3 times less strict than that considered by the EEC working group, if the extraction is made at 100°C, while the two proposals seem nearly equivalent if a 120°C extraction (in autoclave) is chosen. [x)]

Netherlands.

Under consideration is a lead limit of 0.3 mg per dm^2 for cooking ware in a 100°C/3 x 2 hours test, the 3rd extraction being the decisive. No data is available for the evaluation of this procedure against the procedure of the EEC.

United Kingdom.

The British Standard procedure is identical with the proposal considered by EEC apart from a limit of 7 mg/l for the first extract,

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x) Cfr. Appendix

compared to 10, resp. 5 mg/l for the first, resp. second extraction in the working document test.

Thus, it depends on the decrease from 1^{st} to 2^{nd} extraction, whether the British or the EEC working group limits are the more severe. As already mentioned, such decreases are only moderate, and for some objects (those of a fairly constant release) the BS will be milder, while for others (decreasing from 7-10 to 5 mg/l) it will be stricter than the EEC working group test. x)

Ireland and Western Germany.

These countries do not include a specified cookingware test.

3.3 Tableware and cookingware, cadmium release

Turning to the Cadmium limit values, it is noted that the EEC working group throughout operates with limits, which are numerically all related to the corresponding lead limits by a factor (divisor) of 10.

The national standards, legislations or proposals are all established on the same principle, although they differ in their uses of different factors, namely: 15 in Italy and The Netherlands, 14 in Ireland, 10 in the United Kingdom and 3 in Denmark. For comparison it is mentioned that in the recommendations of the FAO/WHO for provisional tolerable weekly intakes, a lead: cadmium ratio of 3 : 0.5 = 6 is applied.

Accordingly, an evaluation of national tests for cadmium would be as follows:

Denmark.

Following the evaluation given for lead, the Danish cadmium limit, which is 1 mg Cd per litre after 3 x 30 minutes extraction at 100°C, is 1.5 times, i.e. slightly more strict than the limit considered by the EEC working group

x) Cfr. Appendix

For objects with a decrease from 1.0 to 0.5 mg/l from the first to the second extraction of 24 hours, the Danish limit is 3 times more restrictive than the EEC working group limit.[x)]

For cookingware, the Danish procedure is 40% milder and the limit 2 times higher than the second limit of the working document. Consequently, for objects with a constant release from 1[st] to second extract, the Danish will be $\frac{5}{3} \times 2 = 3$ times milder than the EEC limit. For objects with a release decreasing from 1 to <0.5, the Danish limit will be 1.7 times milder. [x)]

Italy.

The limit by the third extraction at 40°C for 24 hours is 0.2 mg/l, provided a maximum of 0.5 mg/l in the first extract is not exceeded. Again, assuming a cadmium release temperature relationship equal to that adopted for lead, this means that the Italian cadmium limit for tableware is on the average 9 times lower (stricter) than the EEC working group limit. [x)]

The Italian limit for cookingware is judged to be nearly equivalent to (when 100°C applies) or around 2 times lower (stricter) (at 120°C extraction) than the working group testlimit, cfr. the remarks for lead. [x)]

Ireland.

The Irish cadmiun limit is 0.5 mg/l, or $\frac{1}{14}$ of the Irish lead limit, after 24 hours extraction at 16 - 23°C using 4% acetic acid.

This testlimit is identical to the EEC working group limit, only differing in that the second extract of the latter is decisive. Thus, objects with a release between 1.0 and 0.5 mg Cd per litre in the first extract, and <0.5 mg/l in the second, will pass the working group test, but not the Irish Standard. [x)]

The Netherlands.

For tableware, the cadmium limit is 0.02 mg/dm^2 and the ratio of

x) Cfr. Appendix

cadmium to lead limits is 1 : 15. Referring to the evaluation already given for lead and taking into consideration that the EEC working group deals with a ratio of 1 : 10 for cadmium to lead, the Dutch cadmium limit is therefore judged to be slightly more strict than the working group limit. x)

United Kingdom.

As the ratio between lead and cadmium is the same in the British Standard as in the considerations of the working group, the evaluation given for lead is also valid for cadmium.

In conclusion of this comparison between the EEC working group test and the different national regulations and standards it is a most striking feature, that the degrees of restrictiveness which are imposed by these regulations etc. on the different types of ceramic objects is widely varying, ranging from a factor of about 10 down to the order of $\frac{1}{3}$. x)

This situation is illustrated in table 4 summarizing the results of the survey. As a generalized comment, it seems as if there is an overall tendency for national regulations, especially in the case of tableware, to be more restrictive than the EEC working group limits for both lead and cadmium. Most noteworthy is the severeness which is disclosed in the regulations on tableware in Denmark and Italy, while on the other hand these countries favour a less restrictive attitude towards cadmium, resp. lead from cookingware. x)

x) Cfr. Appendix

Table 4. Ratios estimated on restriction levels of national regulations in relation to EEC working group test (for hollowware <1 litre). x)

	Tableware		Cookingware	
	Lead	Cadmium	Lead	Cadmium
Denmark	5-10x	1.5-3x	1-2x	0.3-0.6x
Italy	4-7x	7-9x	0.3-1x	1-2x
United Kingdom	∿1x	∿1x	∿1x	∿1x
Ireland	1x	1-2x	÷	÷
Western Germany	1x	÷	÷	÷
Netherlands	$\leq$1x	1.5x	÷	÷

x) Cfr. Appendix

Chapter 4

4 Surveying the Quality of ceramic surfaces.

During the later years, several investigations have been made available concerned with surveys of ceramic objects from retail trade in various countries, f.i. Denmark, Italy, The Netherlands, United Kingdom and Western Germany.

Although such surveys do not claim to be representative of the respective market situations for ceramic objects, there do appear to be certain common features, which reveal the location of the major problems connected to the release of lead and cadmium.

In most cases, it is possible to identify the following 4 groups of objects within the various investigations:

1) Pottery, earthenware, faience, porcelain etc., with underglaze decoration or with a plain surface,

2) The same types of objects as under 1), but with an overglaze decoration,

3) Enamelled iron objects, and

4) Crystal glasses or decorated glasses.

In the following a review of the investigations which have been made available will be given, covering some or all of these groups.

4.1 Surveys of ceramics in Italy.

Sampaolo et al. (1973) have presented a survey covering 79 different objects, tested with 3% acetic acid at 40°C for 3 x 24 hours. A summary of the results for lead is as follows.

Type of objects	Plain or underglaze (59 objects)			Overglaze decorated (20 objects)		
Extract	1st	2nd	3rd	1st	2nd	3rd
Lead release mg per litre	Number of objects					
< 1	40	42	42	2	4	6
1 - 2	3	4	5	1	0	1
2 - 3	2	3	3	1	2	1
3 - 5	4	3	2	0	2	1
5 - 7	2	2	1	0	2	2
7 - 10	1	1	1	0	2	2
10 - 20	3	0	0	6	1	4
20 - 40	0	0	1	1	3	2
above 40	4	4	4	9	4	2
Total number	59	59	59	20	20	20
Max. release mg/l	460	130	111	673	120	88

From this table it can be deducted, by transforming the actual test conditions to those considered by the EEC, that 93% of the plain ceramic or underglaze decorated objects and 55% of the overglaze decorated objects in this survey would have passed the EEC working group test. x)

From the discussion above, it was seen that the Italian limits considered in this field was 4 and 7 times more restrictive (for 1st and 2nd extract, respectively), and the corresponding numbers of acceptable samples following the Italian test would have been 85% of the plain ware etc., while only 20% of the overglaze decorated objects would pass the Italian test. xx)

The impact, therefore, of reducing the test limit considerably below the EEC working group level is relatively small for the plain ware/underglaze decorated- group of objects, and it is the <u>second</u> extraction which seems to be the significant for this group. However, there is a considerably greater influence of reducing the limit when dealing with overglaze deco-

x) 50% of the overglaze decorated objects would pass according to EEC-conditions of doc. R/112/75

xx) Cfr. Appendix.

rated ware. The data indicate, that especially the first extraction test is of significance for the latter group of objects.

As far as cadmium is concerned, only 4 (or 7%) of the plain and underglaze decorated objects tested by Sampaolo and coworkers showed releases of this metal in measurable amounts. Among these, 1 would have passed the Italian limit of 0.5 mg/litre in the first extract, and 2 would pass the EEC working group limit of 1 mg/litre.

10 of the 20 overglaze decorated samples released cadmium. Only 3 of them would have passed both the Italian and the EEC working group test for the first extract.

This confirms the general impression presented by most surveys (cfr. f.i. Engberg, 1973), that the problem of cadmium release is mainly concentrated to overglaze-decorated (and enamelled) ware.

Another investigation, however, is in contrast with this impression. This is the survey made in Italy by Ravaglioli et al. (1973), testing 19 multicoloured and 49 plain samples of majolica, earthenware and porcelain vessels. With colours of yellow, green, red and orange, this collection presented rather severe problems of cadmium releases, when they were tested with 3% acetic acid for 3 x 24 hours at room temperature:

Type of objects	Plain		Multicoloured	
Extract	1st	3rd	1st	3rd
Cadmium release mg/litre	Number of objects			
0 - 0.2	22	27	13	13
0.2 - 0.3	1	7		
0.3 - 0.4	0	5		1
0.4 - 0.5	1	0		3
0.5 - 1.0	3	8		2
1.0 - 2.0	6	2		
above 2.0	16	0	6	
Total	49	49	19	19
Max.release	78 mg/l		73 mg/l	

This collection of objects is clearly characterized by a widespreed use of cadmium-containing pigments, and it can be calculated, that only 55% of x) the plain objects would pass the EEC working group limit and 49% (or less, if the test had been performed at 40°C) would pass the Italian limit for the first extract. Thus, the impact of a lowering of the considered EEC limit down to 0.5 or 0.2 mg/litre for the first extract would be relatively small in this case.

13 (or 68%) of the 19 multicoloured samples would pass any of the tests, the release in both the first and the third extract being below 0.2 mg/litre.

In Ravaglioli and coworker's study, the releases of cadmium with the third extract, irrespective of the findings in the first, were nearly all below 1 mg per litre for plain samples as well as for multicoloured. In the first extract, however, up to 20 mg (or 78 mg per litre) of cadmium were found. This emphasizes the importance of a limit for the first extract.

4.2 Surveys of ceramics in the Netherlands.

In 1972, 223 samples of plain ceramics ("aardewerk") were tested by Dutch Food Inspection Services using a room temperature test for 24 hours and measurements of results of lead extraction in mg per litre. A further sampling was made in Haarlem 1974, comprising 8 plain and 13 overglaze decorated objects.

x) 49% of the plain objects would pass the limits proposed in Doc.R/112/75.

The results for lead were as follows:

Type of objects	Plain ceramics (aardewerk)				Onglaze decorated
	Amsterdam 1972	Netherl. 1972	Haarlem 1974	Total	Haarlem 1974
Lead release mg per litre	Numbers of objects				
0 - 1	95	67	0	162	2
1 - 2	6	9	2	22	3
2 - 3	4		1		1
3 - 5	1		0		2
5 - 7	3	11	1	23	1
7 - 10	5		2		1
10 - 20	4	8	1	24	3
above 20	10		1		0
Total	128	95	8	231	13
Max. release	600 mg/l		28 mg/l		

From this table is seen, that about 90% of the plain ware would have passed the EEC working group test of 10 mg/litre suggested for the first extract. x) The impact of a lower limit, f.i. 3 mg/litre for the first extract, imposed on the objects of this collection would be measurable, although not considerable. About 80% of the plain samples would pass also this limit.

For the onglaze decorated group, a greater impact of a reduction of the limit is indicated. However, the number of samples is too small for further evaluations to be made.

For cadmium, it was found in the Dutch survey in 1972, that the release was less than 0.5 mg/litre for 97% of a total of 369 samples of plain ceramics (v.d. Kreek, F.W., (1973)). These 97% would also have been passed by the EEC working group limit, and it can be concluded (cfr. Engberg,1973), that this survey did not present any major problem as far as cadmium release from plain ceramics is concerned, i.e. in contrast to the findings of Ravaglioli et al. (1973) mentioned above.

x) 83% of the plain ware objects would pass the limits of doc.R/112/75.

Coloured enamelled objects were tested for cadmium in the Netherlands in 1971-72, (v.d. Kreek, F.W. (1973)), presenting a number of excessive releases. Out of 17 samples tested, only 3 released cadmium below 0.1 mg/dm^2 (∿0.5 mg/l) and only 4 below 0.2 mg/dm^2 (∿1 mg/l), when boiled for 30 min with 4% acetic acid. If this treatment is taken to be approximately equivalent to a 24 hour extraction at room temperature, only 4 or 24% of the samples would have passed the EEC working group limit of 1 mg/l in the first extract. x)

4.3 Surveys of ceramics in the United Kingdom.

In 1971-72, 34 plain ceramic cassaroles, 35 (onglaze?) decorated plates and 31 enamelled objects were investigated for release of lead, cadmium and other metals by extraction with 4% acetic acid for 24 hours at 20 - 25°C. (Government Chemist, 1971).

The results were as follows:

mg Pb per litre	Ceramics Plain	Ceramics Decorated	Enamel	mg Cd per litre	Ceramics decorated	Enamel
0 - 1	23	13	31	0-0.2	29	21
1 - 2	1	2		0.2-0.3	2	0
2 - 3	2	4		0.3-0.4	0	0
3 - 5	0	1		0.4-0.5	1	0
5 - 7	0	4		0.5-1.0	3	1
7 - 10	1	1		1.0-2.0	0	0
10 - 20	1	1		above 2.0	0	9
above 20	6	9				
Total	34	35	31		35	31
Max.release mg/l	94	395				37

From this table is seen, as far as the plain ware is concerned, that 79% of the tested samples would pass the limit of 10 mg/litre in the first extract, and probably also the 5 mg/litre for the second extract, as they are considered by the EEC working group xx)

x) 3 samples, or 18% would pass the limits of doc. R/112/75

xx) 76% of plain ware samples would pass the limits of doc.R/112/75

The impact of a reduction of the limit for the first extract to f.i. 3 mg/litre would be small, if not insignificant for this choice of plain ceramic objects.

Among the decorated ware, 71% would pass the EEC working group limit of 10 mg/litre in the first extract. x) Here, a reduction of the limit would have a more pronounced influence on the survey evaluation: Only 54% would pass a limit of 3 mg/litre in the first extract.

No lead problem is seen for the enamelled ware. All 31 samples would pass any test.

For both plain and decorated ware, the similarity of survey patterns between this survey and the Dutch survey above is noteworthy.

For cadmium, no releases above 0.03 mg per litre were found for the group of plain ware (not shown in the table) in this English survey.

For the decorated ceramics, 100% would pass the EEC working group limit of 1 mg/litre in the first extract, and 92% were below 0.5 mg Cd per litre in the first test. xx)

Among the enamelled ware, 71% would have passed the EEC working group test xxx), and it would have been of nearly no further consequence to establish a lower limit, as those 9 objects, which did not pass the test, showed cadmium releases out of context with any established limit - up to 36.6 mg/litre.

4.4 Surveys of ceramics in Denmark.

In 1972, a total of 98 samples were tested for release of lead and cadmium by extraction with 4% acetic acid for 3 x 30 minutes at 100°C. The sampling comprised 46 plain ceramic objects, 26 decorated ceramics, 6 enamelled objects and 9 specimens of glassware.

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x) 57% would pass test proposed in EEC document R/112/75

xx) 92% would pass test proposed in EEC document R/112/75

xxx) 68% would pass test proposed in EEC document R/112/75

The results for lead were as follows:

mg Pb per litre	Ceramics Plain	Ceramics Overglaze decorated	Glass, Plain lead crystal	Enamel Plain
<3	28	5 0) + 4 00) = 9	5	6
3 - 6	7	4 + 2 = 6	3	
6 - 9	1	1 + 1 = 2	1	
9 - 15	2	0 + 1 = 1	0	
15 - 21	3	0 + 1 = 1	0	
21 - 30	2	2 + 2 = 4	0	
30 - 60	0	0 + 0 = 0	0	
above 60	3	3 + 0 = 3	0	
Total	46	26	9	6
Max.release mg/l	658			
mg/dm^2		159		

It is noted that for the plain ware, 93% would pass a 30 mg/litre limit which is comparable to the EEC working group limit of 10 mg/litre in first extract at room temperature x). Similarly, at least 83% is estimated to pass the 5 mg/litre limit of the second extract. A considerable impact of lowering the limit to the level of the Danish regulation (i.e. 3 mg/litre by the hot test ∿ 1 mg/litre at room temperature) is seen. Only 67% of the survey samples of plain ware would have passed this limit. 000)

Footnotes:

The first column marked 0) covers mouth rim tests, while second column marked 00) covers tests of the inside surfaces of hollowware.
It is mentioned that the mouth rims are evaluated against a limit in mg per dm^2 which is numerically 5 times lower than a weight to volume limit (0.6 mg/dm^2 ∿ 3 mg/litre). It is further recalled (cfr. the discussion above), that the hot test is evaluated on the average to be 3 times as severe as the 24 hours/room temperature test. Actual releases are therefore evaluated against limits corrected accordingly, i.e. numerically higher (milder) than in other national surveys by a factor of 3.

000) In Danish administrative practice the limit values are considered average values. This means that, based on sampling plans, the effective maximum values per objects are close to 2 times higher than stated. An actual enforcement would thus let about 76% of the survey objects pass as acceptable.

x) 88% would pass the test proposed in EEC document R/112/75

For the overglaze decorated ware, about 80% x) (from 69 - 88%) would expectedly pass the EEC working group limit of 10 mg/litre at room temperature for the first test, and most of the 69% would also pass the second extract limit of 5 mg/litre.

It is in good accordance with the observations from other national surveys, that the impact of a lowering of the lead limit in the Danish survey evaluation would be greater for the overglaze decorated than for the plain ware.

As it was found in the U.K. investigations, no lead problems seem to be connected to the enamelled iron ware.

As for glassware, a majority of plain drinking glasses etc. are to-day manufactured from non-lead constituents. In the Danish survey, therefore, the glassware objects are confined to lead crystal samples, which in few cases give rise to releases moderately above the regulatory limit value. A considerable decrease is always seen from first extract to the second in these cases, and an actual risk of contamination will be negligeable.

A special problem in connection with glassware, however, is presented through the practice of applying decorations on exterior surfaces within the mouthrim area. Such decorations will necessarily come into close contact with the lips and, during use, with a mixture of food (beverage) and saliva.

This question is not presented in the Danish survey results above, which only exemplify mouth rim releases from ceramic ware with decorations. It is therefore mentioned, that unpublished experiments have given evidence, that vast releases of lead (f.i. 100 mg lead per glass) from mouth rim decorated glasses seem to be the rule, rather than the exception. Presumably, the technological practice is inadequate for establishing a sufficiently firm binding of the decoration materials to the glass surfaces.

In the surveys of ceramics in Denmark in 1972 cadmium was included. A special report on this subject was presented to the EEC Symposium

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x) 69% would pass the test proposed in EEC document R/112/75.

on Mercury and Cadmium in Luxembourg, 3.-5. July 1973 to which is referred for further details. From the conclusions of this report, however, it is mentioned that specific uses of cadmium in surfaces of plain ceramic objects generally do not occur very often. However, when cadmium is used for decorated ware or as red, yellow or orange pigments in plain enamels, substantial releases in excess of established limits (Danish and other national limits as well as the considered EEC limit) are most often seen.

4.5 Survey of ceramics in W.Germany.

According to Dömling (1973), 500 samples of decorated porcelain have been investigated since 1972 at the Staatliche Chemische Untersuchungsanstalt, Erlangen.

65% of the samples did not release cadmium in measurable amounts by extraction for 24 hours at room temperature with 4% acetic acid, while 10% released from Zero to 0.5 mg/litre, and for 25%, the release was above 0.5 mg/litre. The maximum release which was found was 100 mg/litre.

In this survey, at least 75%[x)] of the samples would have passed the EEC working group limits, but the impact of lowering the limit cannot be evaluated.

4.6 Summarizing remarks on national surveys.

As already mentioned, these surveys do not necessarily reflect the actual market situations in the respective countries. Qualitatively, however, it seems justified to conclude the survey review on some obvious and general trends as follows.

Lead:

1) For pottery, earthenware, faience, porcelain etc. with underglaze decorations or no decoration, 79 - 93% of the objects presented in the national surveys would have passed the EEC working group limits[xx)] (i.e. 10 mg/litre in the first extract and 5 mg/litre in the second, the latter often being decisive). The impact of a several times stricter limit, as is seen in some national regulations, would only

x) Just 75% would pass the test proposed in document R/112/75

xx) 76-93% would have passed the test proposed in document R/112/75 mean a reduction in the number of acceptable objects by a few percent.

2. For overglaze decorated ceramic objects, 55 - 80%[x)] were estimated to pass the EEC working group limit. Here, the first extract would generally be the decisive.
   This group is vulnerable to a reduction of the lead limit. A reduction of the limit from 10 to 3 mg/litre (at room temperature) would probably mean that only 50 - 58% of the surveyed samples would pass the test.

3. For enamelled iron objects, no problems of lead releases have been presented at all from the surveys.

4. For glassware, the lead crystal glasses do not seem to pose any noticeable problems, due to the steeply decreasing release of lead from the initial to the second extraction.
   The surface qualities of decorated ware, however, may seem questionable, due to the loosely bound lead-based colours which are often used, also within the mouthrims of the objects. It remains to be seen, whether a sufficiently firm binding of lead-based decoration materials to the non-lead glass-surfaces can be technologically feasable.

Cadmium:

1) For plain ceramic ware covered with a cadmium pigmented glaze, a severe release of cadmium is presented in an Italian survey. About one third of 49 plain objects were tested and found to give cause to excessive releases of cadmium. The rather massive amounts of cadmium which could be seen in some 1st extracts, underlined also in this case the necessity of a limit for this extract.

2) For decorated ware, the Italian, British and German surveys indicate that a substantial, but very variable part of the objects would not pass the test considered by the EEC: 30% (Sampaolo et al.), 68% (Ravaglioli et al.) and 100% (U.K. surveys)[xx)], respectively, would meet a 1 mg/litre limit for the first extract, the remaining being objectionable.

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x) 50-69% would have passed the test proposed in EEC document R/112/75

xx) 30%, 68% and 91%, respectively, would have passed the test proposed in EEC document R/112/75.

In these surveys, the effect of reducing the limit for the first extract, f.i. to 0.5 mg/litre, would be small or insignificant. The German survey showed that 75% of 500 samples would pass a limit of 0.5 mg/litre in the first extract.

3) For the enamelled iron ware, the use of cadmium containing pigments is regularly connected with substantial releases of the metal, and it remains to be established whether such uses can be made adequately safe, at least as far as inside surfaces contacting foods are concerned.

4) For glassware, only decorated objects have been of any concern, and the remarks made for lead also apply here.

Chapter 5

5 Characterization of food in relation to migration of metals.

The migration of metals like lead and cadmium into food from ceramic surfaces is a process of highly complex nature, and a description in numerical terms of the individual parameters which determine this process is clearly prohibited. Yet, some basic assumptions can be made, especially with regard to the food acidity.

5.1 Significance of food acidity.

It is generally acknowledged, that one of the most important properties which may determine the aggressiveness of food towards ceramic surfaces, is the acidity. This is mainly connected to the use of lead as the alkaline parts of glaze compositions.

Sampaolo et al. (1973), for instance, deals with this question and mentions as an estimate, that about 10% of the diet belongs to the acid food groups. Such estimate is reasonably agreeing with an evaluation of a typical Danish diet, when the information in table 5 is considered (Danish Home Economic Council, 1974, Statistical Yearbook of Denmark, 1973).

From this table it can be seen, that about 400 grammes or 20% of a total diet (about 2 kg for an adult male person) can be grouped as markedly acid, i.e. pH <4.5. From these, however, some fresh fruit is eaten without coming into contact with ceramic surfaces, while some remaining parts of fruit as well as other acid food items most certainly will come into such contact. As an educated estimate, therefore it seems justified to consider 15% of this diet as the amount of acid food relevant in the present connection. And it seems further to be justified, considering the significance of this parameter, to deal with individual food items as being classified within the following 4 broad groups:

1) Acid (sour) solid food,
2) Non-acid solid food,
3) Acid (sour) liquid food, and
4) Non-acid liquid food,

using a pH of 4.5 as the acidity which divides the groups.

Table 5. Composition of a typical Danish diet

Food group	g/person/day pH <4.5	g/person/day pH >4.5	pH-range	Dominating acids
Milk, milk products non-sour		420 g	6.3-6.6	Citric acid 0.2-0.4%
Milkproducts, sour (buttermilk,youghurt etc.)	80 g		ca. 4.2	Lactic and citric acid
Eggs, cheese		65 g	4.8-9.5	
Meat, fish		230 g	5.5-6.5	Lactic acid
Bread, cereals		187 g	6-9	
Fats		80 g	6-6.5	
Potatoes, vegetables		227 g	5.0-6.0	Oxalic, citric
Fruit	150 g		2.5-3.5	Citric acid, 0.4-0.9%
Canned food, non-sour		60 g	ca. 6	
Canned food, acid	11 g		ca. 3	Citric acid
Beverages:				
Beer		320 g	4.5-5	
Soft drinks, juices	130 g		3.0-3.5	Citric acid
Wine	20 g		3.0-3.5	Tartaric acid
Total (per person)day):	391 g (acid)	1589 g (non-acid)		

Table 6. Stability constants of some food acids

	Lead			Cadmium		
	K_1	K_2	B_2	K_1	K_2	B_2
Acetic acid	2.18		2.92	2.0	0.7	
Citric acid	5.7			2.3		
Lactic acid	2.40	1.40			1.7	
Oxalic acid			6.54			1.77
Tartaric acid	3.78			4.5		

In this connection, it should be mentioned, that not only the acidity of food as measured in pH-values, but also the acid composition (cfr. table 5) may be of interest. This is mainly due to other characteristics, such as f.i. different complexing power of individual acids (and other food components) towards lead and cadmium.

In table 6 this is exemplified for 5 important food acids of which the stability constants with regard to lead and cadmium are given (cfr. Stability Constants, The Chemical Society, London, 1964). Both stepwise (K_1 and K_2) and cumulative (β_2) stability constants are shown and from this can be deducted, that four of these food acids: citric acid, lactic acid, oxalic acid and tartaric acid are all stronger complexing agents for lead, than is the acetic acid. For cadmium only lactic acid is a weaker complexing agent than acetic acid.

Quantitatively, it is noted from the table 6, that the highest stability constant relative to acetic acid is citric acid (for lead), which is also the dominating among food acids, cfr. fruits, juices and even milk products. This underlines the already available experimental evidence, that f.i. a 0.5% aqueous solution of citric acid is equivalent to 5% acetic acid as far as aggressiveness towards lead-containing ceramic surfaces is concerned (cfr. Galler et al., 1939; Ahmad, S. et al., 1964).

Chapter 6

6 Experiments on the release of lead and cadmium into food in relation to simulated test results.

Having reviewed the methods of simulated extractions and the surveys on the quality of ceramic surfaces, it will be attempted to evaluate the migration into food of lead and cadmium found experimentally under conditions of practical use, in so far as these results are - or can be - related to results obtained by the test-methods.

The following investigations have been available:

1) Dömling, H. (1973). For 4 kinds of decorated porcelain plates, the extraction of lead and cadmium with 4% acetic acid was compared to parallel and subsequent exposure with 4 different kinds of acid food.

2) Scholl, W. (1972). For 8 plain plates of different colours, the extraction of lead with 5% acetic acid, 2% citric acid and 15 different sauces (acid and non-acid) was determined.

3) Beyersdorfer, K. (1973). The release of lead from 4 overglaze colours and of cadmium from 1 colour into 4% acetic acid was compared to the release into 3% citric acid and into Coca Cola at $22^{o}C/24h$ and at $100^{o}C/1.5h$.

4) Park, J.R. (1974). The release of lead into 3 non-acid and 1 acid preparations of food was compared to the release into 4% acetic acid by the BS hot-test.

5) Engberg, Å. (1974). The release of lead and cadmium into sour and non-sour, hot and cold food and into beverages was investigated for plain ceramics (serving and oven-heating) and for overglaze decorated porcelain/faience (serving). The results were related to those of a preceding acetic acid test.

Although numerically limited, these investigations comprise a number of individual experiments which in a reasonably adequate way refer to food use situations illustrating combinations of food preparation - food type - utensil type as they are commonly seen in practice. The experiments are concentrated on plain ceramics and overglaze decorated ware, representing the majority of daily used objects and emphasis is placed on hollowware. In table 8 is listed a full series of treatment - food type - object combinations which can all be regarded as regular parts of normal eating practices. For each of the combinations it is indicated, whether experimental evidence has been found in the abovementioned references on lead and/or cadmium migration into the food. These positive illustrations are commented in the following one by one under the headings which are shown in table 8.

6.1 Oven-heating (cooking) of food.

Lead into hot acid food/plain ceramics. This situation is described by Park (1974) and Engberg (1974).

The type of casserole tested by Park (cfr. table 9) released 5.1 mg lead per litre by the BS-test, and the release was reported to be constant from one extract to the following, i.e. it represents such objects which exactly meet the requirements of the EEC working group test. The release of lead into acid food (Rhubarbs) was 1.65 mg/kg after cooking for 2.5 hours and might be estimated to 0.7 mg/kg after 1 hour cooking.

The first object tested by Engberg (table 9) just passed the Danish test, and the lead release into sour food (apricot soup) was 0.75 mg/kg after 1 hour oven-heating. As the EEC considered limit and the Danish regulation in this field are practically equivalent (cfr. page 28), it seems well justified to evaluate the lead release into acid food by 1 hour cooking to be 0.7 mg/kg for objects just passing the limits.

Proportionality between acetic acid test results and releases into food was not demonstrated in this case.

Lead into hot non-acid food/plain ceramics. The three casseroles tested by Park (table 9) were also just meeting the EEC working group limits, and the average lead release into non-acid food (babyfood; vegetables and meat) by 2.5 hours cooking was 0.06 mg/kg. This would

Table 8. Practical use combinations of food treatment-food type-utensil

Type of treatment	Type of food	Type of object	Reference:	Pb	Cd
1. Oven-heating (cooking)	Hot acid	Plain ceramic	Table	9	10b
	Hot non-acid	Plain ceramic	Table	9	10b
2. Serving of food	Hot acid	Overglaze decora.	Table	11	12
	Hot non-acid	Overglaze decora.	Table	11	12
	Cold acid	Plain ceramic	Page	56	-
	Cold non-acid	Plain ceramic	None		
3. Serving of beverages	(Hot acid)	Not usual	None		
	Hot non-acid	Plain ceramic	Table	13	10a
	Cold acid	Plain ceramic	Table	13	10a
	Cold non-acid	Plain ceramic	None		
4. Short storage (keeping) og foods and beverages	Cold acid food	Plain ceramic	None		
	Cold acid food	Overglaze decora.	Table	14	14
	Cold non-acid food	Plain ceramic	None		
	Cold non-acid food	Overglaze decora.	None		
	Cold acid bev.	Plain ceramic	Table	13	10a
	Cold acid bev.	Overglaze decora.	Page	59	60
	Cold acid bev.	Overglaze decora.	Table	14	14
	Cold non-acid bev.		None		

Table 9

Plain ceramics: Oven heating of sour and non-sour food

Comparison of extraction of lead by acetic acid and food

Sour food

	Acetic Acid tests Conditions	Results	Food	Treatment	Pb release % of acetic acid test	Pb release mg/kg food
Parks, J. (1974)						
Casserole	BS2	5.1	Rhubarb	Cooked 2½h	33%	1.65
Engberg, Å. (1974)						
Jug	4% 100°C 3x30 min.	2.8	Apricot soup	175°C 1h	27%	0.75
Bowl	"	5.8	"	"	13%	0.72
Bowl	"	12	"	"	2%	0.24
Bowl	"	27	"	"	6.4%	1.74

Non-sour food

Parks, J. (1974)						
Casserole	BS2	5.1	Tapioca	Cooked 2½h	1.2%	0.06
Casserole	BS2	5.0	Curry	Cooked 2½h	1.2%	0.06
Casserole	BS2	5.0	Heerings	Cooked 2½h	1.0%	0.05
Engberg, Å. (1974)						
Cup	3x30 min. 100°C	3.9	Babyfood (veg.and meat)	175°C 1h	2.6%	0.10
Bowl	"	6.6	"	"	1.8%	0.12
Jug	"	10.7	"	"	3.4%	0.36
Bowl	"	27	"	"	<0.2%	<0.05

correspond to 0.024 mg/kg at a 1 hour cooking, if the release-time relationship is linear.

For the first 3 plain objects tested by Engberg (table 9), the factors with which the Danish limit were exceeded, are 1.3, resp. 2.2 and 3.5. Reduced by these factors, the release into food (baby-food: vegetables and meat) would have been 0.08 mg/kg, resp. 0.05 and 0.10 mg/kg for objects just meeting the test limit of 3 mg/litre. As the two tests are evaluated as practically equivalent, the Danish results are somewhat higher than the English, although not by orders of magnitude (it is noted that the releases found here are near to the detection limit of the analytical methods). An average value of 0.05 mg/kg may be used as a best possible estimate for lead release by cooking of this type of food for 1 hour.

Cadmium into hot acid food/plain ceramics. This combination is only illustrated by one example from Engberg (1974), cfr. table 10b. For an object releasing 2.2 mg cadmium per litre by the Danish test (or 2.2 times the Danish limit), the cadmium release into acid food is 0.36 mg/kg. Provided proportionality between test exposure and migration into food, this would correspond to 0.16 mg per kg of acid food for an object meeting the Danish test limit and 0.07 mg/kg [x)] when meeting the EEC working group limit (cfr. page 30).

Cadmium into hot non-acid food/plain ceramics. Similarly, the one object tested by Engberg cooking baby-food (vegetables and meat) released cadmium into the test solution corresponding to 5.7 times the Danish test limit and 0.075 mg/kg into the food. This would indicate a release of 0.013 mg Cd per kg of non-acid food for an object just meeting the Danish test limit, and 0.006 [xx)] mg/kg for one meeting the EEC proposed limit.

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x) 0.05 mg/kg, according to EEC document R/112/75

xx) 0.004 mg/kg, according to EEC document R/112/75

Table 10 a: Release of cadmium from plain ceramics used for serving and short storage of beverages
Comparison with release by preceding Danish acetic acid test (Engberg, 1974)

Sample no.	Object type	Colour inside	Release of Cadmium Acetic acid test 90 min./100°C	Release of Cadmium Serving of hot, non-acid beverage (tea) 30 min. cooling from 100°C ppm	% of testr.	Release of Cadmium Serving of cold, acid beverage (orange juice) 1 hour at 25°C ppm	% of testr.	Release of Cadmium Short storage of cold, acid beverage (orange juice) 24 hours at 25°C ppm	% of testr.
1864	Mug	brown	0.25	<0.03	<12 %	<0.03	<12 %	0.030	12 %
323	Bowl	orange	2.25	0.032	1.4%	0.094	4.2%	0.029	1.3%
1726	Mug	red	4.65	0.134	2.9%	<0.03	<2 %	0.040	1 %
1725	Mug	red	13.15	0.135	1.0%	0.032	0.24%	0.087	0.67%
		Average (% of testres):			1.7%				

Table 10 b: Release of cadmium from plain ceramics used for ovenheating (cooking) of food
Comparison with release by preceding Danish acetic acid test (Engberg, 1974)

Sample no.	Object type	Colour inside	Release of Cadmium Acetic acid test 90 min./100°C	Release of Cadmium Ovenheating of acid food (apricot soup) 175°C 1 hour ppm	% of testres.	Release of Cadmium Ovenheating of non-acid food (babyfood) 175°C 1 hour ppm	% of testres.
558	Butter jug	red	5.65			0.075	1.3%
305	Jug	red	2.2	0.36	16%		

Table 11: Release of lead from overglaze-decorated plates used for serving

Comparison with release by preceding Danish acetic acid test. (Engberg, 1974)

Sample no.	Object type	Decor. colour inside	Release of Lead Acetic acid test 90 min. at 100°C	Release of Lead Serving of hot, acid food (apricot soup), 5 min., removed with spoon ppm	 % of testres.	Release of Lead Serving of hot, non-acid food (baby food), 5 min. removed with spoon ppm	 % of testres.
F2528	Soup plate	multi-colour	2.1	<0.05	<2.4%		
F1910	Soup plate	multi-colour	2.8			0.07	2.5%
464	Soup plate	Orange/ red	5.5	1.2	22 %		
F 119	Soup plate	red/ Yellow	6.0			0.04	0.7%
F 78	Soup plate	Orange/ red	10.8	1.5	14 %		
F2229	Soup plate	Orange/ red	19.6	1.9	9.7%	0.30	1.5%
F 72	Soup plate	Yellow/red blue/black	23.0	1.0	4.3%	0.02	0.1%
F1986	Soup plate	blue/ black	53.6	0.58	1.1%	0.20	0.4%
		Average (% of testres.):					1 %

6.2 Serving of food.

Lead into hot acid food/overglaze decorated ware.
This subject has been treated by Engberg, (1974). For acid food, 6 plates were tested (cfr. table 11) the results of which indicate that a proportionality between test results and release into food does not exist in the full range of releases. The plates showing high, or even excessive lead releases, clearly demonstrate a tendency to level out as far as the release into food is concerned. Provided, however, that the functional relationship between release into acetic acid and into food can be properly described by a smoothed curve in the moderate ranges around test limits, it can be justified to estimate a release of about 0.7 mg per kg of food for an object just fulfilling the Danish test limit.

Using the conversion factor of 2 for overglaze decorated ware for the Danish hot test related to the 24 hour room temperature extraction considered by the EEC working group, an object fulfilling the EEC limit of 10 mg/litre in the first extract, would be expected to release 20 mg/litre by the Danish hot test. The best estimate for the release into food for such a plate would thus be 1.5 mg/kg [x)] using the smoothed curve in the limited range mentioned above.

Lead into hot non-acid food/overglaze decorated ware. Among 5 soup plates used for serving baby-food, tested by Engberg (1974), cfr. table 11, one plate would be fulfilling the Danish test limit, while 3 [xx)] (up to 19.6 mg lead/litre by hot test) probably would meet the EEC proposed test limit. The corresponding range of releases into food is 0.04 - 0.30 mg/kg.

In this case, too, the releases into food level out, or even decrease, for the two remaining plates with high releases into the test solution. On the average for all 5 plates the release into non-sour food by serving from decorated ware is 1% of the test results, and it may be estimated that 0.03 mg may migrate per kg food for an object meeting the Danish test and 0.2 mg/kg for one meeting the EEC working group test.[xxx)]

x) A release of 1.4 mg/kg would be expected from objects meeting limit in EEC document R/112/75
xx) 2 plates would meet the test limit of EEC document R/112/75
xxx) A migration of 0.1 mg/kg would be expected for objects meeting limit in EEC-document R/112/75

Table 12. Release of cadmium from overglaze-decorated plates used for serving
Comparison with release by preceding Danish acetic acid test (Engberg, 1974)

Sample no.	Object type	Decoration colour	Release of Cadmium Acetic acid test	Release of cadmium Serving of hot, acid food (apricot soup); 5 min, removed with spoon		Release of cadmium Serving of hot, non-acid food (baby-food); 5 min, removed with spoon	
			90 min. 100°C	ppm	% of testres.	ppm	% of testres.
F 72	Soup plate	Yellow/ red/blue/ black	1.87	0.17	9%	0.011	0.6%
464	Soup plate	red/ orange	3.33	0.28	8.4%		
F 78	Soup plate	red/ orange	3.53	0.39	11 %		
F 119	Soup plate	red/ yellow	4.71			0.28	6.0%
F 305	Soup plate	orange/ Yellow/black	7.6	0.47	6.2%	0.30 [1)]	4.0%
F2229	Soupplate	orange	8.3	0.61	7.4%	0.21	2.5%
		Average (% of testres.):			8.4%		3.2%

1) Mashed potatoes.

Cadmium into hot acid food/overglaze decorated ware. Engberg (1974) has tested the release from 5 decorated plates by serving of acid food (apricot soup), cfr. table 12. It is noted that in this case, the release into the food is found to be proportional to the release into test solution, and it can be estimated that for objects just meeting the Danish test limit, the release into acid hot food will be numerically about 8% of this limit, or 0.08 mg Cd/kg of food.

As a pronounced decrease is seen from the 1st to the 2nd extract of cadmium test for the overglaze decorated ware, the ratio 3 (cfr. page 30) should be applied in the transformation of Danish regulation to EEC working group proposal, and a release of 0.24 mg Cd/kg of food would be the estimate for an object just fulfilling the EEC limit.[x)]

Cadmium into hot non-acid food/overglaze decorated ware. The release of cadmium by serving from overglaze decorated plates is estimated from the data by Engberg (1974), cfr. table 12, to be on the average 3% or about 0.03 mg/kg food for objects meeting the Danish test limit. This means that objects fulfilling the limits considered by the EEC working group or the BS test would release about 0.09 mg/kg into non-acid food.[xx)]

Lead into acid cold food/plain ceramics. The release of lead by serving from plain ceramic plates has been treated by Scholl (1972), who investigated a set of 8 earthenware (Steingut) plates with varying colours of the glaze.

Scholl finds that the choice of colour is without influence on the lead release, which is found to be 2.8 mg/litre by extraction with 5% citric acid and 2.5 mg/litre with 2% acetic acid, both solutions tested for both 10 minutes and 2 hours (and presumably at room temperature).

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x) Following EEC-proposal doc. R/112/75, the ratio mentioned would be 1.5 and a release of 0.12 mg Cd pr. kg food is estimated for objects meeting EEC-limit.

xx) A release of 0.05 mg/kg would be expected for objects meeting limit of EEC document R/112/75.

The difference between the results after 10 minutes, resp. after 2 hours is claimed to be small, but is not specified. By applying the same exposure times, the plates were tested with 15 non-specified, different sauces, dressings and organic acids normally used for salad mixtures. Significant, but not specified differences were found between the releases into different sauces. Further to the acidity, the complexing power of the food is mentioned as of importance.

From Scholl's results are seen that the average migration of lead into the acid sauces was 1.5 mg/litre while for all 15 sauces (acid and non-acid) the average was 0.87 mg/litre. These figures indicate extractive powers of 60%, respectively 35% of what is found by Scholl for 2% acetic acid by the same duration and temperature of exposure.

Scholl reports that the decrease of lead releases by continuous extractions was very small. Due to lack of data obtained by usual test methods, however, the information cannot be evaluated to give estimates of releases in relation to specified test methods.

6.3 Serving of beverages.

Lead into hot non-acid beverages/plain objects. Engberg (1974) has investigated the lead release by serving of tea from 8 plain ceramic objects, cfr. table 13. An average of 0.72% of the acetic acid test release is found for the release into tea, the results ranging from 0.2 - 3.6%. At the level of the Danish test limit (3 mg/litre), this would imply that a typical release of lead from an object just meeting this limit would be estimated to be 0.02 mg per litre of tea. For an object meeting the BS or the second extract limit consedered by the EEC working group, a release of about 0.10 mg/litre could be expected. x)

Lead into cold acid beverages/plain objects. Engberg (1974) tested the lead releases by serving and short storage (24 hour keeping) of juice from 8 plain ceramic objects, which had prior been tested with tea (cfr. table 13). An average of 0.9% of the release by acetic

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x) Unchanged by EEC-proposal doc. R/112/75

Table 13. Release of lead from plain ceramics used for serving and short storage of beverages. Comparison with release by preceding Danish acetic acid test (Engberg 1974)

Sample no.	Object type	Colour inside	Release of Lead, Acetic acid test	Release of Lead: Serving of tea, (hot,non-acid bev.) 30 min,cooling from 100°C		Release of Lead: Serving of juice (cold, acid beverage) 1 hour at 25°C.		Release of Lead: Short storage of juice (cold, acid beverage) 1 hour at 25°C.	
			90 min. 100°C	ppm	% of testres.	ppm	% of testres.	ppm	% of testres.
322	Mug	green	3.6	0.13	3.6%	0.07	1.9%	0.07	1.9%
786	Bowl	brown	6.6	<0.05	<0.8%	0.11	1.7%	<0.05	<0.8%
323	Bowl	orange	15.3	0.05	0.33%	0.17	1.1%	0.06	0.39%
1726	Mug	red	20.6	<0.05	<0.24%	<0.05	<0.2%	0.14	0.7%
302	Jug	green	29.2	<0.05	<0.17%	<0.05	<0.2%	0.21	0.7%
F2326	Mug	brown	48.9	0.27	0.55%	0.56	1.1%	1.15	2.4%
F1725	Mug	red	57.2	0.21	0.37%	0.25	0.4%	0.63	1.1%
F1864	Cup	brown	92.4	0.17	0.2%	0.87	0.9%	1.75	1.9%
Average (%					0.72%		0.91%		1.2%

acid test was found, but the release into juice was not clearly proportional to the release in the simulated test. In the best possible judgment, the data would indicate a release of about 0.06 mg/kg (or 2% of the acetic acid test result) for objects just fulfilling the Danish test limit, and 0.17 mg/kg for objects meeting the EEC working group limit considered for second extract. x)

Cadmium into hot non-acid beverages/plain objects. Exemplified by tea, Engberg (1974) finds an average release of cadmium of 1.7% of the result obtained by a preceding acetic acid test, cfr. table 10a. This means that the estimated release of an object fulfilling the Danish test limit is 0.017 mg cadmium/litre tea. This would correspond to about 0.05 mg/litre for objects fulfilling the Working group limit for 1st extract, and 0.025 mg/litre if the second extract limit is decisive. xx)

Cadmium into cold acid beverages/plain objects. This is tested for orange juice, tested by Engberg (1974), cfr. table 10a, who finds cadmium releases in the range 0.24-4.2% of the results obtained by the Danish acetic acid test. The typical release into juice from objects corresponding to the Danish test limit is difficult to estimate due to variations in the experimental data. About 0.03 mg/litre could be proposed as a guided guess. This would correspond to 0.1 mg/litre for objects fulfilling the EEC considered limit for the first extract - and 0.05 mg/litre if the second extract limit is decisive xxx).

6.4 Short storage (keeping) of food and beverages.

For the purpose of these considerations, by short storage, a 24 hours keeping under normal household circumstances is understood.

Lead from plain ceramic objects. 8 objects tested for serving of tea, followed by serving of juice (cfr. table 13) were further tested for lead

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x) Unchanged by EEC-proposal doc. R/112/75

xx) 0.025 mg/kg to be expected for objects meeting limit of doc. R/112/75

xxx) 0.05 mg/litre to be expected for objects meeting limit of doc. R/112/75.

releases during subsequent 24 hour storages by Engberg (1974). For 3 of these objects, which would pass both the EEC working group test and the Danish test, releases were found equal to or lower than the release during the first 1 hour serving period. For the remaining 5 objects showing high to excessive releases, the amounts released by 24 hours storage were about twice the amounts released during the preceding 1 hour. On this basis, the best estimate of the release by short storage in vessels fulfilling the Danish test limit is 0.06 mg/kg juice.

Cadmium from plain ceramic objects. The release into orange juice during a 24 hours storage was found to be 0.03 mg/kg for objects fulfilling the Danish test limit, cfr. Engberg (1974) - table 10a.

Lead from overglaze decorated ware. In the cases so far treated on situations of cooking and serving, it has been characteristic, either that the food migration test was preceded by an acetic acid test on the same objects, or that the release during consecutive acid extractions was constant. Thus, the release into food would not unduly reflect the special conditions during the first ectraction of new objects, but rather the release to be expected by continued use. In the work of Beyersdorfer (1973) this situation is reversed. He compares the extractive power of acetic acid and of Coca Cola under identical test conditions, by measuring the lead releases into the beverage from a new surface, in comparison to the release from a corresponding new surface into acetic acid.

The absolute figures for lead release are not given by Beyersdorfer. It is mentioned that for 4 different overglaze colours, the release into Coca Cola is 57% (range 30 - 86%) of that by acetic acid under the same conditions.

Dömling (1973) has investigated 4 different sets, each of 5 identical overglaze decorated plates (cfr. table 14). All of the plates were first extracted for 24 hours at room temperature with 4% acetic acid. Subsequently, one plate of each set was extracted again with acetic acid, another was exposed to lemon juice, a third to grape juice, and the fourth and fifth to Worcester sauce and apple sauce, respectively. All extractions were made at room temperature for 24 hours.

Table 14. Overglaze decorated ceramic objects
Short storage (24 hr. keeping) of acid foods (Dömling, 1973)x)

LEAD

Object (plate)	First extract.	Second extraction or treatment (all 24 hr/room temp.)					
	Acetic acid,4%	Acetic acid,4%	Lemon juice	Grape juice	Worcester sauce	Apple sauce	Averages (4 sauces)
nr. A	100%	24%	35%	26%	55%	37%	38%
nr. B	100%	40%	42%	62%	83%	55%	61%
nr. C	100%	20%	15%	16%	24%	26%	20%
nr. D	100%	28%	20%	18%	25%	26%	22%

CADMIUM

Object (plate)	First extract.	Second extraction or treatment (all 24 hr/room temp.)					
	Acetic acid,4%	Acetic acid,4%	Lemon juice	Grape juice	Worcester sauce	Apple sauce	Averages (4 sauces)
nr. A	100%	28%	15%	17%	25%	26%	21%
nr. B	100%	42%	30%	42%	64%	45%	45%
nr. C	100%	20%	13%	13%	25%	24%	19%
nr. D	100%	30%	28%	26%	35%	42%	40%

x) No absolute figures given in original reference.

In good accordance with the results given in table 2, page 20, the results of the second acetic acid extraction was on the evarage 28% (range 20 - 40%) of that of the first extraction of the same plates. For comparison, the average for lemon juice extraction was on the average 28% (range 15 - 42%) of the first (acetic acid) extraction result, i.e. the extractive power of lemon juice is found equivalent to that of 4% acetic acid under identical test conditions.

Correspondingly, the extractive power of grape juice is 31% (range 16 - 62%). Of Worcester sauce 47% (range 24 - 83%) and of apple sauce 36% (range 26 - 55%) of the first acetic acid extraction. These

liquids are therefore found to be generally similar to or slightly more aggressive than acetic acid for the plates tested here.

Cadmium from overglaze decorated ware. Beyersdorfer (1973) who measured the release of lead into Coca Cola compared to the release into 4% acetic acid, has included measurement of cadmium release in one of the abovementioned experiments. For one ceramic overglaze colour, he finds a release of cadmium corresponding to 22% of the release into 4% acetic acid in a parallel experiment under the same conditions.

Dömling (1973) in his experiments, also tested the releases of cadmium and compared a first and second acetic acid extraction, as mentioned above under lead. For 4 different types of plates, the result of the second extraction with acetic acid (24 hours/ room temperature) was 30% (range 20 - 42%), of that of the first extraction. For comparison, the releases into lemon juice was 22% (range 13 - 30%), for grape juice 25% (range 13 - 42%), for Worcester sauce 37% (range 25 - 64%) and for apple sauce 34% (range 24 - 45%) of the result for the preceding acetic acid extraction. On the whole, these juices and sauces were found of an aggressiveness similar to that of 4% acetic acid.

Chapter 7.

7 Assessment of a potential total food contamination from ceramic surfaces.

In the preceding chapter, estimates have been made on lead and cadmium migrations into individual foods from ceramic surfaces. In so far as each of these estimates are based on practical use examples, they reflect typical situations from daily eating habits, and they may be taken as representative of potential contaminations of each of the food groups to which they belong and which have been suggested for this study.

Considering the typical Danish diet shown in table 5, page 46, as an example, a breakdown into such groups according to aggressiveness towards ceramic surfaces could be quantitated as follows:

Solid or semi-solid foods:

1. Hot non-acid :	Meat, fish	200 g		
	Fats	40 g		
	Potatoes, vegetables	175 g		
	Canned food	60 g		
	Cereals	35 g	510 g	
2. Hot acid	Fruit dishes etc.	50 g	50 g	
3. Cold non-acid	Egg, cheese	65 g		
	Bread	150 g		
	Fats	80 g	295 g	
4. Cold acid	Milk products	80 g		
	Fruits	50 g		
	Canned food	10 g		
	Meat, fish	30 g		
	Potatoes, vegetables	50 g	220 g	1075g

Beverages:

5. Hot non-acid	Coffee, tea	500 g	500 g	
6. Hot acid	Not common			
7. Cold non-acid	Milk	420 g		
	Beer	320 g	740 g	
8. Cold acid	Soft drink, juice	130 g		
	Wine	20 g	150 g	1390g

If the estimates of migrated lead and cadmium concentrations are combined with these food group figures, a total diet contamination can be estimated based, of course, on the same presuppositions, which applied for the estimates, namely that the utensils were just meeting the specified limits.

Referring to the Danish and the EEC working group test limits, the following total contamination for lead may be calculated: x)

Food Group	Treatment	Type of object	For objects meeting			
			Danish test		EEC prop.test	
			mg/kg	µg	mg/kg	µg
Food:						
1. Hot non-acid	Cooking	Plain ceramic	0.05	26	0.05	26
	Serving	Decorated ware	0.03	15	0.20	102
2. Hot acid	Cooking	Plain ceramic	0.70	35	0.70	35
	Serving	Decorated ware	0.70	35	1.5	75
3. Cold non-acid	Serving	Decorated ware	0.00	0	0.00	0
4. Cold acid	Serving	Plain ceramic	0.06	13	0.17	38
Beverages:						
5. Hot non-acid	Serving	Plain ceramic	0.02	10	0.10	50
6. Hot acid	-	-	-	-	-	-
7. Cold non-acid	Serving	Plain ceramic	0.00	0	0.00	0
8. Cold acid	Serving	Plain ceramic	0.06	9	0.17	26
Total migration per person per day:				143 µg		353 µg
		per week:		∿1.0 mg		∿2.5 mg

For the comparison, the FAO/WHO provisional tolerable weekly intake, as recommended in 1972 (FAO/WHO, 1972) is 3 mg of lead per person.

This means that for the diet, treatment and choice of ceramic objects treated here, a set of objects which is just meeting the requirements of an existing Danish regulation is evaluated to give rise to a contamination of the food corresponding to about 33% of a total tolerable intake. And that, for a set just meeting the test limits considered by the EEC working group, a contamination level would possibly amount to about 2.5 mg/person/week or 80% of the total tolerable intake.x)

x) Cfr. Appendix.

From the set of data based on Danish test limits, it is seen that 60 g per day or about 42% of the total estimated contamination expectedly derive from cookingware objects and the remainder from tableware. In the case of EEC working group limits, the same amount, but then only about 17% of the total lead is estimated to come from the cookingware, while 83% derive from the tableware. x)

This estimate of total contamination from ceramic utensils in "normal" use for food, is to be regarded as a basis, from which both positive and negative deviations neccessarily should be considered.

Among the positive deviations, pointing towards possibly higher contamination levels should be mentioned·

1) It is noted that hollowware limits are used throughout this study. However, some groups of tableware objects would probably be classified into a flatware group of objects, for which somewhat higher limits may be anticipated. Consequently, the contamination from such plates my be expected somewhat higher than indicated above, even if they fulfill the test limits.

2) A potential use of ceramic objects, which has been practised in several cases in which actual lead poisonings have been observed (see next chapter), is not included in this summation of potential, total intakes. This is the short storages (keepings for up to a few days) of acid soft-drinks, beverages etc. which is a food-utensil combination liable to great variations in daily practice, especially as far as volume of consumption is concerned.

3) The use of ceramic objects for long storages of both liquid and solid acid foods is not included in the potential intake evaluation.

On the other hand, negative deviations from the potential intake evaluation, i.e. pointing towards lower contamination levels, should be mentioned:

1) If a certain limit level is established as a maximum level, it can be expected to be the aim of ceramic ware producers, in the positive

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Cfr. Appendix

interest of meeting this limit, to maintain a ceramic surface quality which will guarantee this limit. Statistically this would imply an average level of practical migration in the order of 2 times lower than the limit levels applied in this study.

2) The release of lead is liable to decrease with time. Although, in this study, it has been attempted to base contamination estimates on results connected to continued use, a further decrease of lead releases may still be expected. However, this argument is valid only for objects of a certain surface quality; for less resistant surfaces, it is reminded that significant releases may continue for long periods of practical use.

For cadmium, a total contamination may be calculated as follows:[x)]

Food Group	Treatment	Type of object	For objects meeting			
			Danish test		EEC prop.test	
			mg/kg	μg	mg/kg	μg
Food:						
1. Hot non-acid	Cooking	Plain ceramic	0.013	7	0.006	3
	Serving	Decorated ware	0.03	15	0.09	46
2. Hot acid	Cooking	Plain ceramic	0.16	8	0.07	4
	Serving	Decorated ware	0.08	4	0.24	12
3. Cold non-acid	Serving	Decorated ware	0.00	0	0.00	0
4. Cold acid	Serving	Plain ceramic	0.03	7	0.10	22
Beverages:						
5. Hot non-acid	Serving	Plain ceramic	0.017	9	0.05	25
6. Hot acid	-	-	-	0	-	0
7. Cold non-acid	Serving	Plain ceramic	-	0	-	0
8. Cold acid	Serving	Plain ceramic	0.03	5	0.10	15
Total migration per person per day:				55 μg		127 μg
		per week:		∿0.4 mg		∿0.9 mg

For comparison, the FAO/WHO recommendation on maximum tolerable weekly intake (FAO/WHO. 1972) is 0.4 - 0.5 mg cadmium per person.

Thus, if a person would consume all his food from utensils just fulfilling the Danish test limits, then 80-100% of the total tolerable intake could be expected potentially to be present from this source. And, for a set of

x) Cfr. Appendix.

objects just meeting the EEC considered limits, a contamination level is estimated to amount to the order of 200% of the total tolerable dosis.

The limits, therefore, for cadmium appear to leave no margin at all or may even be exceeded by a factor of 2.

Similar to the remarks made for lead, it is noted that, for the set of data referring to the Danish test limits, 15 μg or 28% of the total estimated contamination is expected to come from cookingware, and the remaining 72% from tableware. If the EEC working group limits apply, the contribution from cookingware will be 7 μg or 6% of the total load. x)

For cadmium, of course, the same remarks as given for lead concerning possible positive and negative deviations from the evaluated total contaminations should be considered. In this case, however, a further remark on the recently discovered influence of light conditions (cfr. page23) would be valid.

Cfr. Appendix

Chapter 8

8 Reported cases of acute poisonings due to migration.

Finalizing this study, it is found appropriate to include a brief discussion of the circumstances under which the use of ceramic household objects has actually led to acute poisonings.

8 such cases published during the years 1958-72 will be reviewed here on the background which is established by the discussion in the preceding chapters. The eitht cases are reported by Whitehead et al., 1960; Harris, 1967; Lewin & Lundin, 1968; Klein et al., 1970; Dickinson et al., 1972; California's Health, 1971; Williams, 1972 and Clark, 1972.

Type, use and origin of suspected objects.

In 6 of the 8 cases, the ceramic objects causing lead poisonings were jugs, pitchers and vessels which were all used for short storages (keepings) of beverages, like soft drinks, juices and home-made wines. In one case, the objectionable object was a glazed mug, used for serving of soft drink, and in the remaining case, cocktail glasses with an interior "frosting" made from lead compounds were used in daily drinking of whisky diluted with soft drink (7-up).

In these cases, 4 examples were connected to normal purchases of commercial ceramic ware in the respective countries in Europe and North America. One example was presented as caused by an amateur-made ceramic mug, while the objects in the 3 remaining cases were all bought as souvenirs in Europe or Latin-America.

Estimates of lead intakes.

The periods of use varied from a few days up to two years, but only in two cases, estimates of the daily lead intakes are given. These are presented by Harris (1967), who describes a 55 years old male, estimated to have taken 3 mg lead/day through a period of 2 years, and by Dickinson et al. (1972), estimating daily doses of 8 mg/person during 6 months.

Persons intoxicated.

In 3 of the reported cases of lead poisoning caused by ceramic ware lead releases, children were involved. One case was fatal, viz. a 2 years old boy (cfr. Klein et al., 1970). In all other cases, recoveries were reported from the varying degrees of abdominal pains, and anemias with fatigue, which were regularly described as the main symptoms.

Test of objects for lead releases.

Most of the suspected objects were tested, for actual lead releases as parts of case investigations, diagnoses etc.:

In the case just mentioned which developed to be fatal, a jug was found to release into apple juice, 157 mg lead per litre during three hours and 1300 mg/litre after 3 days. In one of the cases (Harris, 1967) with an estimated lead intake, a release of about 10 mg lead per litre was found with Coca Cola after 30 minutes extraction at room temperature.

In the case involving cocktail glasses for drinking (Dickinson et al., 1972), 12 mg/litre was released into the drink after 30 minutes, and in a fourth case (Williams, 1972) 40 mg/litre was released into water, while 467 mg/litre migrated into lemon-water in 3 days. In a further instance, (Whitehead et al. 1960) home-made wine contained 7.5 mg lead per litre after having been stored for 48 hours in a ceramic vessel at an early stage of production. This vessel released about 1000 mg/litre into hot 1% hydrochloric acid by an extraction of unspecified duration.

Only in one instance, a legislative test method was used directly (Lewin & Lundin, 1968). This was a jug used for drinking, which, when tested according to Swedish Legislation (3 x 30 minutes boiling with 4% acetic acid) showed a release of 348 mg lead per litre.

In the final two cases were found releases of 1.16 mg of lead into a single washing with 24 ml 5% acetic acid (California's Health, 1971), and 460 mg per litre of 5% acetic acid by a 4 hours/room temperature extraction, (Clark, 1972), respectively.

Summarizing these 8 cases, some conspicious characteristics are connected to them:

1) Several of the lead releases which are reported are excessively high compared to any existing regulatory limits, although some of them are still comparable to maximum recorded releases presented by recent national surveys.

2) In the two cases, where an estimate of the daily intake is presented, this margin between actual releases and regulatory limits was relatively low, however. As an estimate in these cases, a factor of only 10 - 25 x separates the recorded daily intakes (down to 3 mg/day during a 2 years period) connected to manifest symptoms of acute lead-poisoning from such intakes which in this study have been rendered possible as potential migration levels when based on existing or proposed regulations within the EEC.

3) In all cases, the intoxications were due to lead from plain surfaces, released into various sorts of beverages. On the other hand, no cases of cadmium intoxications are recorded as caused by releases from ceramic surfaces.

Such conclusions underline the importance of establishing standards on the quality of ceramic utensils, the primary and immediate aim being to avoid new cases of poisoning. The further aim, however, should be underlined too, as it has been the purpose of this study. Quality standards on ceramic surfaces should be of a character which ensures the proper protection of daily diets against regular contaminations.

It is the general conclusion of the study that ceramic ware as a source of food contamination is not insignificant, even when kept within specified quality standards. Dependant of the details of the standard, of the metal concerned, and of the individual pattern of eating habits, the contribution to the total human load may vary. But it is felt to be substantiated by the study that it will most certainly be measurable, it may be equal to, and it may even in cases moderately exceed the presently recommended levels of tolerable intakes.

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Appendix

Amendments and revisions to the report following the final version for a proposed EEC-directive on lead and cadmium releases from ceramic surfaces. (Doc. R/112/75)

Re page 11, table 1

EEC-proposal for directive deals with ceramic surfaces (type 1), only, under the following circumstances:

Metals	%Acetic acid	Temp.	Duration	Limit Pb	Limit Cd	Remarks
Pb,Cd	4	Room t.	24 hr	1 mg/dm^2	0.1 mg/dm^2	Flatware) Tablew.
				5 mg/l	0.5 mg/l	Holloww.)
				2.5 mg/l	0.25 mg/l	Childrens plates
				0.5 mg/dm^2	0.05 mg/dm^2	Cookingware, Flat
				2.5 mg/l	0.25 mg/l	Hollowware

Re page 25, Section 3.1

EEC-proposal for directive recommends a decisive limit of 5 mg/l for the first extract, only.

Re page 26, Italy

Following the EEC-proposal (R/112/75), the considered Italian limit by 1^{st} extraction is evaluated to be about 2 times more restrictive than the EEC limit. Discussion on EEC 2^{nd} extraction becomes obsolete.

Re page 26, Ireland and U.K.

Following the EEC-proposal (R/112/75), the Irish, British (and German?) limits is evaluated to be about 40% milder than the proposed EEC-limit.

Re page 27, The Netherlands

Following the EEC-proposal (R/112/75), the Dutch limit is estimated to be 2 times milder than that of the EEC document.

Re page 28, Denmark

Following the revision of both limit values and temperature conditions etc. in EEC proposal (R/112/75), the Danish limit for cookingware is evaluated to be equivalent to the EEC proposal.

Re page 28, Italy

Following the EEC-proposal (R/112/75), the Italian consideration of limits connected to hot temperature test is evaluated to be about lo times (for 100°C), resp. 2.5 times (for 120°C) less stringent than the EEC proposal.

Re page 28, United Kingdom

Following the EEC-proposal (R/112/75), the British Standard limit for lead from cookingware is evaluated to be milder than the EEC proposal in the ratio 5 : 7.

Re page 29, Denmark

Following the EEC-proposal (R/112/75), the Danish regulations prescribe a test for cadmium which is about 1.5 times more strict than the EEC proposal as far as tableware is concerned, while about 3 times milder for cookingware.

Re page 30, Italy

Following the EEC-proposal (R/112/75), the considered Italian limit for cadmium from tableware is about 3-4 times more restrictive than the EEC-proposal. In the case of cookingware it is judged to be about 5 times milder.

Re page 30, Ireland

Following the EEC-proposal (R/112/75), the Irish and the EEC proposed limits are practically equivalent.

Re page 30, The Netherlands

Following the EEC-proposal (R/112/75), the Dutch cadmium limit is estimated to be slightly milder than the EEC-proposal.

Re page 31, concluding remarks to chapter 3

Following the proposals of doc. R/112/75, the over-all variation of the degree of restrictiveness is described with a range of factors from about 5 down to the order of 1/5.

For tableware it is noted (cfr. the revised table 4, below) that the Danish and Italian limits are stricter for both lead and cadmium than the EEC proposal, while the limits described from the other countries are equivalent to or slightlv milder. For cookingware, the national limits are equivalent to or milder than those of doc. R/112/75.

Re page 32, table 4

Following the EEC-proposal (R/112/75), a revised table 4 is as follows:

	Tableware		Cookingware	
	Lead	Cadmium	Lead	Cadmium
Denmark	5x	1.5x	1x	0.3x
Italy	2x	4x	0.1°-0.25x°	0.2x
United Kingdom	0.7x	0.7x	~0.7x	~0.7x
Ireland	0.7x	1x	÷	÷
Western Germany	0.7x	1x	÷	÷
The Netherlands	~0.5x	~0.8x	÷	÷

o) 1st extract only

Re page 33-44, Chapter 4

Several minor amendments and revised figures have been added to the text as foot-notes to indicate the evaluations in the light of final version of EEC-proposal doc. R/112/75.

Page 48-63, Chapter 6

Several minor amendments and revised figures have been added to the text as foot-notes to indicate the evaluations in the light of final version of EEC-proposal doc. R/112/75.

Page 65. Table on total lead contamination in diet.

Following the amendments and corrections which have been made necessary in this studv by the final version of EEC proposed directive, doc. R/112/75, the concluding table on potential, total contamination for lead on the typical Danish diet will read as follows:

Food Group	Treatment	Type of object	For objects meeting Danish test mg/kg	µg	EEC prop.test mg/kg	µg
Food:						
1. Hot non-acid	Cooking	Plain ceramic	0.05	26	0.05	26
	Serving	Decorated ware	0.03	15	0.10	51
2. Hot acid	Cooking	Plain ceramic	0.70	35	0.70	35
	Serving	Decorated Ware	0.70	35	1.4	70
3. Cold non-acid	Serving	Decorated Ware	0.00	0	0.00	0
4. Cold acid	Serving	Plain ceramic	0.06	13	0.17	38
Beverages:						
5. Hot non-acid	Serving	Plain ceramic	0.02	10	0.10	50
6. Hot acid	-	-	-	-	-	-
7. Cold non-acid	Serving	Plain ceramic	0.00	0	0.00	0
8. Cold acid	Serving	Plain Ceramic	0.06	9	0.17	26
Total migration per person per day:				143 µg		297 µg
per week:				∿1.0 mg		∿2.1 mg

The revised estimate for the potential weekly intake of lead from objects meeting the proposed EEC-limit is thus 2.1 mg per person, or 68% of the total tolerable intake. 22% of the total amount is estimated to come from the cookingware, while the remaining 78% from the tableware.

A somewhat reduced potential level of contaminations is therefore achieved by the proposed limits of Doc. R/112/75 compared to the working-group considerations. It is noted, however that the reduction is not proportional to the numerical reduction of limit values (cfr. table 4 compared to the revised table 4). This is partly due to the fact, that the change in limit values will be of practical significance for the decorated ware only, while no influence on the plain ceramics is anticipated, and partly connected to the lack of proportionality sometimes found between release of lead into food and into test liquid. Thus, the remaining level of practical migration is still comprising a considerable proportion of the total tolerable intake.

Page 67, Table on total cadmium contamination in diet

Following the amendments and directions which have been made necessary in this study by the final version of EEC proposed directive, doc.R/112/75, the concluding table on potential, total contamination for cadmium on the typical Danish diet will read as follows:

Food Group	Treatment	Type of object	For objects meeting Danish test mg/kg	μg	EEC prop.test mg/kg	μg
Food:						
1. Hot non-acid	Cooking	Plain ceramic	0.013	7	0.004	2
	Serving	Decorated ware	0.03	15	0.05	25
2. Hot acid	Cooking	Plain ceramic	0.16	8	0.05	3
	Serving	Decorated ware	0.08	4	0.12	6
3. Cold non-acid	Serving	Decorated ware	0.00	0	0.00	0
4. Cold acid	Serving	Plain ceramic	0.03	7	0.05	11
Beverages:						
5. Hot non-acid	Serving	Plain ceramic	0.017	9	0.025	13
6. Hot acid	-	-	-	0	-	0
7. Cold non-acid	Serving	Plain ceramic	-	0	-	0
8. Cold acid	Serving	Plain ceramic	0.03	5	0.05	7
Total migration per person per day:			55 μg			67 μg
per week:			∿0.4mg			∿0.5mg

In the case of cadmium it is thus estimated that the potential intake from objects meeting the proposed EEC limit is 0.5 mg per week per person, i.e. equal to the total tolerable intake. 5 μg per day or about 8% of this amount is estimated to come from cookingware.

The reduction in potential cadmium release into the total diet according to doc. R/112/75 compared to the working-group document is estimated to be more pronounced than was the case with lead, and the influence of the limit changes is more evenly distributed among the various eating situations. It is noted, however, that the total potential amount is still of a sizable order of magnitude compared to tolerable intake.